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The Growth and Opto-Electrical Characterization of SILAR-grown Iron Copper Sulphide (FeCuS) Ternary Thin Films

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Abstract: This paper reports the growth and characterization of Iron Copper Sulphide (FeCuS) ternary thin films prepared by Successive Ionic Layer Adsorption and Reaction (SILAR) technique onto glass substrate at room temperature of 300 K with varied molar concentrations of Fe^{2+} (0.7 M and 1.0 M) at varied SILAR cycles of deposition (20, 30 and 40 cycles) from aqueous solution of ferrous nitrate, cuprous chloride and thiourea, ammonium solution, EDTA and TEA. The grown thin films were characterized using an AVALIGHT-DH-S-BAL Avantes UV-VIS spectrophotometer and KEITHLEY 4ZA4 2400 Source-meter Four-point probe machine. The results of this study revealed that the reflectance, transmittance and absorbance of the films exhibited appreciable change for Fe^{2+} concentration at the varied SILAR cycles. However, the energy band gaps for direct transitions (ranges from 3.61-3.84 eV) of the thin films decreased with increase in SILAR cycles for the Fe^{2+}.

Keywords: Thin films; Iron concentrations (Fe^{2+}); Iron Copper Sulphide (FeCuS); SILAR technique; Characterization

1 Introduction

Time awaits no one as numerous developments has been made towards meeting the global energy demand with an increasing percentage supplied by renewable resources. Though, the majority of the world's energy consumption seems to be supplied from fossil energy [1]. Photovoltaic (PV) solar cells removes the barrier of climate change vis-a-vis greenhouse effects and improves constant supply of energy needed for the system [2]. Successive Ionic Layer Adsorption and Reaction (SILAR) technique had made large-scale rural electrification not impossible and increased rural area electrification. A Successive Ionic Layer Adsorption and Reaction (SILAR) is required for making uniform and large area thin films, which is based on immersion of substrates into separately placed cationic and anionic precursors. Some of the numerous advantages of SILAR technique are but not limited to, uniform film deposition, control of thickness, deposition temperature maintenance (precisely), low cost and reduction in wastage of materials, deposition of compound materials on a variety of substrates like insulators, semiconductors and metals and many more. To the best of our knowledge, a simple solution based SILAR method has not yet been employed to synthesize a technologically important iron copper sulphide (FeCuS) and this motivated this study. In this study, FeCuS thin films were grown using SILAR technique at varied iron ion (Fe^{2+}) concentrations and SILAR cycle. The optical properties of the grown thin films such as absorbance (A), reflectance (R) and transmittance (T), which were used to calculate other properties such as absorbance coefficient (α). Band gap energy(Eg) of the as-deposited iron copper sulphide (FeCuS) were extrapolated from the coordinates. Electrical characterization of the as-deposited thin films was also investigated and these properties were calculated [3], [4].

2 Experimental Details

2.1 Materials

Laboratory reagents (LR) grades of Ferrous Nitrate, Cuprous Chloride and Thiourea were the precursors and sources of Fe^{2+}, Cu^{2+} and S^{2-} respectively, while ethylene diamine tetraacetate (EDTA) and triethanolamine (TEA) were used as complexing agents. (which slowed down the reactions for the formation of the films) and aqueous NH_3 was added for stabilizing the pH of the mixtures with deionized water.

2.2 Deposition Method of the Film

FeCuS ternary thin films were grown on soda-lime glass substrates with dimension 76.2 mm x 2.5 mm x 1.2 mm when

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immersed into the precursors. The deposition processes were observed using a four-beaker system (Beakers I, II, III and IV) at room temperature (300 K). Figure 1 shows the schematic diagram of SILAR technique for the deposition processes. The glass substrates were first cleansed with concentrated HNO_3 for about two days, rinsed in detergent solution, later with deionized water and air-dried in order to remove the organic and inorganic impurities on them. A four-beaker system solution was obtained by first preparing 5 ml of 1.0 M ferrous nitrate, 5 ml of 1 M cuprous chloride, 3 ml of 14 M ammonia solution, 3 ml of 7.4 M TEA and 3 ml of 0.1 M EDTA were placed into 50 ml beaker (Beaker I) and magnetically stirred at room temperature to obtain a homogenous solution. 20 ml of deionized water was put into two 50 ml beakers differently (Beakers II and IV). Finally, 20 ml of 1 M thiourea was placed into another 50 ml beaker (Beaker III). The solutions in beakers I and III served as cationic and anionic precursors with pH and temperature of 9.14 and 31.9 °C; 9.10 and 30.5 °C respectively which were observed with Mettler Toledo AG 8603 pH meter. The same precursors were prepared by only changing the molarity of ferrous nitrate to 0.7 M.

