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EFFECT OF SILAR CYCLE ON THE CRYSTALLINE PHASE AND STRUCTURAL PROPERTIES OF COPPER ZINC SULPHIDE (CuZnS) THIN FILMS

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Abstract

Crystalline phase and structure of Copper Zinc Sulphide (CuZnS) thin films deposited on soda-lime glass substrates at room temperature via successive ionic layer and reaction (SILAR) technique was investigated. This study used X-ray diffraction (XRD) analysis to determine the phase purity and crystallinity of the synthesized CuZnS thin films. Using XRD characteristics, the structural properties of CuZnS were examined at 10, 20, and 30 SILAR cycles. The X-ray diffraction pattern, according to the result, varied from $2\theta = 5.34$ at 10 SILAR cycles to $2\theta = 8.206$ at 30 SILAR cycles. The XRD patterns indicated that the synthesized CuZnS films were polycrystalline, exhibiting orientation along various planes and phases. Consequently, the crystalline characteristics of the formed thin films were enhanced with an increase in SILAR cycles. This study showed that the deposited CuZnS thin films may be good candidates for absorbance layers in solar cells as a result of its amorphous structure.

Key words: CuZnS thin films, SILAR cycle, glass substrates (SLG), crystalline phase, structural properties.

1.0 Introduction

There is need to create new types of solar energy conversion materials because of the global energy problems and rising energy demand. Devices with high power and energy density conversion could serve as a renewable energy backup. The world's energy needs are constantly growing as a result of the population's rapid growth and the depletion of natural resources, such as fossil fuels. When paired with appropriate optical and electrical characteristics, copper, zinc, and sulfur—all of which are cheap, non-toxic, and abundant in the earth—make a potential absorber material for thin-film solar cell construction (Jose & Santhosh Kumar, 2017). Several strategies have lately been used to identify the search for thin film materials for solar energy conversion and other related applications. Because of their many uses, ternary chalcogenide compounds have been prepared and their physical characteristics studied more recently (Adeniji *et al*., 2021; Fowodu *et al*., 2024). Some transition metal ternary compounds, including $Cd_{x-1}Mg_xS$ (Waleed, 2010), CuAgS (Chukwuemeka, 2011), CuZnS (Odunaike *et al*., 2021), CuMnS (Nwori *et al*., 2021), and FeCuS (Olayiwola *et al*., 2024), have recently been studied for a variety of applications. Ternary compounds are discovered to be acceptable material for optoelectronic device applications and good material for window layer solar cells (Woon-Jo & Gye-Choon, 2003). Ternary chalcogenide thin films have their prospective applications in solar cells, light emitting diodes (LEDs) and non – linear optical devices (Ezema, 2004; Lacomi *et al*., 2006).

Both physical and chemical techniques can be used to deposit thin films on a substrate. Because it is less expensive and less complex than other film deposition techniques, the chemical bath deposition (CBD) approach has been utilized extensively for the deposition of both binary and ternary chemicals. There is considerable interest in the deposition of ternary derivative materials, due to the potential of tailoring both the lattice parameters and the band gap by controlling depositions parameters (Sankapal & Lokhande, 2002). Many techniques have been successfully employed for these purposes: chemical vapour deposition (CVD) (Firgo *et al*., 1989), successive ionic layer adsorption and reaction (SILAR) (Adeniji *et al*., 2020; Fowodu *et al*., 2025) and chemical bath method (Ezenwa & Okoli, 2015). We shall report here the successful growth of crystalline Copper Zinc Sulphide (CuZnS) thin films by SILAR technique on sodalime glass substrates and the compositional properties studied.

2. Materials and methods

2.1 materials

Granulated or powdery form of copper, (cuprous chloride), zinc, (zinc chloride) and sulphur, thiourea ($[NH_2]_2CS$), triethanolamine (TEA), ammonia solution (NH_4OH), ethylenediaminetetraacetate (EDTA) (all were purchased from Sigma Aldrich, Germany and are of 99.99% purity) and with laboratory prepared deionized water were used in this study.

2.2 Methods

2.2.1 Preparation of Glass Substrate

SILAR technique was used in depositing CuZnS. Four beaker systems (Beakers I, II, III, and IV) were used to synthesize CuZnS thin films on sodalime glass substrates (measuring 75 by 26 *mm* and about 1 *mm* thick) that were submerged in the precursors at ambient temperature. The glass substrates were extensively cleaned and degreased for 48 hours by soaking in hydrochloric acid (HCl), in order to eliminate both organic and inorganic contaminants from the surface. After being cleaned and dried in air, the substrates were rinsed in distilled water, which provided them with the benefit of acting as nucleation sites for the development of thin films that were uniformly deposited and extremely sticky.

