Journal of Multidisciplinary Engineering Science and Technology (JMEST)
ISSN: 3159-0040
Vol. 2 Issue 6, June - 2015

Effect Of The Applied Voltage On The Optical Properties Of Zinc Sulphide Thin Films Deposited On Conducting Glasses Using Electrodeposited Method

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***Abstract*— Zinc Sulphide (ZnS) thin films have been deposited successfully on conducting glass substrates at various applied voltage using electrodeposition method. The XRD confirm the presence of ZnS thin films. Effect of applied voltage on the optical properties of ZnS thin films was investigated. Optical characterization of the films showed low absorption at low photon energy with value of 0.09, 0.32, 0.22 and 0.06 for the film deposited at 1V, 5V, 7V and 9V respectively and high absorption at high photon energy with value of 0.40, 0.81, 0.59 and 0.31 for the film deposited at 1V, 5V, 7V and 9V respectively. Thicker film was formed at 5V which indicates more favourable condition for the formation of ZnS thin films. The broadening in the XRD peaks as the applied voltage is increased showed that the crystalline size of ZnS decreases.**

Keywords—ITO, XRD, UV-VIS Spec., Cubic structure.

I. INTRODUCTION

Semiconducting chalcogenide thin films especially sulphide and selenides have been investigated extensively owing to their interesting optoelectronics properties. Also these chalcogenides thin films have been widely studied for their unique properties, both physical and chemical. The synthesis of materials with controlled sizes, morphologies and size distribution is always potentially important in the synthesis of materials suitable for optoelectronics and luminescent applications [1], [2], [3], [4], [5]. Zinc Sulphide (ZnS) is one of the most important II – VI group semiconductor, with room temperature bulk band gap of 3.54eV (Cubic) and 3.91eV (Hexagonal) and refractive index of ~ 2.4 is a good candidate for photo- and electro-luminescence properties and promising applications in optoelectronics [6], [7]. Dimensionality, size and size distribution are known to play important roles in determining the physical and chemical properties of ZnS thin film materials. ZnS thin films with grain size range of 10 – 0.1 nm are becoming attracting increasing attention from researchers all over the world because of their superior properties and sometimes completely new compared to those of conventional coarse grained materials [8], [9]. ZnS films have been synthesized by various methods such as pulse laser technique, silar method, chemical bath deposition, spray pyrolysis, vacuum evaporation and self-catalytic liquid solid growth. Also molecular beam epitaxy, metalorganic, solvothermal, organometallic vapour phase epitaxy and atomic layer deposition. Electrodeposition method has many advantages like free from porosity, rapidity, high purity, industrial application, potential to overcome shape limitations or allows the production of free-standing parts with complex shapes, higher deposition rates, produce coatings on a widely different substrates, ability to produce composition unattainable by other techniques, the possibility of forming simple low cost multilayers and no postdeposition treatment amongst others [10], [11], [12], [13], [14]. In this research work, electrodeposition method is explored and the effect of applied voltage on the optical properties of ZnS thin films was studied

II. EXPERIMENTAL

All reagents were used as purchased and solvents were distilled prior to use. ZnS films were deposited on indium doped tin oxide (ITO) (conducting glass) at various deposition conditions. Prior to use, the substrates were cleaned with detergent solutions, rinsed with distilled water and then rinsed with acetone, methanol and distilled water and dried before use. An area of about 6.00 cm^2 of the substrate was dipped into the electrolyte (solution). The electrodeposition bath system is composed of Zinc Trioxonitrate V Hexahydrated $Zn(NO_3)_2$ as source of cation (Zn^{2+}), Potassium Tetraoxo Sulphate VI (K_2SO_4) as a source of anion (S^{2-}), and distilled water. p-XRD studies were performed on an Xpert diffractometer using Cu-Kα radiation. The samples were mounted flat and scanned between 20^o and 60^o with a step size of 0.05^o and various count rates. Absorbance spectra data of the films were obtained using Agilent HP8453 UV – VIS spectrophotometer. From the absorbance, various other optical parameters which include: Optical band gap, Refractive index, Coefficient of absorption, and Optical conductivity were derived.

A. Preparation of solution

0.1M solution of $Zn(NO_3)_2.6H_2O$ was prepared by dissolving 14.87g of it in 500ml of distilled water and when thoroughly shaken, it dissolved completely. Again 0.1M solution of (K_2SO_4) was prepared dissolving 8.71g of it in 500ml of distilled water and it dissolved completely with a clear solution.

