Growth and Characterization of Zinc Silver Sulphide Thin Films Prepared by Chemical Bath Deposition Technique

A.I. Ibeh. D.D.O. Eya and C.Iroegbu

Department of Physics, Federal University of Technology, Owerri, Nigeria.

ibehthony@yahoo.com, eyadom2003@yahoo.com

Abstract

Zinc Silver Sulphide thin films have been successfully prepared by the chemical bath deposition technique. The reaction bath consists of solutions of $Zn(COOH)_2$, $AgNO_3$, CH_3CH_2NS, TEA, and NH_3 in 50ml beakers. The films are shiny dark brown in colour and are strongly adhered to the substrates and retain their properties for a long period of time. The films have high absorbance at the UV region and can be used as UV filters. The thin film annealed at 373K has the highest absorbance of 2.7% at the UV region. The thin films have low transmittance in the UV region due to the high absorbance. The film sample annealed at 423K has the highest transmittance in the visible region (about 80%). These properties make the films suitable for solar window control applications. The XRD studies show that the films are crystalline in nature and the range of the grain size obtained is from 0.752nm to 1.145nm. The band gap obtained is in the range of 1.9eV to 2.45eV which gives it potential application in solar cell fabrication.

Keywords- band gap, optical properties, solar cell, thin films, xrd, zinc silver sulphide

1. Introduction

The impact of energy crises since the industrial revolution has kept researchers busy on how to solve these problems (energy crises). A promising source of energy identified is solar energy, but the efficient mode of tapping this energy turned out to be another problem.

Solar cell was successfully fabricated in the late 1950's from silicon to tap the solar energy. However, the low conversion efficiency and high cost of fabricating the cell impeded the popularization of this achievement. Efforts to bring the cost down led to the development of thin-film technology, which is now being diversified to source for good materials for solar cells and other electronic devices. The successful development of this technology and the low percentage solar cell efficiency achieved with silicon motivated researchers to use the technology to search for other materials that could give better results than silicon. All these culminated into the growth and characterization of thin films of various materials.

Many ternary chalcogenide thin films have been prepared by the chemical bath method of deposition. This is because the thin films have properties suitable for the fabrication of solar cells (Uhuegbu and Babatunde, 2010), linear optical devices, light emitting diodes etc. (Ezenwa, Ezenwa and Okoli, 2015) deposited FeCuS thin films, metal chalcogenides by (Mane and Lokhande, 2000), (Fajimi and Adelabu, 2009; Okoli, Ezenwa, Elekalachi, Okpaneje, and Okoye, 2016) deposited Cadmium silver sulphide. In this work, chemical bath deposition technique was employed to deposit ZnAgS thin films on glass slides. This technique has been found to be an economical, simple, and low-temperature method that can be applied to produce quality thin films that are good for device applications (Oriaku and Osuwa, 2008). Also, the CBD technique is a slow process which facilitates the better orientation of crystallites with improved grain structure (Awodugba, Adedokun, and Sanusi, 2012). The optical and structural properties of the films were studied after annealing to find out if they are useful potential materials for solar cells and semiconductor electronic device applications.

2. Experimental Details

2.1. Sample Preparation

ZnAgS thin films were prepared using the chemical bath deposition technique. The reaction bath is constituted in a 50ml beaker which contained 3ml of 1M zinc acetate ($Zn(COOH)_2$) solution, 3ml of 1M silver nitrate ($Ag(NO_3)$) solution, 3ml of 1M thioacetamide (CH_3CH_2NS) solution and 3ml of triethanolamine (TEA) which was used as the the complexing agent. 3ml of 88% ammonia was also used, which helped in stabilizing the pH. The substrates consist of microscopic glass slides of dimension $76\text{mm} \times 26\text{mm} \times 1\text{mm}$. Before the usage of the slides, they were degreased by soaking them in aqua regia, a mixture of concentrated HNO_3 and HCl acids in the ratio 1:3. The substrates were removed after 48 hours and washed properly in a detergent solution, rinsed in distilled water and drip-dried in air. The properly degreased and cleaned substrate surface has the advantage of producing highly adhesive and uniform films. The $Zn(COOH)_2$ served as the precursor for the Zn^{2+} ion, the $AgNO_3$ served as the precursor for the Ag^+ ion while the CH_3CH_2NS served as the precursor for the S^{2-} ion. The $Zn(COOH)_2$ solution was colourless. The colour changed to a light pink solution when the $AgNO_3$ solution was poured into the beaker. The colour remained the same when the TEA and the ammonia were poured in turns. But when the CH_3CH_2NS solution was poured into the beaker, the solution turned to a shiny dark brown colour immediately. The mixture was stirred rigorously with a glass rod to obtain uniform solution. The glass slides were placed vertically in the reaction bath with the help of synthetic foams. After 24 hours, the glass slides were removed, rinsed with distilled water and dried in air. The reaction mechanism is as follows:

