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Optical and Solid State Properties of Manganese Sulfide Thin Films Deposited Using Chemical Bath Method

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Abstract— *Manganese Sulfide (MnS) thin films were successfully deposited on glass substrate at room temperature via a simple, cheap technique; chemical bath method. The baths contained manganese sulphate ($MnSO_4$. H_2O) of different concentrations (0.1M, 0.2M 0.3M), thiourea [SC (NH2)2] and Ammonia (NH3) solution which acted as the complexing agent. The effects of the bath concentration on the optical and solid state properties of the films were investigated. The as-deposited films was characterized by the 752N England UV-VIS Spectrophotometer in the wavelength range of 200-1000nm. The results showed that films deposited at 0.1M was found to posses high values of absorbance, absorption coefficient, refractive index , extinction coefficient and optical conductivity. Transmittance and reflectance values were low. Films deposited at 0.2M and 0.4M, showed an inverse of these properties. The band gap energy of the material was found to increase as concentration increases. It was found to be in the range of 2.4eV - 2.8eV. These properties make MnS thin film suitable as Spectral Selective Surfaces for Solar Energy Application.*

Index Terms— Chemical bath method, Concentration, manganese Sulfide, solid state Properties, Solar , thin films, glass

1 INTRODUCTION

THIN film is a layer with a high surface-to-volume ratio ranging from fractions of a nanometre (monolayer) to several micrometres in thickness. It is formed from the process of atom–by-atom, molecule–by–molecule, ion–by–ion, or cluster of species–by–cluster of species condensation [1].Thin film materials exhibit crystalline or amorphous nature depending on their deposition conditions.

Recently, the studies on the optical properties of metal chalcogenide semiconductors have received a lot of attention due to their significant roles in different areas of technology.

Manganese sulphide with the chemical formula MnS, belongs to this group of materials. It has interesting properties such as direct wide band gap of about 3.1eV, exhibition of combination of magnetism and semi conductivity, abundance in nature and absence of toxicity .The electrical resistivity of the film is of the order of 10^6–10^7 Ωcm with *p*-type electrical conductivity[2],[3]. MnS exist in three phases, a green stable α-MnS form (alabandite) with a rock salt (RS) structure, β-MnS and γ-MnS (both pink) which are both meta-stable modifications with zinc blend (ZB) and wurtzite (W) structures, respectively[4]. The cubic *a*-phase of MnS appears to be stable above room temperature, but when they are turned to α -phase of MnS, they can be prepared at low temperature. The γ -phase of MnS can be prepared at low temperature, but they turn to α -phase above 200°C. The α -phase is retained at all temperatures[4],[5].

Manganese Sulphide finds application in devices such as solar cell [2] ,as selective coatings, photoconductors, sensors [6] and anti-reflection coatings [7] Several physical and chemical techniques are available for the growth of manganese sulphide thin films, such as nebulized spray pyrolysis [8] radio-frequency sputtering [9], hydrothermal[10] SILAR [11] , solution growth technique **[**12**]** and chemical bath deposition [13] [7] [14] Amongst these methods chemical bath deposition is the most promising technique for depositing thin films and nanomaterials since it is one of the simplest and cheapest methods as it does not depend on expensive equipment and can be employed for large area deposition. Chemical bath deposition method is based on the controlled precipitation from solution of a compound on a suitable substrate. The substrates are immersed either in an alkaline or acidic solution which contain the metal ion, chalcogenide source and a complexing agent. However, the deposition condition such as bath composition, reagent composition, temperature, pH,deposition time, etc. strongly influences the film stoichiometry, microstructure and crystallinity. These characteristics determine the optical and electrical properties of the deposited films.

Deposition of Mns using CBD is based on the slow release of Mn^{2+} ions and S^{2-} ions in an aqueous alkaline bath and the subsequent condensation of these ions on substrates suitably mounted in the bath. The slow release of Mn^{2+} ions is achieved by adding a complexing agent (ligand) to the Mn salt to form some magnesium complex species which, upon dissociation, results in the release of small concentrations of Mn^{2+}ions.