B. Electrodeposition

Deposition of ZnS on conducting glass (ITO) substrate was carried out using electrodeposition technique. 20ml solution of $Zn(NO_3)_2.6H_2O$ was measured in 100ml beaker and again 20ml solution of (K_2SO_4) was measured in the same 100ml beaker and stirred to achieve uniformity with a pH value of 2.6 and the resultant solution was used for the deposition.
The substrate, ITO, was used as the cathode while carbon electrode was used as the anode. The deposition was done at room temperature (27^oC) under 1V, pH of 2.6 and the deposition took place for 180secs. The same process was repeated with the voltage of 5V, 7V and 9V.
The possible reaction mechanism is shown below:

$$\mathbf{Zn(NO_3)_2.6H_2O + K_2SO_4 = ZnS + 2KNO_3 + 2O_2 + 6H_2O}$$

At the end of deposition, the coated substrates were washed well with distilled water and air dried at room temperature. The thickness of the deposited films was determined gravimetrically. The deposited films were taken for structural characterization using Cu-Kα (λ = 0.154nm) on an MD-10.3 diffractometer and optical characterization using Janway 6405 UV-VIS spectrophotometer.

III. RESULTS AND DISCUSSION

Figure 1 shows the plot of the calculated optical thickness against the applied voltage. As the applied voltage is increased, from 1V to 5V, the thickness of the deposited thin film increases from 307nm to 775nm but when the applied voltage is increased further from 5V to 9V, the thickness of the films decreases from 775nm to 247nm, this can be attributed to the fact that the particle size of ZnS decreases as the applied voltage is increased from 5V to 9V. This observation is seen in the broadening of the peaks in the XRD pattern of ZnS thin film. **Figure 2** shows the variation of optical absorbance of the films deposited, at different deposition voltage, with photon energy. This variation reveals low absorption in the lower photon energy with value of 0.09, 0.32, 0.22 and 0.06 for the film deposited at 1V, 5V, 7V and 9V respectively. The absorbance tends to be high in high photon energy with value of 0.40, 0.81, 0.59 and 0.31 for the film deposited at 1V, 5V, 7V and 9V respectively. The optical absorbance increased with thickness of the deposited films. The high absorbance in the UV region makes ZnS useful in forming p – n junction solar cells with other suitable thin film materials for photovoltaic applications and a good window layer for solar cell application [11] [12], [15], [16]. The low absorption of energy makes ZnS films useful for optical components in higher laser window and multispectral applications, proving good imaging characteristics [17]. **Figure 3** shows the spectral transmittance (%) of the films. From the figure, it is observed that the transmittance decreases as the thickness of the film increases. The transmittance spectra reveal a low transmittance in the UV region for all the films and a high transmittance in the near infra-red region for all the films. The higher transmittance in the visible region makes it a strong candidate for use in opto-electronic devices, The wide transmission range of ZnS film makes the material useful in manufacturing optical components, windows, mirrors, lenses for high power IR laser [3] [13], [18], [19], [20], [21].
The refractive index of the deposited ZnS thin films were calculated and plotted. **Figure 4** showed that the refractive index of the film deposited at 1V and 9V is 1.8 at low photon energy and increased to 2.6 at high photon energy. Film deposited at 7V showed approximately constant refractive index at any photon energy whereas the refractive index of the film deposited at 5V showed a refractive index of 2.6 at low photon energy and 1.4 at high photon energy. The high refractive index possessed by ZnS films made it suitable as anti-reflection coatings. The extinction coefficient of the films was estimated using the formula **k** = $\frac{\alpha\lambda}{4\pi}$ **figure 5** whereas the optical conductivity was estimated using $\boldsymbol{\sigma_0 = \frac{\alpha nc}{4\pi}}$ **figure 6.** Where $\boldsymbol{\alpha}$ is the coefficient of absorption, **λ** is the wavelength of photon energy, **n** is the refractive index of ZnS film and **c** is the speed of light. Figures 5 and 6 showed that both the extinction coefficient and optical conductivity increased with the photon energy. The figures also showed that the films have least absorption in the lower energy level, (VIS-IR region) but very high rate of absorption in the high energy level (UV region). These optical properties makes ZnS thin films nice glazing materials for maintaining cool interior in buildings in warm climate regions while still keeping the rooms well illuminated [15].

