Optical and Morphological Properties of Electrodeposited Thin Films of ZnS

M.L. Madugu*1, Abdullahi Lawal2, H.M. Ndahi3

1. Department of Physics, Gombe State University, P.M.B. 127, Gombe
2. Department of Physics, Federal College of Education Zaria, P.M.B 1041, Zaria, Kaduna State
3. Department of Physics, Federal College of Education, Eha Amufu, P.M.B. 2001, Enugu State.

*Corresponding author, maduguu2@gmail.com

Abstract. Zinc sulphide (ZnS) thin films were grown on glass/fluorine-doped tin oxide (FTO) substrates using the simple and inexpensive electrodeposition technique. The deposition electrolytic bath was prepared from aqueous acidic solution of ZnSO4 and (NH4)2S2O3. The work was carried out to investigate the optical and morphological properties of ZnS layers. The deposition temperature and the pH values were respectively 30°C and 1.50. It was observed that optical properties vary with variation in growth voltage. It was observed that bandgap decrease with increase in growth voltage since the higher the growth voltage, the higher the current density. As the deposition temperature in increased, the bandgap is seen to decrease. After annealing, the bandgaps are seen to increase and the absorption edges can be seen to have smoothened out. Increase in annealing temperature play a significant role in achieving desired results especially when it is meant for device application. As expected, the layer thickness is seen to increase with increase in deposition temperature.

Keywords: optical, morphology, electrodeposition, ZnS

1.0 Introduction

Zinc sulphide (ZnS) is a binary semiconductor material with a wide and direct optical bandgap of 3.70 eV [1]. This bandgap fits very well as a window layer in solar cells [2], [3]. ZnS has also found applications in the areas of electroluminescent devices [4] and in antireflective coatings [5]. ZnS can be obtained in both n-type or p-type in electrical conductivity [6] depending on the preparation parameters. This material usually grows in zinc blende and/or wurtzite crystal structures, which in both cases show a direct energy bandgap [7]. In solar cells, ZnS can be used as a buffer or window layers in CdTe and CIGS based solar cells.

ZnS thin films have been grown using different techniques such as chemical bath deposition (CBD), successive ionic layer adsorption and reaction (SILAR), spray pyrolysis and
electrodeposition (ED). In the present work, potentiostatic electrodeposition using a simple two-electrode system was employed to deposit electronic device-quality ZnS thin. The strengths of this technique include its simplicity, intrinsic doping, low cost, low-temperature processing, low chemical waste generation and application in large-area optoelectronics.

This work presents the optical and morphology studies of ZnS thin films grown using potentiostatic electrodeposition technique with 2-electrode configuration. This experiment was carried out in the Materials and Engineering Research Institute (MERI), Sheffield Hallam University, UK.

2.0 Preparation of deposition electrolyte

The deposition electrolyte for the preparation of ZnS thin films was made by dissolving 0.15 M ZnSO$_4$ of purity 5N (99.999%) and 0.15 M (NH$_4$)$_2$S$_2$O$_3$ (purity 98%) in 400 ml of deionised water. The beaker containing the 400 ml of the electrolyte was housed in water bath of 1000 ml glass beaker. All chemicals and the glass/FTO substrates used in this work were purchased from Sigma-Aldrich, UK.

Substrate preparation

The substrates used for the deposition of ZnS are glass/FTO with sheet resistance of 7 or 15 $\Omega$/square. The glass/FTO substrates were cleaned using soap solution to degrease and remove dust particles, rinsed in de-ionised water then cleaned with methanol and again rinsed in de-ionised water and dried in air before the deposition process. After the cleaning process, each of the glass/FTO substrates (working electrode) was attached to carbon electrode using polytetrafluoroethylene (PTFE) tape before insertion into the electrolyte. The cleaning of the substrates before deposition is important so that dust and other contaminants on the substrate surface are thoroughly removed before deposition. If the cleaning is not properly done, it may affect the deposited layer property in many ways ranging from layer non-uniformity, voids which can result in poor contact between the FTO and the deposited layers and it can also introduce pinholes. These effects become obvious in heat treated layers where the pinholes appear clearly and may also result to peeling of the layer due to poor adhesion. Substrate cleaning should be taken seriously especially when incorporated in solar cells since the output of of this device depends largely on the electronic property of the interface. This cleaning procedure is implemented prior to the deposition of all layers.