The cationic and anionic solutions were initially deep green and whitish in colour but later changed to deep brown and yellow respectively during the deposition process while the deionized water in the beakers II and IV was initially colourless which later changed to dark brown and golden yellow respectively during the deposition process. The substrate was kept vertically in each beaker at every immersion to prevent it from slanting or falling into the beaker and the deposition was done at room temperature for 80 seconds dip time per cycle. One SILAR cycle comprised of four steps: (i) adsorption of both iron and copper species for 20 s, (ii) rinsing with deionized water for 20 s to remove excess adsorbed (iii) reaction with thiourea precursor solution for 20 s to form stable FeCuS, and (iv) rinsing with purified water for 20 s to unreacted species of FeCuS. By repeating such deposition cycle 20, 30 and 40 times, FeCuS thin films were obtained respectively. After the deposition, the SLG substrates were removed, rinsed with deionized water (to confirm the deposition) and allowed to air-dried. The as-deposited samples at 20, 30 and 40 cycles with varied molar concentrations of iron (Fe^{2+}) ions (1.0 M and 0.7 M) were labeled FeCuS-20(1.0M), FeCuS-30(1.0M), FeCuS-40(1.0M), FeCuS-20(0.7M), FeCuS-30(0.7M) and FeCuS-40(0.7M) respectively.

3 Results and Discussion

3.1 Results

The optical analyses data of the thin films were obtained from an AVALIGHT-DH-S-BAL Avantes UV-VIS spectrophotometer (in the wavelength range 200-1000 nm) and the electrical characterization was done with the aid of KEITHLEY 4ZA4 2400 Source-meter four point probe machine (manufactured by Tektronix Company).

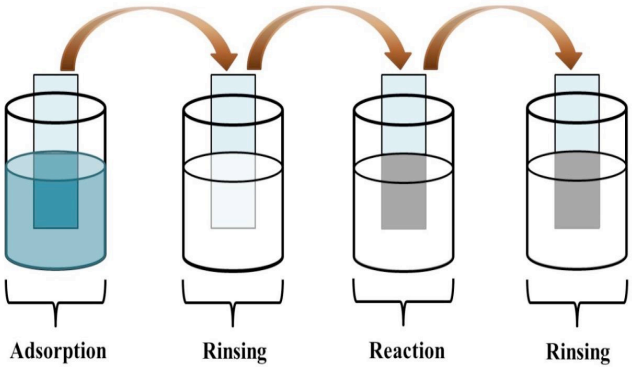

Fig. 1: Schematic diagram of SILAR technique.

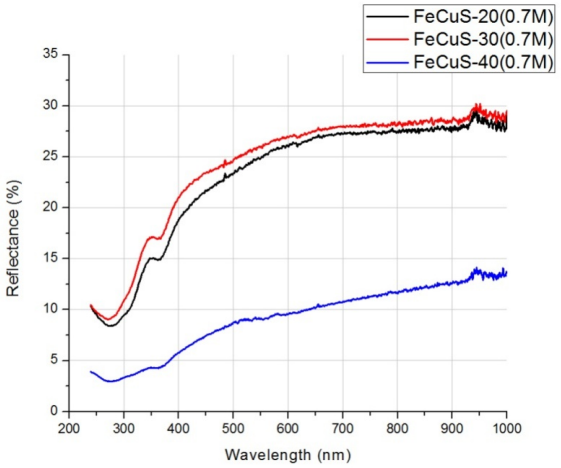

Fig. 2: Reflectance against wavelength of the as-deposited thin films for 0.7 M of Fe ion concentration at 20, 30 and 40 cycles.