$$\mathrm{Zn(COOH)_2 + AgNO_3 + TEA \leftrightarrow [ZnAgTEA]^{2+}} \quad (1)$$

$$\mathrm{[ZnAgTEA]^{2+} \leftrightarrow Zn^{2+} + 2Ag^+ + TEA} \quad (2)$$

$$\mathrm{CH_3CH_2NS + 2OH^- \leftrightarrow SH^- + CH_2CN + 2H_2O} \quad (3)$$

$$\mathrm{SH^- + OH^- \leftrightarrow S^{2-} + H_2O} \quad (4)$$

$$\mathrm{Zn^{2+} + 2Ag^+ + S^{2-} \leftrightarrow ZnAg_2S} \quad (5)$$

Several samples of the ZnAgS thin films were deposited using the same technique. Some of the thin films were annealed at 373K and 423K after deposition.

2.2. Characterization

The optical absorbance and transmittance of the annealed thin films were investigated using a dual-beam Shimadzu UV-1600 spectrophotometer within the wavelength range of 200nm-1200nm. The structural properties of the films annealed at 373K and the as-deposited films were studied using a Shimadzu 6000 model diffractometer.

3. Results and Discussion

The chemical bath deposition is based on controlled precipitation of the desired compound (ZnAgS in this case) from the reaction solution (Eya, Ekpunobi, and Okeke, 2005). Fast precipitation implies that a thin film cannot be formed on a substrate immersed in the solution. However, if the reaction is slow, neutral atoms would be formed on the substrate if the equilibrium condition of the bath is optimized. The thin film samples were shiny dark brown in colour and adhered strongly to the substrates. The absorbance and transmittance as functions of wavelength are shown in figures 1 and 2.

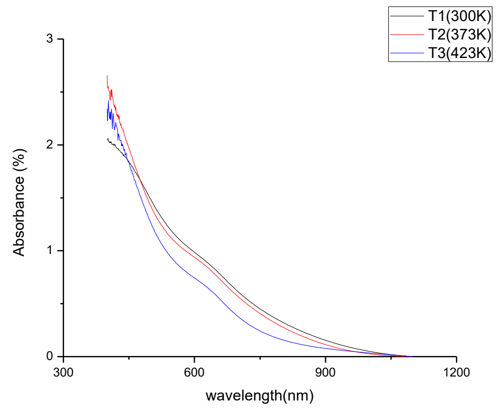

Figure 1: Absorbance as a function of wavelength under different thermal treatments.

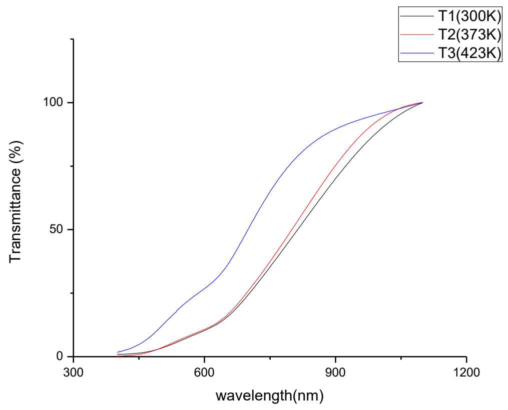

Figure 2: Transmittance as a function of wavelength under different thermal treatments.