3.0 Experimental procedure

3.1 Optical studies

The optical properties of ZnS layers grown on glass/FTO substrates were studied using a cary 50 UV-Vis spectrophotometer at room temperature. A bare glass/FTO was used as a baseline before using the glass/FTO/ZnS substrates. The investigation of the optical properties in these thin films is very important especially when they are intended to be used as optoelectronic devices like solar cells. The properties of interest in this work are optical energy bandgap of the layers.
3.2 Effects of growth voltage on the optical properties of ZnS layers

This experiment was carried out to investigate the effect of variation in growth voltage on electrodeposited ZnS thin films. To perform this experiment, three layers were grown at three different growth voltages of 1400, 1450 and 1500 mV including the optimum growth voltage. The samples were grown for one hour.

After growth, each sample was divided into two smaller samples, one was left as-deposited and the other annealed at 350°C for 15 minutes in air. Figures 1 (a) and 1(b) show respectively the optical bandgap spectra for as-deposited and heat treated ZnS layers grown at different growth voltages. The bandgaps were estimated by plotting absorption coefficient ($\alpha$) vs. photon energy ($h\nu$) and by extrapolating the straight line portion of the absorption coefficient ($\alpha$) to the photon energy ($h\nu$) axis (at $\alpha=0$) [8].

![Figure-1: Absorption coefficient Vs photon energy ($\alpha$ vs $h\nu$) for (a) as-deposited and (b) absorption coefficient Vs photon energy ($\alpha$ vs $h\nu$) for the annealed ZnS layers grown at different voltages.](image)

It is observed that the optical bandgaps in the as-deposited samples as estimated from Figure 1(a) vary in the range (3.75-3.80) eV which are in agreement with reported values of ZnS thin films in the literature [9]–[11]. The sample grown at a cathodic voltage of 1400 mV shows the larger bandgap of 3.80 eV while layers grown at 1450 and 1500 mV both indicate similar bandgaps of 3.75 eV. This slight variation in the bandgap is attributed to the variation in the deposition current density which increases with increase in growth voltage as mentioned earlier. Therefore, materials grown at lower voltages are expected to show a higher bandgap due to low film thickness that can allow the passage of all wavelengths of light through the layer which translates to a wider bandgap. Layers grown at higher voltages will show lower bandgaps due to incorporation of more material on the cathode especially Zn which tends to reduce the bandgap due to its metallic nature. Irrespective of the large differences in the growth voltages, the bandgaps exhibited by all the layers are within the reported bandgap of...
ZnS thin films. This also shows that ZnS can be grown over a wide range with similar optical properties. The errors in the bandgap measurement is within ±0.02 eV.

After annealing (Figure 1(b), the bandgaps of all the layers were observed to have increased. The estimated bandgaps of the layers show that the layer grown at 1400 mV show a bandgap of 3.80 eV while the other two layers grown at 1450 and 1500 mV show similar values of 3.70 eV which matches closely with the bulk \( E_g \) of ZnS [1]. The improvement in the bandgaps of the layers after heat treatment could be due to annealing out defects and improvement in structural and electronic properties of the layers.

3.3 Effects of growth temperature on the optical properties of ZnS thin films

The influence of growth temperature on the optical properties of ZnS layers was carried out by growing ZnS layers at three different temperatures of 30, 60 and 80°C at the growth voltage of 1450 mV. Growth duration for all layers was one hour. After growth, the as-deposited sample at each growth temperature was cut into two halves which were then cleaned and dried in air within the laboratory ambient temperature. The first set was left as-deposited and the other set annealed at 300°C for 10 minutes in air.