2.2.2 Preparation of CuZnS

Copper chloride was the source of copper ions (Cu^{2+}) during the deposition. 17.048 gdm^{-3} was prepared and 5 *ml* of 1 M of it was used which served as the ionic precursor. Zinc chloride served as the source of zinc ions (Zn^{2+}) during the deposition. 13.62 g/dm^3 was prepared and 5 *ml* of 1 M of it was used. Both the copper chlorides of copper and zinc served as the cationic precursor. The pH and the temperature of the cationic solutions were 9.51 and 26.9°C respectively. More so, thiourea was used as the source of sulphur ions (S^{2-}) during the bench work which is the anionic precursor. 7.612 gdm^{-3} was prepared and 20 *ml* of 1 M of it was used at 5.5 pH and 26.9°C. The pH and the temperature were measured using a portable multifunction EZ-9902 TDS/EC/pH/TEMP meter.

2.2.3 Deposition and Characterization of the Thin Films

A four-beaker system solution was obtained by first preparing 5 *ml* of 1 M zinc chloride, 2 *ml* of 1M cuprous chloride, 3 *ml* of 14M ammonia solution, 3 *ml* of 7.4 TEA and 3 *ml* of 0.1M EDTA were all placed in to a 50 *ml* beaker (Beaker 1) and followed by magnetic stirring at room temperature, a homogenous solution was obtained which served as cationic precursor. Then, 20 *ml* of distilled water was also put in to two different 50 *ml* beaker (Beaker 2 and 4). Finally, 20 *ml* of 1 M thiourea was placed in to another 50 *ml* beaker (Beaker 3) and this solution served as the anionic precursor. The pH and temperature of the precursor was noted with EZ-9902 TDS/EC/pH/TEMP meter. The zinc chloride, cuprous chloride and thiourea served as source of Zn^{2+}, Cu^{2+} and S^{2-} respectively while the TEA and EDTA as complexing agents in other to slow down the reactions for the formation of the thin films on the substrates whereas NH_4OH stabilizes the pH of the homogenous mixtures.

At every immersion, the substrate was maintained vertically in each beaker to avoid slanting within the beaker. For 120 seconds of dip time per cycle, the deposition was done at room temperature. A single SILAR cycle comprised of four stages: a 30-second adsorption phase for both Zn^{2+} and Cu^{2+} species, followed by a 30-second distilled water rinse to eliminate any surplus adsorbed or loosely bounded Zn^{2+} and Cu^{2+} species, a 30-second reaction with thiourea precursor solution to generate stable CuZnS, and a 20-second purified water rinse to eliminate any excess or unreacted species or powdery CuZnS. Thin films of CuZnS were synthesized, respectively, by repeating this deposition cycle 10, 20, and 30 times. The substrates were taken out and given time to air out after the deposition. In addition, a substrate without any film was used as control, making the samples obtained four. Figure 1 displays the schematic experimental set-up for the SILAR deposition of CuZnS.

The phase purity and crystallinity of the prepared CuZnS ternary nanostructured thin films were identified by X-ray diffraction analysis. The XRD patterns of the CuZnS films, synthesized at different SILAR cycles of 10, 20 and 30 are shown in Figures 2 (a) - (d).