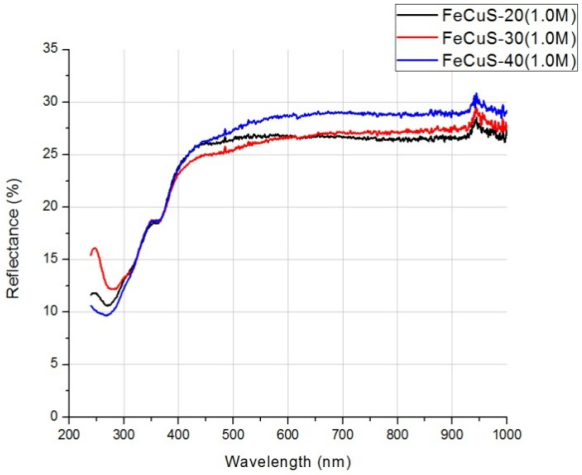

Fig. 3: Reflectance against wavelength of the as-deposited thin films for 1.0 M of Fe ion concentration at 20, 30 and 40 cycles.

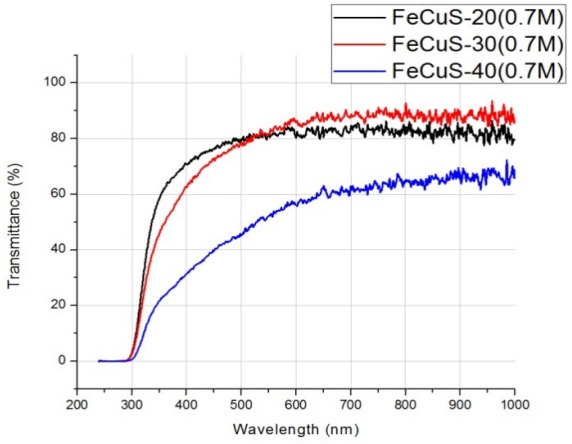

Fig.4: Transmittance against wavelength of the as-deposited thin films for 0.7 M of Fe ion concentration at 20, 30 and 40 cycles.

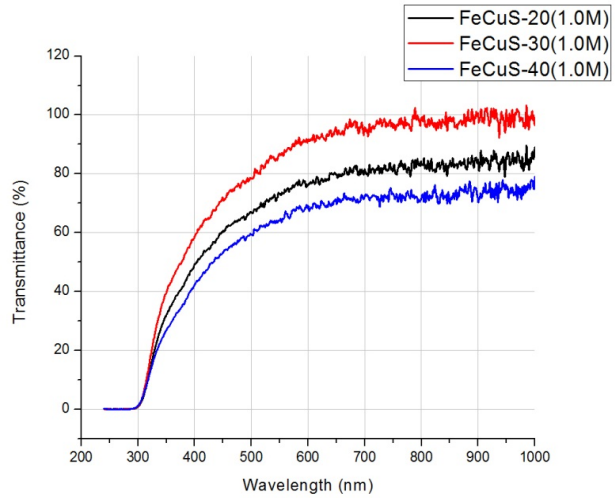

Fig. 5: Transmittance against wavelength of the as-deposited thin films for 1.0 M of Fe ion concentration at 20, 30 and 40 cycles.

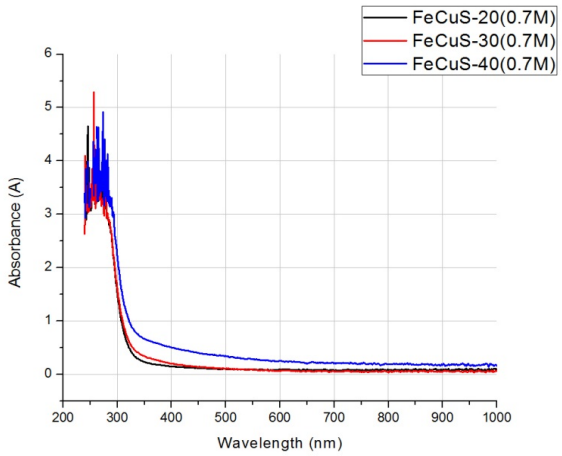

Fig. 6: Absorbance (A) against wavelength of the as-deposited thin films for 0.7 M of Fe ion concentration at 20, 30 and 40 cycles.

