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Effect of Different Silar Cycle on Chemically Deposited ZINC Copper Sulphide (ZnCuS)

Kola Odunaike[1] , *Q. A. Adeniji*[2,*], *A. L. Sheu*[3], *T. O. Fowodu*[1] *and T. A. Alabi*[4]

1Department of Physics, Olabisi Onabanjo University, Ago-Iwoye, Nigeria
2Department of Physics, Federal University of Kashere, Gombe State, Nigeria
3Department of Physics, Emmanuel Alayande College of Education, Oyo, Nigeria
4Manufacturing Department, Scientific Equipment Development Institute, Minna, Nigeria

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Abstract: Ternary thin films of ZnCuS were grown on soda lime glass (SLG) substrate by Successive Ionic Layer Adsorption and Reaction (SILAR) technique at room temperature with one molar concentration of zinc (Zn) ions (1 M) at varying SILAR cycles (20 and 30 cycles) of deposition. Zinc chloride, copper (II) chloride dihydrate (cuprous chloride) and thiourea serves as precursors for zinc, copper and sulphur ions respectively with EDTA, TEA and NH4OH as complexing agents. The thin films grown were characterized using Avantes UV-VIS spectrophotometer (in wavelength range of 200 nm – 1000 nm) and Four Point Probe machine. The results suggest that the reflectance, transmittance and absorbance of the films show appreciable change for varying the SILAR cycles. The optical properties showed that the thin films have high reflectance (with a peak value of 30%) in the UV-region and low reflectance in the VIS-NIR-regions. The transmittance was 80% around 500 nm wavelengths. However, it was observed that the energy band gap decreased as the SILAR cycle increases (range from 3.87 eV and 3.58 eV). In addition, it was also observed that the grown thin films exhibited high absorbance (between 2.5 and 3.4) in the UV region of the electromagnetic spectrum between wavelength of 200 nm to 300 nm which show a decrease with increase in wavelength of solar radiation and the films showed relatively low absorbance in the VIS-NIR region of the spectrum. The electrical result of the thin films shows that resistivity decreases while conductivity increases as the SILAR cycle increases.

Keywords: Growth, Zinc Copper Sulphide (ZnCuS), SILAR Technique, Thin films, Characterization.

1 Introduction

Searching for novel semiconductor materials for efficient solar energy conversion, ternary thin films have been investigated extensively [1]. The preparation and study of physical properties of ternary chalcogenide compounds have increased in recent years due to their wide range of applications. Ternary compounds are found to be suitable materials for optoelectronic device applications and good materials for window layer solar cells [2]. There are possible applications of Ternary chalcogenide thin films to solar cells, light emitting diodes (LEDs) and non-linear optical devices [3]. Different chemical techniques including Chemical Bath Deposition (CBD), Spray Pyrolysis (SP), electrodeposition and many more have been used to synthesize thin films. All these experimental techniques either demand stringent reaction conditions such as high temperature and pressure, and hazardous chemicals or both [4;5]. Among the different methods for film deposition, the relative simplicity of the Successive Ionic Layer Adsorption and Reaction (SILAR) method and its potential application for large area deposition make it very attractive [5]. Easy control on film thickness by adjusting number of deposition cycles is the beauty of this method [4]. Using SILAR method to prepare thin films, substrates are immersed into separately placed cationic and anionic precursors and precipitate formation in the solution, thus wastage of the material would be avoided [6]. The first report on Successive Ionic Layer Adsorption and Reaction (SILAR) was made by [7] and it is a method that could be effectively used to deposit nanomaterials thin films. It is also useful for the deposition of thin films of chalcogenide groups such as I–VI, II–VI, III–VI, V–VI, VIII–VI binary and I–III–VI, II–II–VI, II– III–VI, II–VI–VI and II–V–VI ternary chalcogenides and composite films. In SILAR method, substrates are immersed into separately placed

*Corresponding author E-mail: qadeniji@yahoo.com

cationic and anionic precursors and precipitate formation in the solution. Wastage of the materials are always avoided.
Many research works have been carried out on Zinc Copper Sulphide (ZnCuS) thin film using different techniques. Among the techniques that have been used for synthesizing ZnCuS nanostructures include Chemical Bath Deposition (CBD), patterned catalytic growth, substrates-induced vapor deposition, solution-phase deposition, chemical reaction etc. These methods require high temperature, expensive substrates, tedious procedures, sophisticated equipment and rigorous experimental. Hence it is necessary to find out a simple method to synthesize ZnCuS nanostructures to tackle these anomalies. In view of this, a simple, environmentally friendly, solution-based method with some modifications to produce ZnCuS thin film using Successive Ionic Layer Adsorption and Reaction (SILAR) techniques was employed for this study.