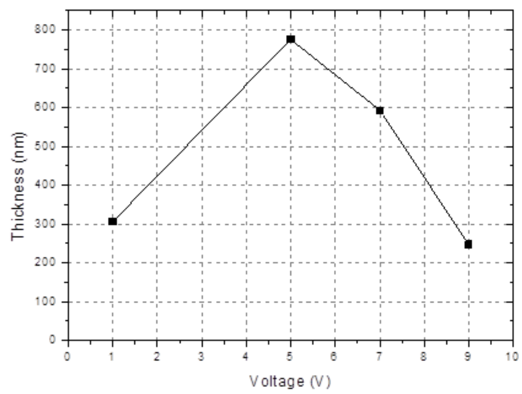

Figure 1 *Plot of the thickness of the deposited films versus applied voltage.*

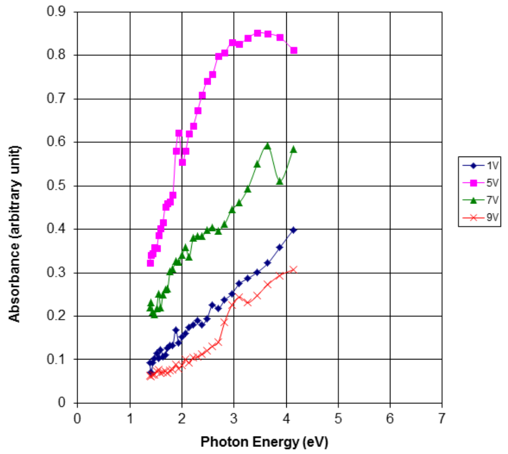

Figure 2 *Spectral absorbance of ZnS films deposited at different applied voltage*.

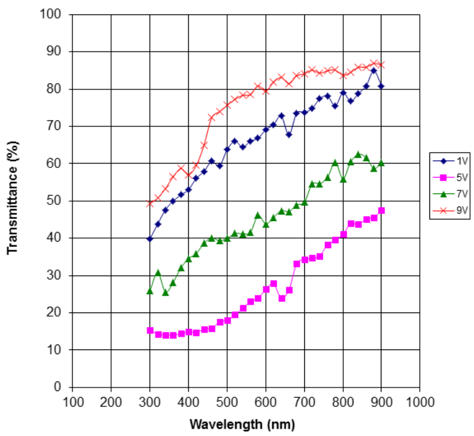

Figure 3 *Spectral transmittance of ZnS films deposited at different applied voltage.*

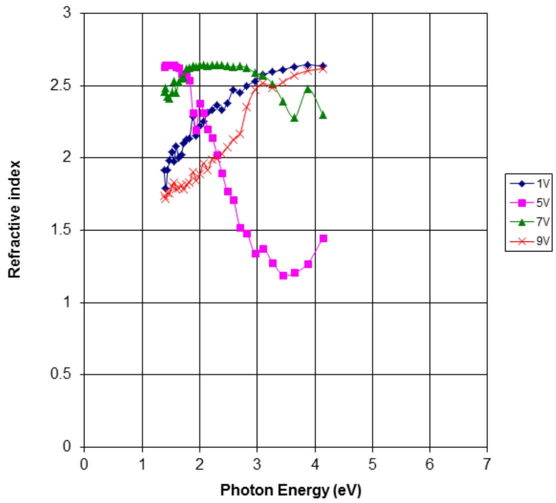

Figure 4 *Plot of refractive index versus photon energy for the films deposited at 1V, 5V, 7V and 9V.*

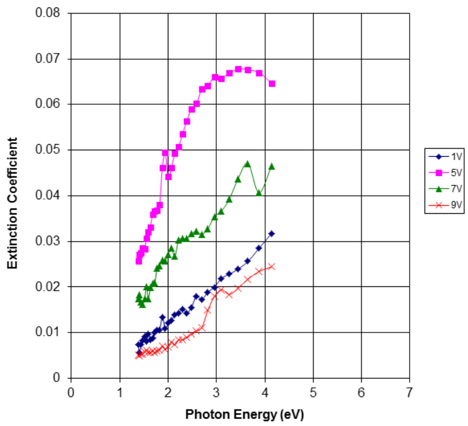

Figure 5 *Plot of extinction coefficient versus photon energy for the films deposited at 1V, 5V, 7V and 9V.*

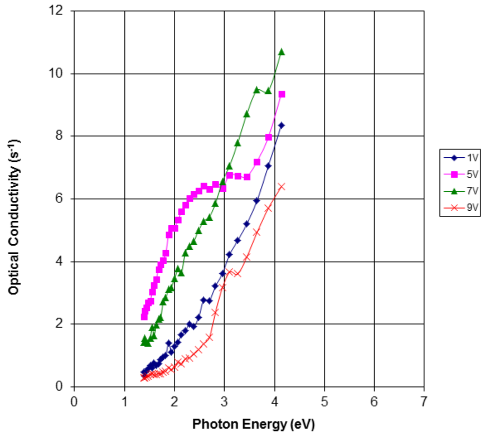

Figure 6 *Plot of optical conductivity versus photon energy for the films deposited at 1V, 5V, 7V and 9V.*

Figures 7 – 8 show the variation of the dielectric constants (real (ε_r), Imaginary (ε_i)) with photon energy. It is observed that the imaginary dielectrics increased as the photon energy increases with an exception of the film deposited at 5V which peaked at photon energy of 2.1eV. It is also observed that the real dielectrics of the films deposited at 1V and 9V increased as the photon energy increase while the film deposited at 5V had its real dielectrics decreased with photon energy. The plot of the absorption coefficient squared against photon energy showed that the deposited films have optical band gap of 3.2eV as shown in **Figure 9**. The XRD pattern of the deposited films under the experimental optimum conditions at 1V, 5V, 7V, and 9V is shown in **figure 10**. The observed diffraction peaks in these patterns can be indexed to cubic ZnS structure. Three prominent planes of reflection are indexed to (111), (200) and (220). Again it is also observed that the broadening of the peaks increases as the applied voltage increases, this shows that the grain size of the deposited films decreases with increase in the applied voltage.