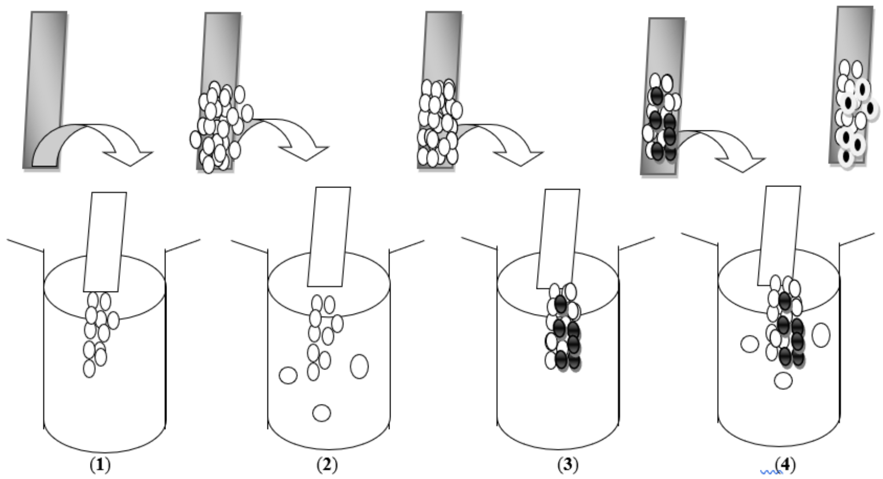
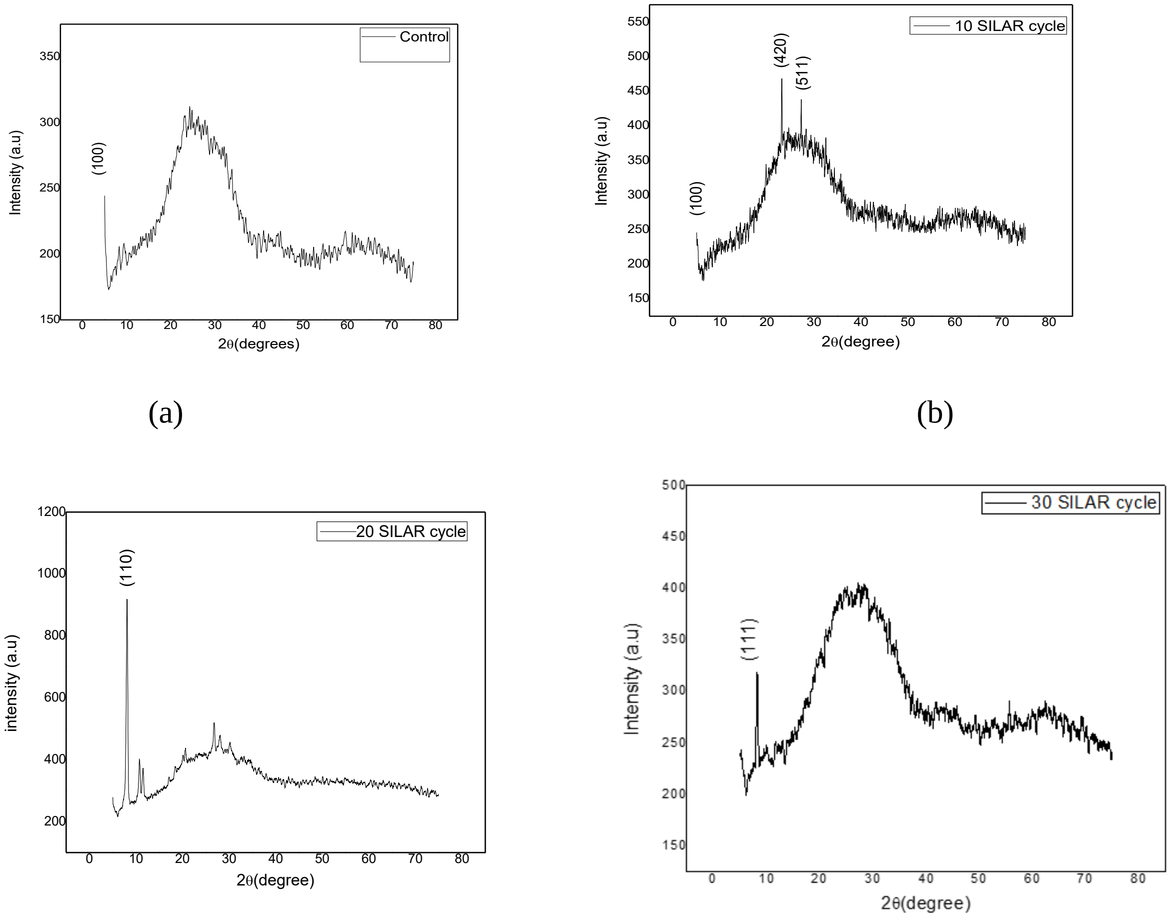


Figure 1: Schematic experimental set-up for the SILAR deposition process of CuZnS thin films

3.0 Results and discussion



(a)

(b)

(c)

(d)

Figure 2: X-ray diffraction pattern of SILAR-grown CuZnS thin film at (a) Control (b) 10 cycles (c) 20 cycles (d) 30 cycles

Figure 2(a) shows the X-ray diffraction peaks of the control at 2θ = 5.08121^0 indexed at (100). The structure showed a humped amorphous structure with a weak intensity, this is because there was no deposition done to the control soda lime glass substrate (SLG).