2 Experimental Details

Also the reagents for SILAR technique were Stoichiometric quantities of analytical grade reagents of zinc chloride ($ZnCl_2$), copper(II)chloridedihydrate (cuprous chloride) ($CuCl_2.2H_2O$) and thiourea ($(NH_2)_2CS$) serves as precursors, ethylenediaminetetraacetate (EDTA) ($C_{10}H_{16}N_2O_8Na_2.2H_2O$) and triethanolamine (TEA) ($N(CH_2CH_2OH)_3$), were used as complexing agents with deionized water and ammonia solution (NH_4OH). The films were deposited on glass substrate (76.2mm × 2.5mm × 1.2mm) when immersed into the precursors. The deposition of ZnCuS thin film was carried out using four beakers system labelled (Beaker I, II, III and IV) at room temperature. Figure 1 shows the experimental set-up of SILAR techniques for the deposition process. In order to remove the organic and inorganic impurities, the glass substrates with dimension 76.2 mm × 2.5 mm × 1.2 mm were first degreased in concentrated trioxonitrate (V) acid (HNO_3) for 48 hours, washed with detergent, rinsed in distilled water and dried in air. The degreased dry surface provides nucleation center for the growth of the film, hence yielding highly adhesive and uniformly deposited film on the surface of the substrates. A four-beaker system solution was obtained by first preparing 5 mls of 1.0M zinc chloride, 5 ml of 1.0M cuprous chloride, 3ml of 14M ammonia solution, 3 ml of 7.4 M TEA and 3ml of 0.1 M EDTA. These were placed into a 50ml beaker (Beaker I) and was stirred with magnetic stirrer at room temperature to get homogeneous solution which served as cationic precursor with respective pH and temperature of 9.09 and 31.9 ºC. Then 20ml of distilled water was put into two different 50ml beakers (Beaker II and IV). The last beaker (Beaker III) contains 20 ml of 1 M thiourea which serves as anionic precursor with pH and temperature of 9.49 and 30.3 ºC. The pH and temperature of the precursors were measured with Mettler Toledo AG 8603 pH meter. The zinc, cuprous chloride and thiourea serves as source of Zn^{2+}, Cu^{2+} and S^{2-} respectively while the TEA and EDTA as complexing agent slowed down the reaction for the formation of solid thin film on the substrate and the ammonia solution (NH_4OH) served to stabilize the pH of the mixtures.The cationic and anionic solution were deep blue and whitish in colour while the distilled water in beaker II and IV was initially colourless but later beaker II changed to light blue during the deposition process. The substrate was kept vertically in each beaker at every immersion to prevent it from slanting or falling in the beaker. The deposition was done at room temperature for 80 seconds dip time per cycle. One SILAR cycle will consist of four steps: (i) adsorption of both zinc and copper species for 20s, (ii) rinsing with distilled water for 20s to remove excess adsorbed or loosely bounded zinc and copper species, (iii) reaction with thiourea precursor solution for 20s to form stable ZnCuS, and (v) rinsing with purified water for 20s to remove excess or unreacted species. By repeating such deposition cycle 20 and 30 times, ZnCuS thin film were obtained respectively. After deposition, the substrates were removed and left to air-dried. The samples deposited at 20 and 30 cycles were labeled ZnCuS-20and ZnCuS-30 respectively.

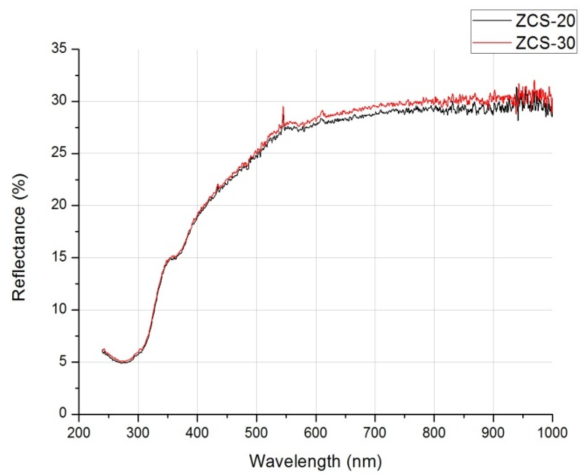

Fig.1: Reflectance against wavelength for ZnCuS thin films deposited for 20 and 30 cycles.

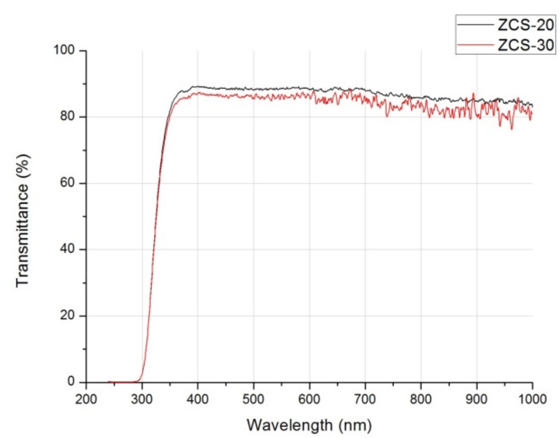

Fig.2: Transmittance against wavelength for ZnCuS thin films deposited for 20 and 30 cycles.