Anuar and HO [14] deposited MnS thin films on indium tin oxide glass substrate using chemical bath deposition technique. The influence of bath temperature was investigated to determine the best conditions for deposition process. . From the optical properties analysis, the band gap energy was found to be dependent on the bath temperature.

The solution growth technique was used to deposit thin film of manganese sulphide on micro-slides at different bath parameters using Manganese chloride ($MnCl_2.4H_2O$), sodium thiosulphate ($Na_2S_2O_3$), distilled water, and ethylenediamine tetraacetic acid (EDTA) which served as the complexing agent [12]. The optical and solid state characteristics revealed that films of manganese sulphide (MnS) have low absorbance ~ 0.033 – 0.40, high transmittance ~ 4 – 99%, and low reflectance ~ 0 – 20% throughout the ultraviolet, visible, and infrared region energy band gap, Eg ~ 2.60 –3.90eV

The effect of Triethanolamine on the structural and optical properties of nebulized spray deposited MnS thin films was studied by Girish et al., [8]. Manganese acetate and thiourea was used as the source materials .The as-deposited and annealed films were characterized using X-ray diffraction (XRD), UV-Vis spectroscopy and photoluminescence. The formation of mixed cubic and hexagonal phase MnS was confirmed by XRD analysis. The energy band gap of films varies between 3.47eV and 3.65eV.

Usoh and Okujagu [13] synthesized and deposited binary thin films of Manganese Sulphide (MnS) on glass substrates at 300k by varying molar concentrations of solution. The spectral analysis showed that the transmittance 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.

In this study, we report the deposition of MnS thin films on microscope glass slides at room temperature by chemical bath deposition (CBD) method and the effect of bath concentration on the optical and solid state properties of the as-prepared MnS thin films were investigated.IS document is a template for Microsoft Word versions 6.0 or later. If you are reading a

2 Materials and Methods

Manganese sulphide thin films were deposited on glass substrates which had been previously degreased in concentrated HCl for 24 hours, washed with detergent, rinsed with distilled water and dried in air.

In this experiment, three reaction baths were used which contained different concentrations of the Mn^{2+} (0.1M, 0.2M and 0.4M). The Manganese sulphide thin films were prepared from an alkaline bath using aqueous solutions of manganese sulphate ($MnSO_4.H_2O$) and thiourea [$SC(NH_2)_2$] which acted as a source of Mn^{2+} and S^{2-} ions, respectively. The complexing agent used was NH_3. Deposition of MnS thin films was carried out at room temperature (25^0C) using the following procedure: 10 ml of 0.1M manganese sulphate solution was placed in a 50 ml beaker. Then, 5ml of NH_3 was added to the beaker and was stirred continuously using the glass stirrer. Thereafter, 8mls of 1.0M thiourea [SC(NH2)2] was then added and stirred gently to ensure uniformity of the mixture The mixture was then topped to 50mls level by addition of 27ml of distilled water. This procedure was repeated for 0.2M and 0.4M of Mn^{2+}. A glass substrate was dipped vertically into all of the three reaction baths with the aid of a synthetic foam cover. Each bath was allowed to stand for twenty four hours, after deposition, the films were rinsed with copious amounts of distilled water, dried in air and kept in an air tight container to avoid contamination.

After the films were deposited, they were characterized using a 752N England UV-VIS spectrophotometer in the wavelength range (200-1000nm) using blank glass slide as reference. The optical and solid state properties studied in this work include: Absorbance (A), Transmittance (T), Reflectance (R), Absorption coefficient (α). Others are the band gap, refractive index (n) ,extinction coefficient (k) and Optical conductivity (σ_o).

3. Results and Discussion

Data obtained from the optical characterization of the films in the wavelength range 200 to 1000 nm were used to plot the following graphs.