Figure 2(a) and 2(b) show the absorption coefficient vs photon energy (\( \alpha \) vs \( h\nu \)) for as-deposited and annealed layers respectively. In the as-deposited layers, the estimated bandgaps were found to be 3.85, 3.70 and 3.05 eV for layers grown at temperatures of 30, 60 and 80°C respectively. It can be observed that the bandgap values decreased with increase in growth temperature. This is attributed to layer thickness due to variation in growth temperature. Low temperature grown layers are relatively thinner than those grown at high temperature. It is known that increase in temperature of the deposition electrolyte, results in the increase in the electrochemical reaction between the constituents ions of the electrolyte which influences surface diffusion of the adsorbed atoms (adatoms) [12] on the cathode surface. In this way, the variation of growth temperature can affect the optical properties of materials, with layer thicknesses increasing with increase in deposition temperatures.

![Figure -2: Plots of (a) optical absorbance Vs wavelength (\( \alpha \) Vs \( \lambda \) for (a) as-deposited and (b) annealed layers for samples grown at different temperatures.](image-url)
After annealing (Figure 2(b), the optical bandgaps of the layers grown at 1400, 1450 and 1500 mV were 3.80, 3.70 and 2.70 eV respectively. It can be seen that there is an increased in the bandgap in each of the layers after annealing. The slight increase in the bandgaps could be attributed to the amorphous nature of the material. However the smoothening of the absorption edges of the films after heat treatment especially in sample grown at 30° C is observed. The bandgaps in these layers are in agreement with reported bandgaps of ZnS in the literature [13].

3.4 Effects of annealing temperature on the optical properties of ZnS thin films

This experiment was carried by growing a ~500 nm thick ZnS layer. The as-deposited layer was divided into three smaller samples for heat treatment at three different temperatures (100, 200 and 300°C). All samples were annealed for 15 minutes in air.

Figure 3(a) and 3 (b) are respectively the absorbance vs wavelength (A Vs λ) and absorption coefficient Vs photon energy (α vs hν) of the three ZnS layers. Figures 3(a) shows that absorbance decreased with increase in annealing temperature. The layer annealed at 100°C shows higher absorbance while the layer annealed at 300°C shows the least absorbance. It is observed that improved absorbance is recorded as the annealing temperature increases from 100 to 300°C. This could be due to improvement in structural properties of the layers or possibly due to material sublimation reducing the layer thickness. Figure 3(b) shows that, the samples heat treated at a temperature of 100°C show a bandgap of 3.70 eV while samples annealed at 200°C and 300°C showed similar bandgap of 3.75 eV.

![Figure 3](image)

**Figure -3:** The plots of (a) absorbance Vs wavelength (b) absorption coefficient vs photon energy (α Vs hν) spectra for ZnS layers heat treated at different temperatures for 15 minutes in air.

The results show that the heat treatment temperature is a very important parameter from which desired optical properties of layers can be achieved if properly optimised. The transmittance obtained in the layer annealed at 300°C shows a very good transmittance range.
required for buffer layers so that absorption of photons at the window layers is minimised for increased photocurrent and overall conversion efficiency of the solar cell.

4.0 Morphological studies

Effects of growth temperature on the surface morphology of ZnS thin films

Figure 4 shows the surface morphology of as-deposited (AD) and heat treated (HT) thin films of ZnS grown at different growth temperatures for one hour on glass/FTO substrates. There is virtually no difference between the surface images of the as-deposited and annealed layers grown at each growth temperature. However, it is observed that layer thickness increases with increase in growth temperature. This is due to an increase in surface diffusion as the deposition temperature increases from 30°C to 80°C. The layer grown at 30°C (Figure 4(a) and 4(b)) shows a thin layer of ZnS for both the (a) as-deposited and (b) heat treated samples. The layer thickness continues to increase with increase in temperature with the thicker layer observed in samples grown at 80°C.

As mentioned earlier the variation in the layer thicknesses was attributed to an increase in surface diffusion due to an increase reaction rate between the ions as the growth temperature increases. The morphologies remained virtually the same even after heat treatment for each growth temperature which further confirmed the amorphous behaviour of these layers. However few pinholes are observed in the sample grown at 80°C after heat treatment which could be due to material loss or sublimation after heat treatment.
Figure -4: SEM images of glass/FTO/ZnS layers grown at different growth temperatures (a,c,e) as-deposited and (b,d,f) annealed samples.