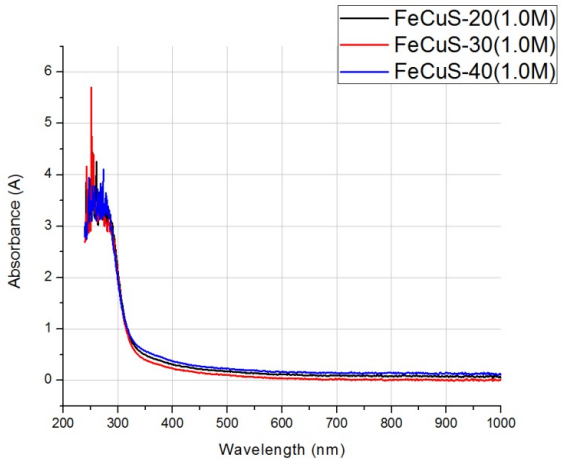

Fig. 7: Absorbance (A) against wavelength of the thin films for 1.0 M of Fe ion concentration at 20, 30 and 40 cycles.

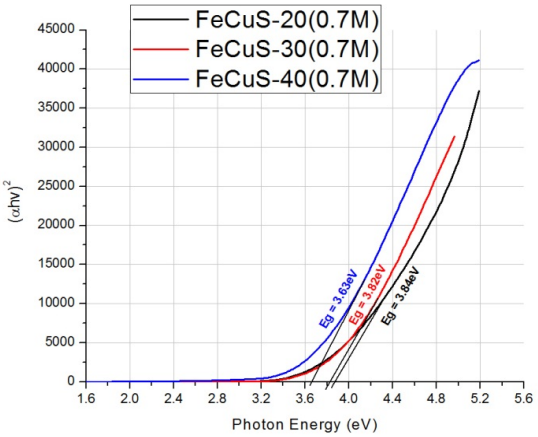

Fig. 8: $(\alpha h\nu)^2$ against Photon energy in eV of the as-deposited thin films for 0.7 M of Fe ion concentration at 20, 30 and 40 cycles.

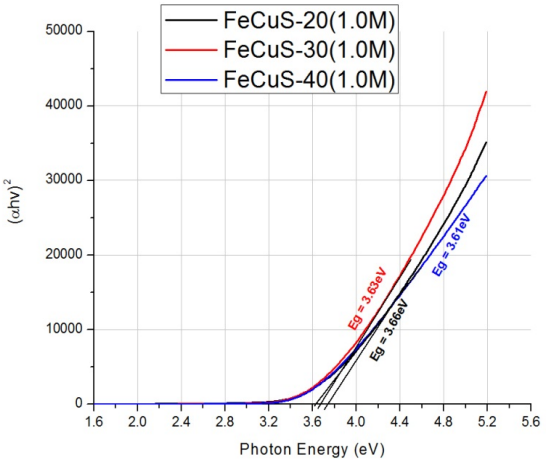

Fig. 9: $(\alpha h\nu)^2$ against Photon energy in eV of the as-deposited thin films for 1.0 M of Fe ion concentration at 20, 30 and 40 cycles.

Table 1: Grown FeCuS thin films Electrical results.

Thin film Samples	Voltage (v)	Current (A)	Sheet resistance, R_s (Ωm^{-2})	Resistivity (Ωm)	Conductivity (Sm^{-1})
FeCuS-20(0.7M)	3.737×10^{-1}	2.226×10^{-8}	7.608×10^{7}	1.522×10^{7}	6.572×10^{-8}
FeCuS-30(0.7M)	3.739×10^{-1}	4.152×10^{-8}	4.082×10^{7}	8.163×10^{6}	1.225×10^{-7}
FeCuS-40(0.7M)	2.159×10^{-1}	3.349×10^{-8}	2.922×10^{7}	5.843×10^{6}	1.711×10^{-7}
FeCuS-20(1.0M)	4.053×10^{-1}	2.650×10^{-8}	6.934×10^{7}	1.387×10^{7}	7.210×10^{-8}
FeCuS-30(1.0M)	3.107×10^{-1}	3.400×10^{-8}	4.141×10^{7}	8.282×10^{6}	1.207×10^{-7}
FeCuS-40(1.0M)	2.473×10^{-1}	3.598×10^{-8}	3.116×10^{7}	6.232×10^{6}	1.605×10^{-7}