Figure 2(b) illustrates XRD pattern of the CuZnS thin films deposited at 10 SILAR cycles. The pattern exhibits two broad peaks, observed at around 2θ = 5.34^0, 23.174^0 and 27.27^0 corresponding with the reflections of CuZnS with major reflection around (100), (420) and (511). The presence of the peaks indicated the crystal nature of the deposited thin film. Increased intensity was observed as SILAR cycles increased from 0 to 10. This showed improvement in the crystallinity as a result of increase in film thickness as SILAR cycles increased. The improvement in the crystallinity could be of the films as SILAR cycles increased (Egwunyenga, 2021).

Figure 2(c) is the XRD pattern at 20 SILAR cycle of deposition, the sample have a crystal grown at 2θ = 8.04866^0 indexed at (110) orientation plane this indicates a peak suppression of the two peaks from this sample, this phenomenon may occur due to changes in the crystal symmetry or lattice distortion caused by the higher SILAR deposition cycles.

In Figure 2(d), the peak shifted to 2θ = 8.206^0 indexed at (111). Shift occurs due to changes in the crystal lattice parameters caused by the substitution of Cu or S atoms with Zn atoms and it can also be observed as a slight deviation from the expected positions of CuS peaks. It is observed from the XRD patterns that the CuS, CuZnS and ZnS films are polycrystalline with orientation along different planes and phases. The crystalline of these thin films are improved with increasing SILAR cycles.

Conclusively, increase in the number of SILAR cycles leads to thicker films and can affect structural properties like crystallinity, grain size, and porosity. The 10, 20, and 30 SILAR cycles result in improved crystallinity, larger grain size, and reduced porosity as the film becomes more compact. These changes could enhance the material's electrical, optical, and catalytic properties, making it more suitable for various applications like solar cells, sensors, and photocatalysis (Ali *et al*., 2014).

4. Conclusion

CuZnS thin films were deposited at room temperature and natural atmospheric condition using SILAR approach and the structural characterization were analyzed. It can be said that the ternary films are polycrystalline with a better peak at 10 and 20 SILAR cycles.

The characterization of the thin films was not sufficiently performed in this work due to the lack of laboratory instruments and funds. For this reason, selected samples were chosen for characterization techniques where other properties of the deposited thin films such as thickness, optical properties and Hall Effect were not investigated. The characterization of such properties should be carried out in order to know the bulk properties of the thin films.

Reference

Adeniji, Q.A., Odunaike, K, Fowodu, T.O., and Talabi, A.T. (2020). Influence of SILAR cycle on the Energy bandgap of Iron Copper Sulphide (FeCuS)

Thin Films deposited on SLG Substrate. *Nano World Journal*, 5(4), 49-52, https://doi.org/10.17756/nwj.2019-072.

Ali, A.I., Ammar, A.H., and Abdel Moez, A. (2014). Influence of Substrate Temperature on Structural, Optical Properties and Dielectric Results of Nano-ZnO Thin Films prepared by Radio Frequency technique. *Superlattices and Microstructures*, 65, 285-298. https://doi.org/10.1016/j.spmi.2013.11.007.

Jose, E. and Santhosh Kumar, M.C. (2017). Room temperature deposition of highly crystalline ZnCuS thin film for solar cell application using SILAR method. *Journal of Alloys and Compounds*, 712, 649-656, https://doi.org/10.1016/j.jallcom.2027.04.097.

Egwunyenga, N.J., Onuabuchi, V.C., Okoli, N.L. and Nwanko, I.E. (2021). Effect of SILAR Cycles on the Thickness, Structural, Optical Properties of Cobalt Selenide Thin Films. *International Research Journal of Multidisciplinary Technovation*, 3(4), 1-9, https://doi.org/10.34256/irjmt2141.

Ezenwa, I.A. and Okoli, L.N. (2015). Synthesis and Characterization of Chemically Deposited Iron Copper Sulphide (FeCuS) Thin Films. *Asia Pacific Journal of Research*, I(XXI), 14-21. ISSN: 2320-5504, E-ISSN-2347-4793.