3.1. Absorbance

In spectroscopy, the absorbance (also called optical density) of a material is a logarithmic ratio of the amount of radiation falling upon a material to the amount of radiation transmitted through the material [15].Optical absorption study of materials provides useful information to analyze some
features concerning the band structure of materials.

Figure 1 shows the plot of Absorbance versus Wavelength of the deposited MnS thin film. It is observed that the spectral absorbance of the specimens vary with wavelength in similar manner. It is found to have very low absorbance between 200- 340nm which increased rapidly between 340-400nm of the UV region, and gently decreases as the wavelength increases. The spectra also indicate that absorbance increased with decrease in Manganese ion concentration. Film H 0.1, with lowest concentration showed highest absorbance peak of 1.0. All the films show a sharp absorption edge below 400 nm. This property makes MnS thin film useful in applications such as protective coating.

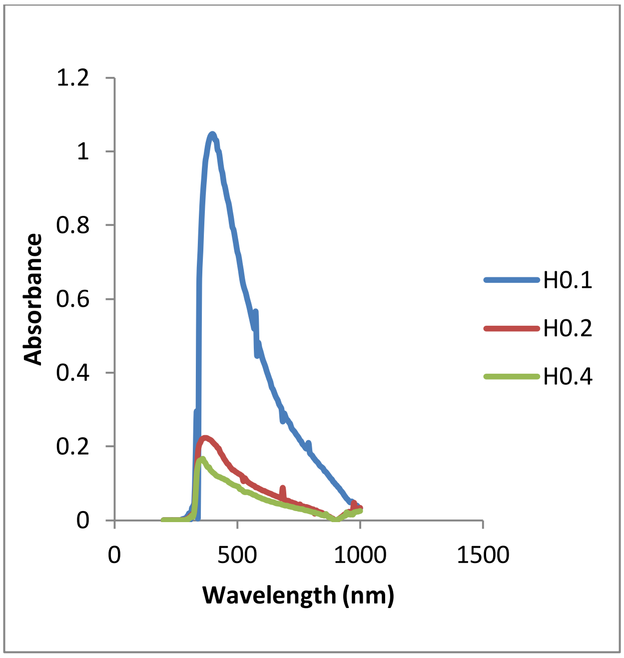

Figure 1. Plot of Absorbance versus Wavelength

3.2. Transmittance

The transmittance (T) of a specimen is defined as the ratio of the transmitted flux (I_t) to the incident flux (I_o) that is,

$$T = I_t/I_o \quad \text{------------------------------------} \quad 3.1$$

vary in similar manner. It decreased from a value of about 99% at 250nm to various minimum values of 8% at 400nm for H0.1, 59% at 365nm for H0.2 and 68% at 360nm for H0.4 before increasing rapidly throughout the VIS/NIR region. All deposited films showed a high transmittance in the NIR region. The low transmittance of the specimen deposited at 0.1M makes it useful as a cold mirror coating, while the high transmittance in VIS/ NIR Figure 2 shows the transmittance spectra of the MnS film. It is observed that the transmittance of the specimens regions exhibited by films deposited at 0.2M and 0.4M makes them useful aesthetic window glaze materials.

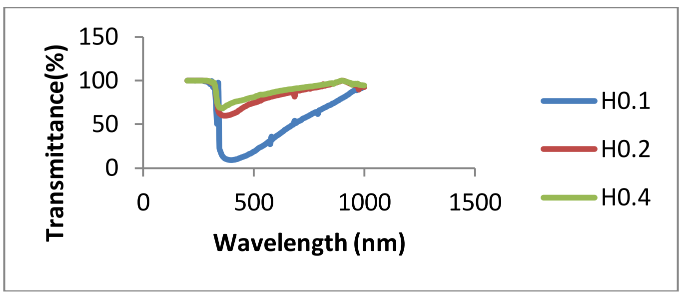

Figure 2. Plot of Transmittance versus Wavelength

3.3. Reflectance

Reflectance is the fraction of the incident radiation of a given wavelength that is reflected when it strikes a surface. A relation between transmittance (T), spectral absorbance (A) and spectral reflectance (R), according to the law of conservation of energy is given by