Figure 1 shows the absorbance spectrum of the ZnAgS thin films at different annealing temperatures. The films showed similar absorption pattern with the thin film annealed at 373K having the highest absorbance of about 2.7% in the UV region. The absorbance has high values in the UV region and decreases exponentially through the visible (VIS) region into the near-infrared (NIR) region. Since the films absorb most of the UV rays, they can be used as UV filter or shields to protect the skins of man and other animals. The transmittance of the thin films is low for wavelength less than 450nm but increases almost linearly with wavelength in the VIS region and tends to saturate in the NIR region as shown in figure 2. The film annealed at 423K has the highest transmittance in the visible region (about 80%). The low transmittance in the UV region is due to the high absorbance. The high transmittance in the visible region makes the films good glazing materials for the illumination of the interior of a house or room. The admittance of infra-red rays by the thin films suggests that the films can be a good material for the warming of the interior of poultry houses which helps to keep the chicks warm. Figure 3 shows the reflectance as a function of wavelength. It shows a high reflectance in the UV and visible regions. The reflectance decreases steeply from the VIS region to low values down to zero in the near-infrared region. The films annealed at 373K and the as-deposited films have higher reflectance values, for instance 86% at 619nm, in the visible region. The high reflectance in the visible region implies that the thin films can be used in the construction of driving mirrors and in the windscreen of cars to avoid dazzling light entering the driver's eyes at night which might cause accidents. The refractive index versus wavelength under different thermal conditions is shown in figure 4. The refractive index is high in the first part of the visible region with the thin film annealed at 373K having the highest value of about 1.45 at the wavelength of 401nm. The refractive index of the films decreases exponentially to zero in the NIR region. The high refractive index suggests that the films can be promising materials for making photovoltaic devices.

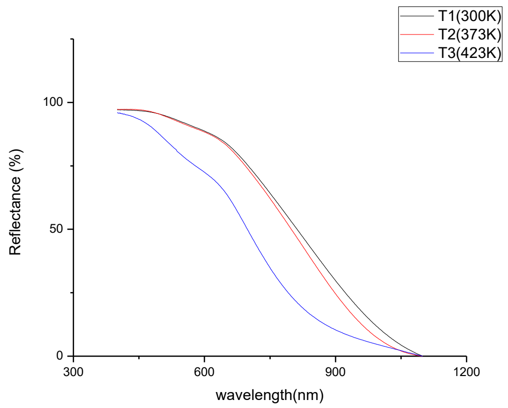

Figure 3: Reflectance as a function of wavelength under different thermal treatments.

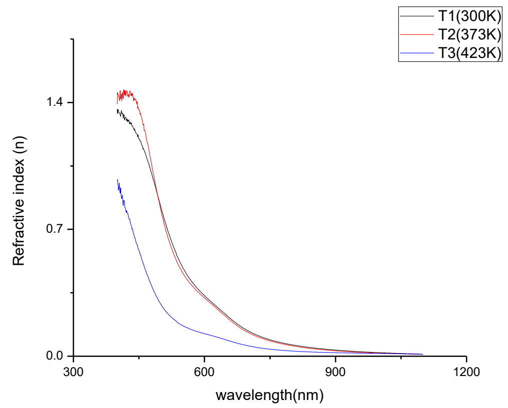

Figure 4: Refractive index as a function of wavelength under different thermal treatments.

Figures 5 and 6 show the absorption and the extinction coefficients as functions of wavelength. The absorption coefficient for all the samples shows high values in the UV region but decreases exponentially through the visible region into the NIR region. The extinction coefficients of the films are very high in the UV and the first half of the VIS regions which show that the films absorb much of the electromagnetic radiation that passes through them. The film annealed at 373K has the highest extinction coefficient value of about 201 at a wavelength of 400nm. The extinction coefficient of the films decreases to zero from UV region to the NIR region. The figure also shows a steep linear relationship indicating sharp increases in the absorption with increasing wavelength, and it conforms to the relation:

$$K = \frac{\alpha\lambda}{4\pi} \qquad (6)$$

where K is the extinction coefficient, α is the absorption coefficient, and λ is the wavelength.

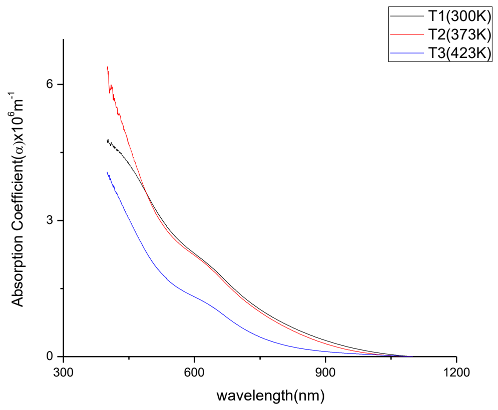

Figure 5: Absorption coefficient as a function of wavelength under different thermal temperatures.

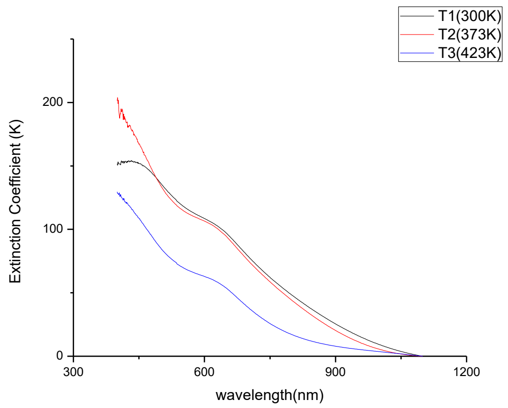

Figure 6: Extinction coefficient as a function of wavelength under different thermal treatments.