Firgo, D.M., Khan, O.F.Z. and O'Brien, P. (1989). Growth of epitaxial and highly oriented thin films of cadmium and cadmium zinc sulfide by low pressure metal organic chemical vapor deposition using diethylthiocarbamates. *Journal of Crystal growth*, 96, 989, https://doi.org/10.1016/0022-0248(89)90662-3.

Fowodu, T.O., Adeniji, Q.A., Adelaja, A.D., Odunaike, K., Okusanya, A.A., Falayi, E.O., Akinsipo, O.B., Bamidele, K.J., Ogunneye, A.L., Olayiwola, O.G., Saheed, R.A., Leshi, D.A. and Fagbohun, M.A. (2024). Opto-electrical Investigation of Thallium Cuprate (Tl_2Cu) Binary Chalcogenide Thin Films via Chemical Bath Deposition Technique. *Journal of Science and Information Technology (JOSIT)*, 18(1), 177-184, https://journals.tasued.edu.ng/index.php/josit/article/view/96.

Fowodu, T.O., Adeniji, Q.A., Olayiwola, O.G., Adelaja, A.D., Bamidele, K.J., Emegha, J.O., Saheed, R.A., Borah, D.J. and Ikeme, E.K. (2025). Influence of Varying Iron Ion Concentration and Silar Cycle on the Optical Properties of Iron Copper Sulphide (FeCuS) Thin Films on Different Substrates. *Nigerian Journal of Environmental Sciences and Technology (NIJEST)*, 9(1), 278 – 289. ISSN (Print): 2734-259X; ISSN (electronic): 2734-2603, https://doi.org/10.36263/nijest.2025.01.36.

Https://nijest.com/wp-content/uploads/2025/08/278-289_36_Vol.-9-No.-1_NIJEST.pdf.

Iacomi, F., Salaoru, I., Apertroaei, N., Vasile, A., Teodorescu, C.M., Macovei, D. & Optpelectr, J. (2006). Physical Characterization of CdMnS Nanocrystalline thin films grown by vacuum thermal evaporation. *Journal of Optoelectronics and Advance Materials*, 8(1), 266.

Nwori, A.N., Ezenwaka, L.N., Ottih, I.E., Okereke, N.A., Umeokwona, N.S., Okoli, N.L. and Obimma, I. O. (2021). Study of the Optical and Solid-State Properties of Copper Manganese Sulphide (CuMnS) Thin Film Semiconductors for Possible Optoelectronics Applications. *Journal of Physics and Chemistry of Materials*, 8(3); 23-33. E-ISSN: 2348-6341. Available at: https://www.isroset.org.

Odunaike, K, Adeniji, Q. A., Sheu, A. L., Fowodu, T. O., and Alabi, T. A. (2021). Effect of Different SILAR cycle on Chemically Deposited Zinc Copper Sulphide (ZnCuS). *International Journal of Thin Film Science and Technology*, 10(2), 117-120, http://dx.doi.org/10.18576/ijtfst/100208.

Olayiwola, O. G., Odunaike, K., David, T. W., Talabi, A. T., Adeniji, Q. and Fowodu, T. O. (2024). Synthesis of Iron Copper Sulphide (FeCuS) Thin Film and its Characterization. *Nigerian Journal of Physics (NJP)*, 33(1), 43-47. ISSN online: 3027-0936. ISSN print: 1595-0611, https://doi.org/10.62292/njp.v33i1.2024.199.

Sankapal, B.R. and Lokhande, C.D. (2002). Effect of annealing on chemically deposited Bi_2Se_3-Sb_2Se_3 composite thin films. *Materials Chemistry and Physics*, 74, 126-133, https://doi.org/10.1016/S0254-0584(01)00414-X.

Chukwuemeka, U. C. (2011). Solid state properties of copper silver sulfide ternary thin film deposited by solution growth techniques. *Journal of Emerging Trends in Engineering and Applied Science.* 2(1), 113-116, ISSN: 2141-7016. Available at: https://www.jeteas.scholarlinkresearch.org.

Waleed, B. S. (2010). The study of optical properties of thin films $Cd_{x-1}Mg_xS$ prepared by Chemical spray pyrolysis technique. *Journal of University of Anbar for Pure Science*, 4(2), 34-50.

Woon-Jo, J. and Gye-Choon, P. (2003). Structural and electrical properties of $CuGaS_2$ Thin Films by electron beam evaporation. *Solar Energy Materials and Solar Cells*, 75(1-2), 93-100, https://doi.org/10.1016/S0927-0248(02)00110-1

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