$$A + T + R = 1 \quad \text{-----------------------------------} \quad 3.2$$

Figure 3 shows the plot of Reflectance versus Wavelength of the deposited MnS thin film. The reflectance of the sample deposited at 0.1M of Mn^{2+} ion decreased from about 19% at about 335 nm sharply to a minimum value of -13 % at 400 nm thereafter, increased to 20 % at 675 nm before decreasing gently with wavelength. For samples deposited at 0.2M and 0.3M, the maximum reflectance of about 17% and 15% was observed at 380nm and 355nm respectively.

Generally all the films show a low reflectance throughout the UV/VIS/NIR region. The low reflectance exhibited by this material makes it useful for anti-reflection coating for consumer optics (spectacle lenses, camera objectives, and binoculars) [16].

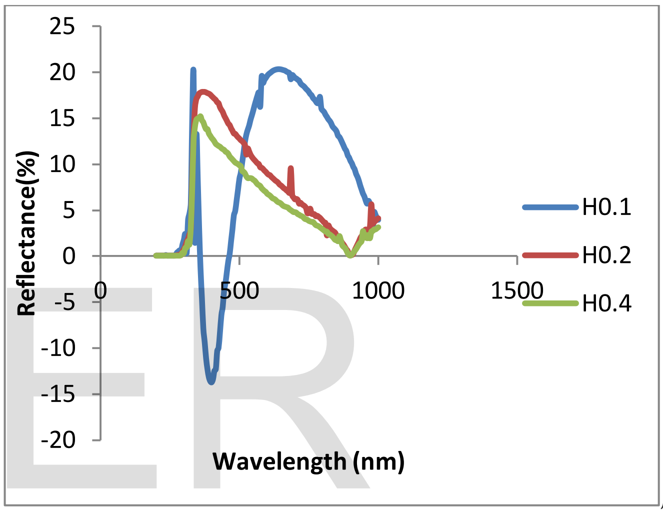

Figure 3. Plot of Reflectance versus Wavelength

3.4 Absorption Coefficient

The absorption coefficient curves for MnS thin films deposited at different concentration are displayed in figure 4. From the spectra, It is observed that the absorption coefficients vary in the same manner. It increased from 0.074×10^6 m^{-1} at 1.2eV to a maximum value of 2.40×10^6 m^{-1} at 3.06eV before decreasing to 0.0011×10^6 m^{-1} at 4.68eV for H0.1. That of H0.2 increased from a value of 0.078×10^6 m^{-1} at 1.2eV to a maximum value of 0.51×10^6 m^{-1} at 3.4eV before decreasing to a minimum value of 0.0011×10^6 m^{-1} at 4.68eV. While that of H0.4 increased from a value of 0.058×10^6 m^{-1} at 1.2eV to a maximum value of 0.36×10^6 m^{-1} at 3.4eV before decreasing to 0.001×10^6 m^{-1} at 3.4eV.