5.0 Conclusions

Successful deposition of ZnS thin films from aqueous acidic solution was achieved using a simple 2-electrode system in a single cell configuration. Surface morphology studies using SEM show little or no improvement of the layers even after heat treatment. This indicates the amorphous nature of this material. Optical properties investigated show slight improvement in the optical bandgaps of the layers after heat treatment. The energy bandgaps obtained are in the range (3.0-3.80) eV as investigated under different conditions.

Reference

[1] K. H. Yasuda and H. Kukimoto, “Low Resistivity Al-doped ZnS Grown by MOVPE,” J. Cryst. Growth, vol. 77, pp. 485–489, 1986.

[2] O. K. Echendu, F. Fauzi, A. R. Weerasinghe, and I. M. Dharmadasa, “High short-circuit current density CdTe solar cells using all-electrodeposited semiconductors,” Thin Solid Films, vol. 556, pp. 529–534, 2014, doi: 10.1016/j.tsf.2014.01.071.

[3] O. K. Echendu and I. M. Dharmadasa, “Graded-bandgap solar cells using all-electrodeposited ZnS, CdS and CdTe thin-films,” Energies, vol. 8, no. 5, pp. 4416–4435, 2015, doi: 10.3390/en8054416.

[4] A. Ates, M. A. Yildirim, M. Kundakci, and A. Astam, “Annealing and light effect on optical and electrical properties of ZnS thin films grown with the SILAR method,” Mater. Sci. Semicond. Process., vol. 10, no. 6, pp. 281–286, 2007, doi: 10.1016/j.mssp.2008.04.003.

[5] S. Tec-Yam, J. Rojas, V. Rejón, and a. I. Oliva, “High quality antireflective ZnS thin films prepared by chemical bath deposition,” Mater. Chem. Phys., vol. 136, no. 2–3, pp. 386–393, 2012, doi: 10.1016/j.matchemphys.2012.06.063.

[6] O. K. Echendu, A. R. Weerasinghe, D. G. Diso, and F. Fauzi, “Characterization of n -
Type and p-Type ZnS Thin Layers Grown by an Electrochemical Method,” vol. 42, no. 4, pp. 692–700, 2013, doi: 10.1007/s11664-012-2393-y.

[7] N. K. Abbas, K. T. Al-Rasoul, and Z. J. Shanan, “New method of preparation ZnS nano size at low Ph,” Int. J. Electrochem. Sci., vol. 8, no. 2, pp. 3049–3056, 2013.

[8] J. Tauc, “Optical Properties and Electronic Structure of Amorphous Germanium,” Phys. stat. sol., vol. 15, no. 627, 1966.

[9] S. Lindroos, A. Arnold, and M. Leskelä, “Growth of CuS thin films by the successive ionic layer adsorption and reaction method,” Appl. Surf. Sci., vol. 158, no. 1, pp. 75–80, 2000, doi: 10.1016/S0169-4332(99)00582-6.

[10] M. Y. Nadeem and W. Ahmed, “Optical Properties of ZnS Thin Films,” Turk J Phy, vol. 24, pp. 651–659, 2000, doi: 10.1088/0022-3727/7/13/312.

[11] A. Goktas, F. Aslan, E. Yasar, and I. H. Mutlu, “Preparation and characterisation of thickness dependent nano-structured ZnS thin films by sol-gel technique,” J. Mater. Sci. Mater. Electron., vol. 23, no. 7, pp. 1361–1366, 2012, doi: 10.1007/s10854-011-0599-z.

[12] D. Philip and P. Laurence, “Advances in Electrochemical Science and Engineering, http://www.wiley-vch.de/books/sample/3527328599_c01.pdf,” in Applications of Electrochemistry in the Fabrication and Characterization of Thin - Film Solar Cells, C. A. Richard, M. K. Dieter, L. Jacek, and N. R. Philip, Eds. 2010.

[13] H. A. Bioki and M. B. Zarandi, “Effects of Annealing and Thickness on the Structural and Optical Properties of Crystalline ZnS Thin Films Prepared by PVD Method,” Int. J. Opt. Photonics, vol. 5, no. 2, pp. 121–128, 2011.