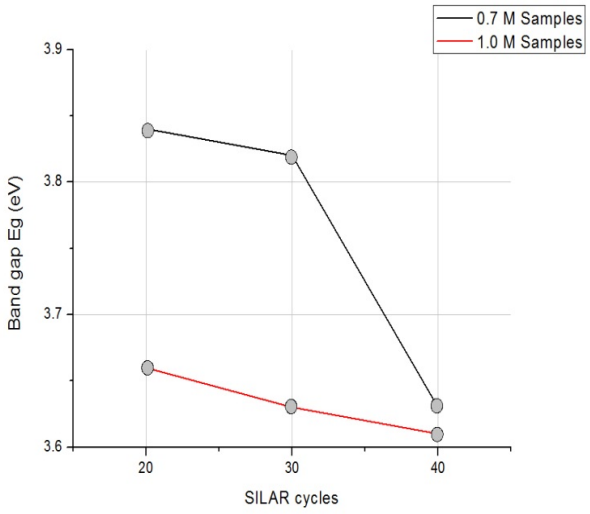

Fig. 10: Variation of Eg in the grown FeCuS**.**

3.2 Discussion

From Figures 2 and 3 for 0.7 M of Fe ion concentration, the samples exhibited reflectance values which were less than 12 % and 31 % (with the samples as-deposited at 40 and 30 cycles having the least and highest values of 4 % and 30 % respectively) for both at the UV and NIR regions respectively while for 1.0 M of Fe ion concentration, the samples exhibited reflectance values which are less than 17 % and 32 % (with the sample as-deposited at 40 cycle having the least and highest values of 10.5 % and 31 %) for both at the UV and NIR regions respectively. Results from reflectance spectra exhibited varied concentrations of Fe^{2+} in FeCuS thin films mostly decreased and sometimes increased the reflectance properties of the thin films. And these properties mostly increased and at times decreased with SILAR cycle. This provides wide latitude for applications of the thin film. Average reflectance was found to be below 30% for all films.[5] and [6] reported similar results for the thin films. The as-deposited thin films are useful material for the window layer part of solar cells. The wavelength above 500 nm was observed from the transmittance graphs (Figures 4 and 5) with that of 0.7 M of Fe^{2+} concentration, the samples as-deposited at 20 and 30 cycles have the highest transmittance values of 80 % and 90 % respectively followed by the sample as-deposited at 40 cycles with transmittance 70 %. And for 1.0 M of Fe^{2+} concentration, the sample deposited at 30 cycles has transmittance about 100 % (highest), 85 % for sample deposited at 20 cycles and about 75 % for the sample as-deposited at 40 cycles. However, this means that the transmittance varies most times as concentration and SILAR cycle and in some cases inversely proportional. In all the film samples, below 400 nm, there was a sharp fall in the percentage transmittance of the as-deposited thin films. From the transmittance graphs, average transmittances at wavelength (λ) = 800 nm were found to be between 80% and 90%. These values of fairly low and high transmittances in UV and VIS-NIR regions respectively are in agreement with the work of [6] who employed CBD technique to deposit FeCuS and reported same, the optical and solid state parameters for use as photovoltaics and also agrees with the position of [5] who deposited same thin films by solution growth technique (SGT) for solar cell applications. However, the high values suggest the suitability of the films for window layers in solar cells. From the optical absorption spectra of the thin films shown in Figures 6 and 7, it was observed that all the as-deposited thin films exhibited high absorbance in the UV region of the electromagnetic spectrum between wavelengths of 200 nm and 300 nm which decreased with increasing wavelength of solar radiation. However, the absorbance of the thin films is between 2.5 and 5.4 and 2.5 and 5.7 in order of increasing Fe ion concentration. The increase in absorption occurs when the photon energy reaches the value of the energy gap where electronic transfers occur between the valence band and conduction band. The films show relatively low absorbance in the NIR regions of the spectrum (less than 1.0). This is in