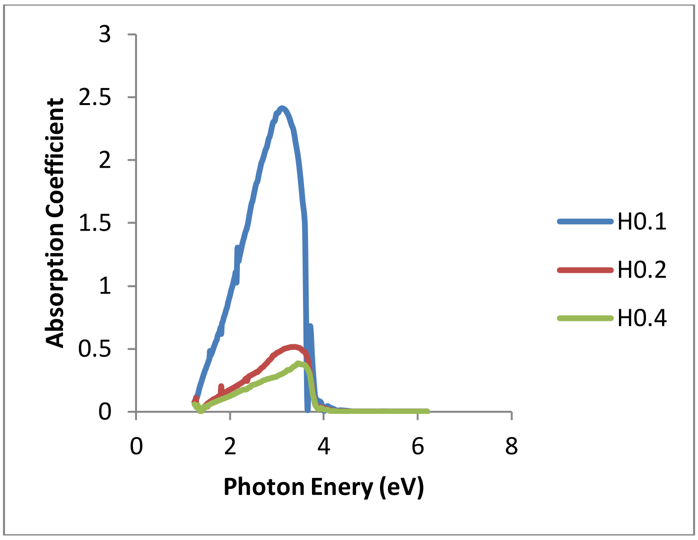

Figure 4. Plot of Absorption Coefficient versus Photon Energy

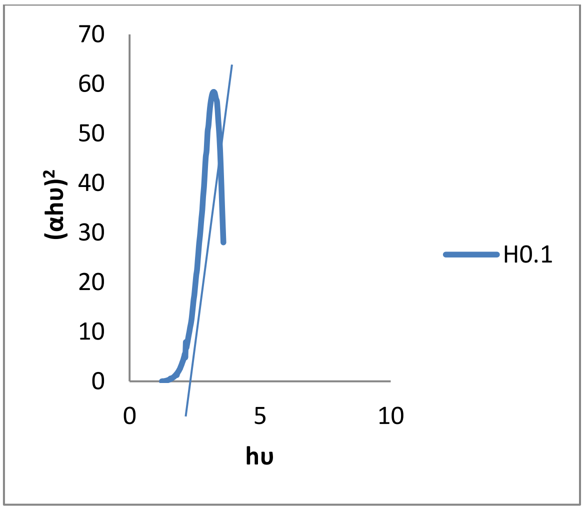

Figure 5(a) Plot of $(\alpha h\upsilon)^2$ versus hυ for 0.1M

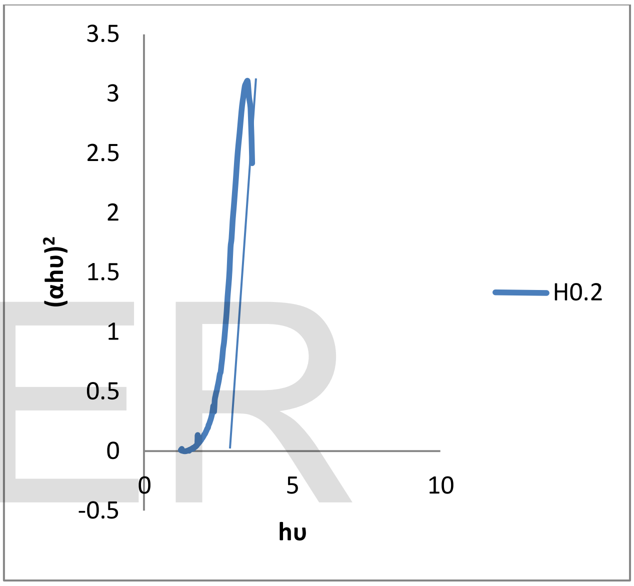

Figure 5(b). Plot of $(\alpha h\upsilon)^2$ versus hυ for 0.2M

3.5 Optical bandgap of the deposited MnS

The value of the optical band gap can be determined from the fundamental absorption of the material which corresponds to the excitation of electrons from the valence band to the conduction band.

The optical bandgap energy of the deposited films can be determined from the following equation;

$$\alpha hv = A\left(hv - E_g\right)^n \text{ ----------------------------- 3.3}$$

where A is constant, E_g is the optical bandgap of the material, and n assumes values of ½, 2, 3/2, and 3 for allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions, respectively. For allowed direct transition, n = ½, which supports the direct bandgap nature of the semiconductor [17]. The band gap was determined from the intersect of straight line portion of $(\alpha h\upsilon)^2$ versus hυ.

The curves of $(\alpha h\upsilon)^2$ versus hυ were plotted and are shown in Figure 5 (a, b and c) for 0.1M ,0.2M and 0.4M respectively. The optical bandgap of the deposited MnS thin films were found to be 2.4eV, 2.6eV and 2.8eV for 0.1M, 0.2M and 0.3M respectively, this values are in agreement with the values obtained by [7],[12]. The plots indicate that the bandgap increased as higher the concentration of the Mn^{2+} increased.