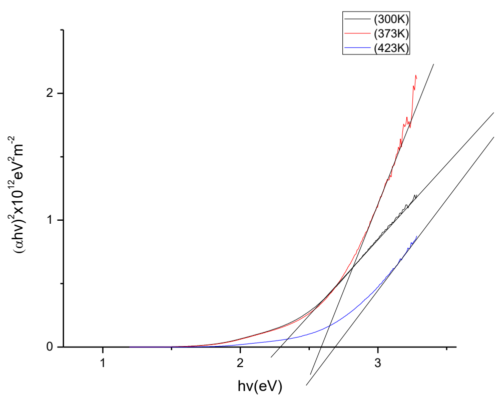

Figure 7: A plot of $(\alpha hv)^2$ as a function of photon energy (hv).

The band gap of the ZnAgS was determined by plotting $(\alpha hv)^2$ as a function of hv as shown in figure 7. Extrapolating the linear portion of the curve to $(\alpha hv)^2 = 0$ gives the band gap energy. The band gaps obtained are 1.9eV, 2.45eV, 2.4eV for the as-deposited film and those annealed at 373K, 423K respectively. The range of the band gap indicates that ZnAgS thin films could be applied in solar cell fabrication.

The results of the structural studies of ZnAgS thin films were carried out using the Shimadzu model 6000 diffractometer. The as-deposited thin film has (100), (100) and (210) strongest peaks while the film annealed at 373K shows (100), (100), (211) strongest peaks as shown in figure 8 and 9.

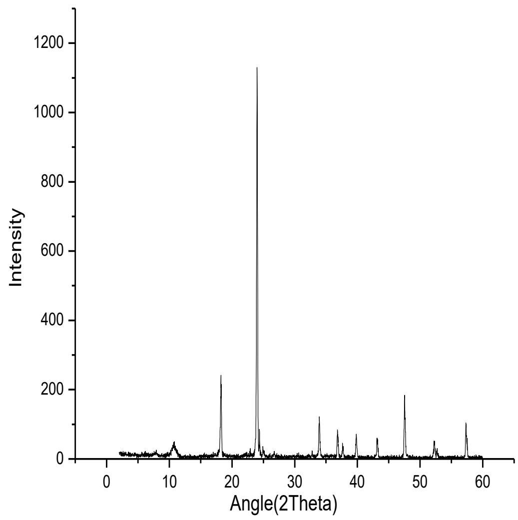

Figure 8: X-ray diffraction spectra for the as-deposited ZnAgS thin film.

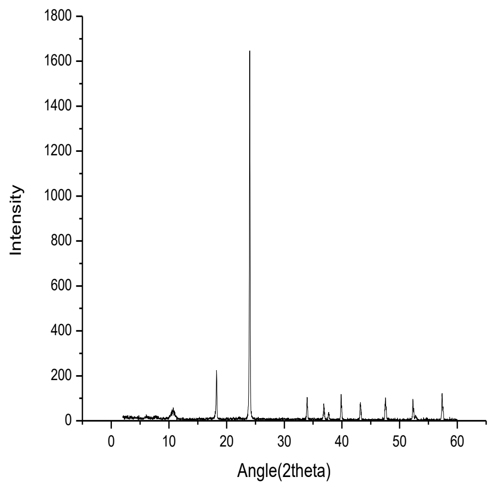

Figure 9: X-ray diffraction spectra for the ZnAgS thin film annealed at 373K.

The intensity of the peaks increased as the annealing temperature increases. The many peaks shown in the diffractograms reveal that the thin films grown in this study are crystalline in nature. The grain size D was calculated from Scherrer's formula (Ezugwu, Ezema, and Asogwa, 2010), which is given as:

$$D = \frac{K\lambda_x}{\beta\cos\theta} \quad (7)$$

Where K is a dimensionless constant, 2Θ is the diffraction angle, λ_x is the X-ray wavelength and β is the full width at half maximum (FWHM) of the diffraction peak. The grain sizes of the different diffraction peaks are shown in Table 1.

Table 1: Deposition parameters and grain size of the ZnAgS thin films.