consonance with the reports of [5] and [6] as they also observed similar results in their experiments using chemical bath deposition and solution growth techniques respectively. The band gaps of the samples were obtained directly by taken the intercept of the extrapolation of $(\alpha h\nu)^2$ against $h\nu$ coordinates (Figures 8 and 9). On extrapolations, it was observed that the as-deposited thin films have direct band gap of 3.84 eV, 3.82 eV and 3.63 eV for 0.7 M of Fe^{2+} concentration samples and 3.66 eV, 3.63eV and 3.61eV for 1.0 M of Fe^{2+} concentration samples deposited at 20, 30 and 40 cycles respectively. The graph of the variation of the band gap energies of the thin films grown at various molar concentration of Fe^{2+} with increasing order of cycles as shown in Figure 10 indicated relatively high energy values. It was observed that the band gap values decreased with increase in both SILAR cycle and Fe^{2+} concentration. And the values reached the peak (3.84 eV) when the Fe ion concentration was 0.7 Mol. at 20 cycles. There is an obvious contrast between the range of these direct band gap values (3.61eV – 3.84eV) and the results of previous researchers [4], [5] and [6] as these values are greater than what they reported (2.40 eV–2.80 eV; 2.50eV–2.80eV; 2.56eV–2.75eV; 2.50eV–2.80eV respectively). The reason for this variation may be due to the variation in the molar concentrations of the precursors used, the deposition time, and impurities from the environment where the experiment was carried out. Meanwhile, there is need to ensure that window layer does not absorb any of the incident light coming from the cell and to give out maximum photon energy so as to reach the absorber layer where electrons could be generated [7]. From the electrical results (Table

1), the resistivity and conductivity of the grown thin film samples varied from 5.843 x 10^6 Ωm to 1.522 x 10^7 Ωm and 6.572 x 10^{-8} Sm^{-1} to 1.711 x 10^{-7} Sm^{-1} respectively. The electrical results of films deposited showed that resistivity decreased while conductivity increased with increase in SILAR cycle for each Fe ion concentration. This enhances the electrical property of the film and makes it a good material for solar applications as resistivity.

4 Conclusions

The growth and characterization of FeCuS thin films via SILAR technique have been successfully achieved. This study unraveled the fact that, varied concentrations Fe^{2+} in the as-deposited thin films mostly brought about increase and sometimes decrease in some properties of the as-deposited films at different SILAR cycles. This provides wide latitude for applications of the thin films in solar cell fabrication. as a result of its high absorbance. Coating of poultry buildings, eye glasses coating, solar thermal conversion, solar control, anti-reflection coating and window layers in solar cells are also applicable. It is hoped that the doping of FeCuS thin films with required specific concentration of Fe^{2+} could enhance its properties and lead to numerous applications of the ternary compound semiconductor.

5 Recommendations

This study recommended that ITO and FTO should be employed as substrates in the future growth of FeCuS thin films. Deposition techniques such as physical vapour deposition, radiofrequency (RF) magnetron sputtering and so on, be used and results compared with that of this study. Thin film characterizations such as Energy Dispersive X-ray analysis (EDX), X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD) of FeCuS as-deposited via SILAR and investigate the effect of annealing on the thin film. Use of concentrations of the precursors greater than 1.0 mole for FeCuS thin film deposited via SILAR is also recommended for future work.

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References

[1] Gabriel, E. Fabrication and Characterization of Gradient Oxide Thin Film. University Honors Theses. Paper., 327. (2016).

[2] Blakers, A. and Armour, T. Flexible silicon solar cells. Solar Energy Materials and Solar Cells, 93, 8; 1440-1443. (2009).

[3] Chauhan, K. A., and Chaudhary R. P. Structure and Optical Properties of Zn1-xnixo Nanoparticles by Co-precipitation Method. *Journal of Optoelectronics and Biomedical Materials*., **3(1)**, 17-23 (2011).

[4] Obasi, B. I., Osuwa, J. C. and Odu, D. A. Effects of Varying Copper (Cu) Ion Concentrations of Ternary Compound of Copper Iron Sulfide (CuFeS) Thin Films. *International Journal of Science and Technology*., **5(8)**, 369-373 (2016).

[5] Uhuegbu, C. C. Solution growth technique for iron copper sulphide ternary thin film and its optical characteristics. *Am. J. Sci. Ind. Res.,* 1(3); 392-396. ISSN: 2153-649X. DOI:10.5251/ajsir.2010.1.3.392.396. (2010).

[6] Ezenwa, I. A. and Okoli, L. N. 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 (2015).

[7] Adeniji, Q. A., Kola Odunaike, Fowodu, T. O. & Talabi, A. T. Influence of Silar Cycle on the Energy Bandgap of Iron Copper Sulphide (FeCuS) Thin Films deposited on SLG substrate. *NanoWorld Journal Research Article* Open Access https://doi.org/10.17756/nwj.2019-072., 49-52 (2020).