3.5. Refractive index

The refractive index (η) is one of the fundamental properties of an optical material because of its close relationship to the electronic polarization of ions and the local field inside materials. Evaluation of the refractive indices of optical materials is considerably important for applications in integrated optic devices, such as switches, filters, and modulation, among others, in which η is a key parameter for the device design [18] .

The value of η for thin films can be calculated from their reflectance by using simple approximations [19].

$$\eta = \frac{(1+\sqrt{R})}{(1-\sqrt{R})} \text{ --------------------------------3.4}$$

The plot for Refractive index (η) against Photon energy for

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MnS thin films are shown in Figure 6 Film show maximum refractive index of 2.2, 2.04 and 1.84 for 0.1M, 0.2M and 0.3M respectively.

It is observed that the refractive index vary in similar manner for H0.2 and H0.4. It increased from a value of 1.1 at 1.2eV to a maximum value of 2.04, and1.84 at 3.4eV for H0.2 and H0.4 respectively. It then decreased to a minimum value of 1.05 at 2.1eV. That of H0.1, increased from a value of 1.15 at 1.2eV to a maximum value of 2.2 at 3.4eV before decreasing to a minimum value of 0.7 at 2.8eV. Thereafter, it increased to another maximum value of 2.2 at 3.7eV before decreasing to 1.0 at 4.8eV. The high refractive index possessed by MnS films makes it suitable for use as anti-reflection coatings.

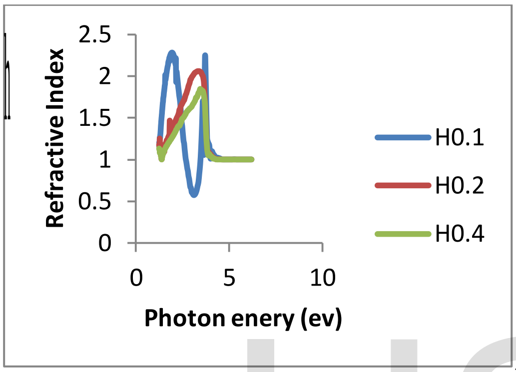

Figure 6. Plot of Refractive index versus hυ

3.6. Extinction Coefficient

Figure 7 shows the variation of extinction coefficient of the MnS film against Photon energy.The extinction coefficient allows for estimation of the molar concentration of a solution from its measured absorbance. Films deposited at 0.1M showed a high extinction coefficient of 79.19 at 2.99eV it then decreases slightly from 3.1eV to 3.7ev until it is almost zero at the boundary point. While films deposited at 0.2M and 0.4M were observed to exhibit low extinction coefficient property all through. Since k decreases with increasing wavelength in the VIS region, it indicates that the transparent films seem to behave like transparent insulators preventing high energy UV and high temperature NIR radiation into a building while allowing only visible light.

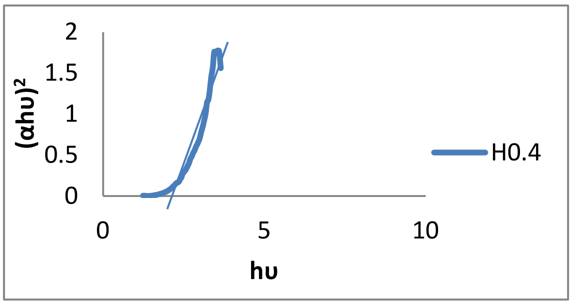

Figure 5(c). Plot of $(\alpha h\upsilon)^2$ versus hυ for 0.3M

3.7. Optical Conductivity

The optical conductivity (σ) is obtained using the relation [20];

$$\sigma = \frac{\alpha \eta C}{4\pi} \quad \text{--------------------- 3.5}$$

Where c is the velocity of light in the space; η is the refractive index and α is the absorption coefficient. Fig.8 shows the variation of optical conductivity with the incident photon energy. The optical conductivity increases as the concentration decreases, also shown is the increase in optical conductivity with increase in photon energy. The increased optical conductivity at high photon energies is due to high absorbance of film in that region.