Diffraction peaks	D values for Y01(nm)	D values for Y02(nm)
100	0.752	
100	0.826	
210	0.934	
100		0.947
100		1.072
211		1.145

where Y01 and Y02 represent the as-deposited film and the film annealed at 373K.

The compositional characterization of the films was done in Ife, Osun state, Nigeria. Figure 10 shows the RBS of the ZnAgS thin film. The results, as shown in table 2 reveal the compositional percentage of the elements in the deposition. From the results gotten, we can can say that the as-deposited film is ZnAgS thin film with small amount of Pb impurities.

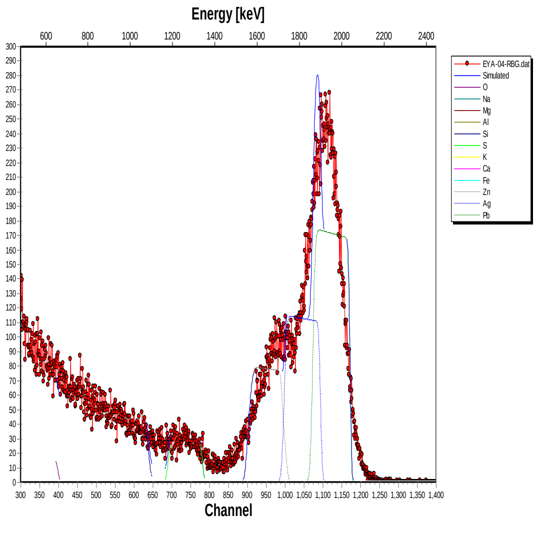

Figure 10: **The RBS spectrum for ZnAgS thin film.**

Table 2: Elemental composition of ZnAgS thin film sample.

Element	Percentage Composition
Zn	31.66%
Ag	18.95%
S	39.71%
Pb	9.68%

4. Conclusion

The deposition of ZnAgS thin films was successfully done using the chemical bath deposition (CBD) technique. The films were strongly adhered to the substrates and retain their properties for a long time. Literatures on ZnAgS were rare to get maybe because not much studies has been carried out on it and hence, this work will form a basis for further research applications. It has been observed from the results gotten that the ZnAgS thin films are crystalline in nature and are useful material for use as UV shields, construction of poultry houses, in driving mirrors. It also finds application in solar cell technology.

5. References

1. Awodugba, A.O., Adedokun, O., Sanusi, Y.K. (2012). Study of Optical and Crystallogaphic Properties of CBD grown CdS thin films. *International Journal of Research and Reviews in Applied Sciences*. 12(3).
2. Eya, D.D.O., A.J. Ekpunobi, and C.E. Okeke. (2005). Structural and Optical properties and applications of Zinc Oxide thin films prepared by chemical bath deposition technique. *Pacific Journal of Science and Technology*. 6(1), 16-22.
3. Ezenwa, I., A. Ezenwa, and Okoli, L.N. 2015. Synthesis and Characterization of Chemically deposited Iron Copper Sulphide (FeCuS) thin films. *Asia Pacific Journal of Research*. 1(16), 14-21.
4. Ezugwu, S.C., Ezema, F.I., and Asogwa, P.U. (2010). Synthesis and Characterization of ternary $CuSbS_2$ thin films: Effect of deposition time. *Chalcogenide letters*. 7(5), 341-348.
5. Fajimi, G.R, and J.S.A. Adelabu. 2009. Preparation and Characterization of Chemically deposited Cadmium Sulphide thin films. *Pacific Journal of Science and Technology*. 10(2), 817-822.
6. Mane, R.S, and Lokhande, C.D. (2000). Chemical deposition Method for Metal Chalcogenide thin films. *Materials Chemistry and Physics*. 65(1), 1-31. https://doi.org/10.1016/s0254-0584(00)00217-0
7. Okoli, L.N., Ezenwa, I.A., Elekalachi, C.I., Okpaneje, O.T., and Okoye, V.C. (2016). Time Optimization of Chemically deposited Cadmium Silver Sulphide (CdAgS) ternary thin films at Room Temperature. *American Institute of Science, Physics Journal*. 2(2), 88-95.
8. Oriaku, C.I., and Osuwa, J.C. (2008). Analysis of thin Chalcogenide PbS films prepared from chemical
9. bath. *Pacific Journal of Science and Technology*.
   9(2), 461-467.
10. Uhuegbu, C.C. and babatunde, E.B. (2010). Spectra analysis of copper zinc sulphide ternary thin film grown by solution growth technique. *American Journal of Scientific and Industrial Research*. 1(3), 397-400.