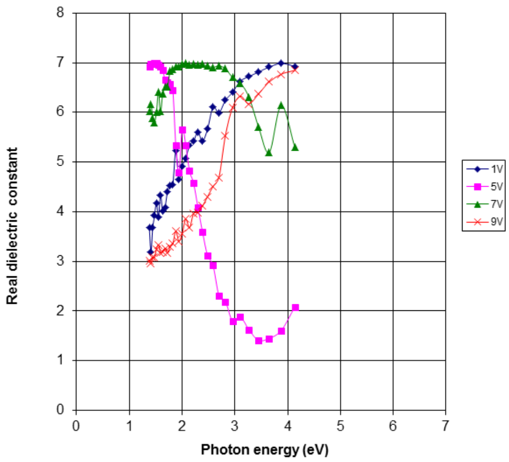

Figure 7 *Plot of optical conductivity versus photon energy for the films deposited at 1V, 5V, 7V and 9V.*

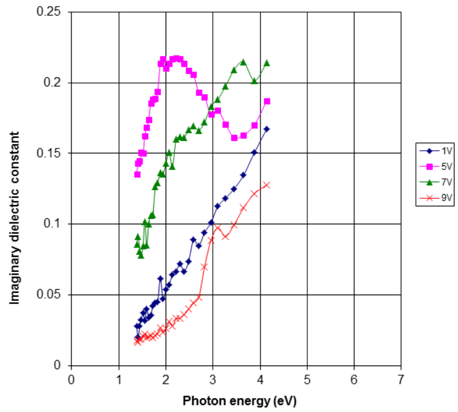

Figure 8 *Plot of optical conductivity versus photon energy for the films deposited at 1V, 5V, 7V and 9V.*

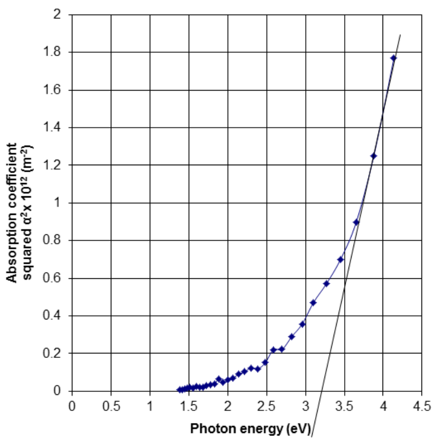

Figure 9 *Plot of α^2 versus photon energy of deposited ZnS film.*

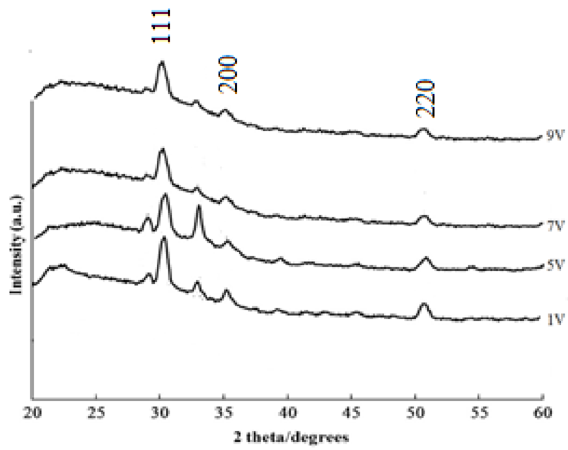

Figure 10 *X-ray diffraction patterns of ZnS thin film deposited on conducting glass (ITO) substrate at various applied voltage.*

IV. CONCLUSION

Electrodeposition technique has been used to deposit polycrystalline of ZnS thin film under different applied voltage. XRD pattern of the deposited films showed that polycrystalline cubic ZnS thin films were formed with preferred orientation on (111), (200) and (220) planes. The broadening of the peaks as the applied voltage is increased showed that the crystallite decreases. Optical characterization of the deposited films showed that, ZnS films have low absorption in the low photon energy and the absorption tends to be high at high photon energy. The transmittance spectra reveal a low transmittance in the UV region for all the films and a high transmittance in the near infra-red region for all the films. The value of the refractive index depends on the applied voltage. From the results, we can conclude that applied voltage has significant effect on the optical properties of ZnS thin film.

ACKNOWLEDGMENT

The authors are grateful for the assistance of the staff of Engineering Material Development Institute, EMDI, Akure, Ondo State were the characterization was done.

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