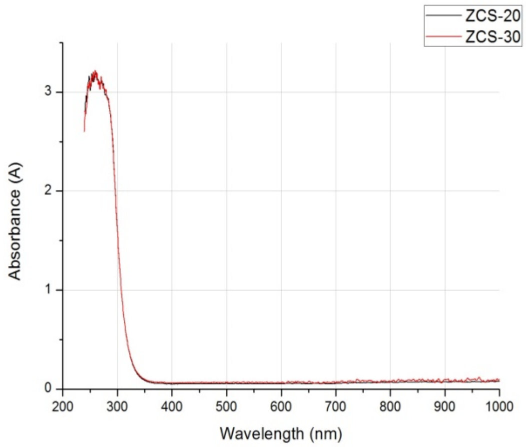

Fig. 3: Absorbance (A) against wavelength for ZnCuS thin films deposited for 20 and 30 cycles.

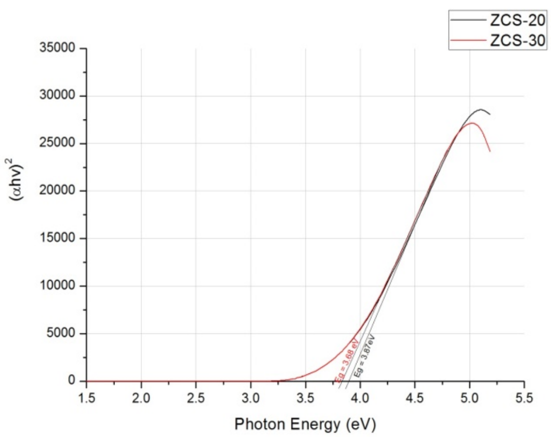

Fig. 4: Graph of $(\alpha h\nu)^2$ against Photon energy for ZnCuS thin films deposited for 20 and 30 cycles.

Table 1: Electrical Result of the deposited ZnCuS thin films.

Samples	Voltage (v)	Current (A)	Sheet resistance, R_s (Ω/m^2)	Resistivity (Ωm)	Conductivity (Sm^{-1})
ZnCuS-20	0.14	8.50×10^{-8}	7.47×10^{6}	1.49×10^{6}	6.70×10^{-7}
ZnCuS-30	0.36	8.40×10^{-8}	1.94×10^{7}	3.86×10^{6}	2.57×10^{-7}

From Figure 1, it was observed that average reflectance was below 30% for both 20 and 30 SILAR cycles deposited films. They both have the same reflect at the initial until the 30 SILAR cycle thin film was slightly greater than the one with 20 SILAR cycle at about 550 nm wavelength, this made the thin film to be a good material for the window layer part of the solar cell. Figure 2 shows the transmittance for the ZnCuS thin films. Both thin films 20 and 30 SILAR cycles exhibited transmittance above 80% for wavelength around 500 nm. There was a fall in the percentage transmittance of the films around 750 nm, They both have the same transmittance at the initial until the 20 SILAR cycle thin film was slightly greater than the one with 30 SILAR cycle at about 350 nm wavelength, this could be attributed to an indication of a strong increase in absorption due to the rapid change in the optical absorption coefficient, and is an indication that some states have been created in the region between the conduction and valence band. The optimum transmittance at λ=900 nm was found to be 85%. This transmittance value of the thin film is good for the window material to be used in solar cells. Figure 3 show that ZnCuS films have good absorption at short wavelength region between 250 nm and 300 nm. The absorption decreased with increasing wavelength of solar radiation. From the figure there was a decrease in absorbance up to a wavelength, λ=990 nm, then a slight increase in absorption. The deposited ZnCuS Thin film of 20 and 30 SILAR cycle have the same absorbance of 3.4% at wavelength 300 nm. Figure 4 shows the estimated energy band gap values of 3.87 eV and 3.58 eV for 20 and 30 SILAR cycle respectively. The extrapolated band gaps energy values for ZnCuS thin films vary from the range of 3.82 eV to 3.91 eV. It was observed that the band gap value decreased as the SILAR cycle increases. Table 1 shows the sheet resistance calculated from the I-V characteristics for the ZnCuS thin film as deposited for 20 and 30 SILAR cycle with values of 7.47×10^6 Ωm to 1.94×10^7 Ωm respectively. From the table, it was observed that resistivity decreased with increase in SILAR cycle and it was between 1.49×10^6 Ωm and 3.86×10^6 Ωm. The respective conductivities are 6.70×10^{-7} Sm^{-1} and 2.57×10^{-7} Sm^{-1}. This shows that conductivity increases as the SILAR cycle increases which enhances the electrical properties of ZnCuS thin films. This surely made the ZnCuS a good material for solar cell fabrication.

4 Conclusions

The thin films Zinc Copper Sulphide (ZnCuS) deposited through Successive Ionic Layer Adsorption and Reaction (SILAR) varying the SILAR cycle mostly increased and in some times decrease the properties of the thin film. These provide wide range of application of the thin film in the following: solar cell fabrication, screening off UV radiation that is harmful to human beings and animal due to its high absorbance, low transmittance and low reflectance in UV region, coating of poultry building, eye glasses coating, solar thermal conversion, solar control, anti-reflection coating and window layers in solar cells.

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