It is observed that the optical conductivity of H0.2 and H0.4 vary in similar manner. It increased from 0.022 $\times10^{14}s^{-1}$ at 1.2eV to a maximum value of $0.25\times10^{14}s^{-1}$ at 3.4eV before decreasing to $0.0034\times10^{14}s^{-1}$ at 4.1eV for H0.2. That of H0.4 increased from 0.015 $\times10^{14}s^{-1}$ at 1.2eV to a maximum value of $0.15\times10^{14}s^{-1}$ at 3.5eV before decreasing to $0.00139\times10^{14}s^{-1}$ at 4.1eV. While that of H0.1 increased from a value of $0.020\times10^{14}s^{-1}$ at 1.2eV to a maximum value of $0.60\times10^{14}s^{-1}$ at 2.2eV before decreasing to a minimum value of $0.33\times10^{14}s^{-1}$ at 3.1eV. Thereafter, it increased to a maximum value of $0.59\times10^{14}s^{-1}$ at 3.5eV before decreasing to $0.001\times10^{14}s^{-1}$ at 4.5eV.

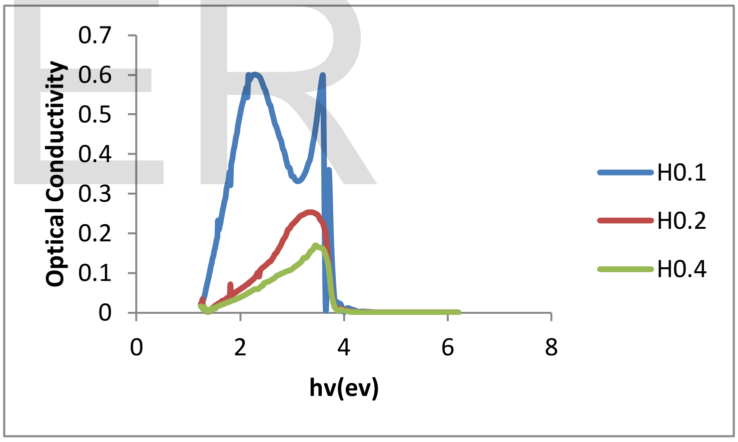

Figure 8. Plot of Optical Conductivity versus hυ

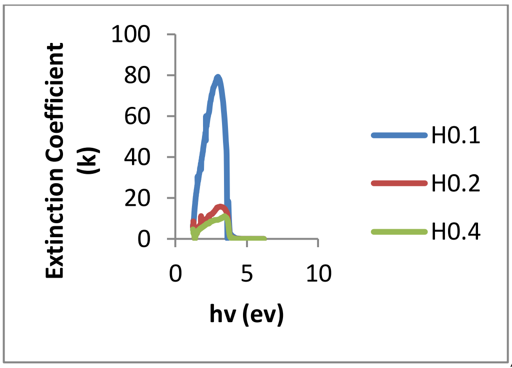

Figure 7. Plot of Extinction Coefficient versus hυ

4. Conclusion

Thin films of MnS were successfully deposited on glass substrate using chemical bath deposition technique. The deposited films were optically characterized using 752N England spectrophotometer. The results shows that bath concentration have effect on the optical and solid state properties of MnS thin films deposited. The band gap energy of the material was found to increase as concentration increases. Films deposited at 0.1M was found to posses high values of absorbance , absorption coefficient, refractive index , extinction coefficient and optical conductivity. Transmittance and reflectance values were low. For films deposited at 0.2M and 0.4M, showed a decrease in the properties obtained when concentration was 0.1M. . The band gap was found to be in the range, 2.4eV - 2.8eV for the concentrations. These properties exhibited by MnS thin film at different concentrations makes it suitable as spectral selective surfaces for solar energy applications.

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