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OPTICAL PROPERTIES OF CUS THIN FILMS PREPARED USING SILAR METHOD

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Abstract: **CuS thin films were successfully deposited on glass substrate by Successive Ionic Layer Adsorption Reaction (SILAR) technique. The chemical compositions and thicknesses of the films were obtained using Rutherford backscattering spectrometer while the topography of the films was obtained by scanning electron microscopy while the optical transmittance data were obtained using UV double beam spectrophotometer 1800 series. The sample deposited at 273K, layer (1) which is the sample deposited on the glass recorded a thickness of 386.03nm. The chemical compositions of the materials that were analysed by Rutherford backscattering spectrometry are Lead (Cu: 3.33%), and Sulphur (S: 1.46%). The deposited films were analysed with Scanning Electron Microscope. The micrograph revealed a polycrystalline nature and the deposited films were found to be non-homogeneous. It also show that the microstructure were spherical in shape. The films as observed on the surface region indicate that the films were more on glass substrate, as the kinetics of film formation on the substrate was not uniform. It was also observed that CuS thin films have energy band gaps 2.5±0.05eV-2.4±0.05eV .CuS thin films have transmittance in the ranges of 0.434-0.628 and, reflectance ranges from 0.3326-0.484 at wavelength of 350nm-1100nm respectively. The other optical properties that were investigated are; reflectance, absorption coefficient, extinction coefficient, refractive index, optical conductivity, and dielectric constants. Based on the spectral qualities, these thin films may be used in cold and heat mirror applications, active layer in various types of solar cells, liquid crystal displays, flat panel displays for opto-electronic applications .**

Keywords: **Absorbance, Reflectance, Absorption Coefficient, Extinction Coefficient, Refractive Index, Optical Conductivity.**

I. INTRODUCTION

Energy is important to economic growth of the world. We have basically two major types of energy; renewable and non-renewable energy. Non-renewable energy resources are the major sources of energy global warming. And due to its negative effect on the world climate, research is ongoing as to find alternative energy resources which are environmental friendly. The solar, wind, and thermal energies come under the umbrella of the renewable energy, which is considered to be better alternatives to the conventional energy. Solar energy which is an aspect of renewable energy is a promising solution to world energy problem. Photovoltaic materials are capable of converting solar radiation into electricity. One major advantage with the use of renewable energy is that as it is renewable and it is therefore sustainable and so will never run out. Renewable energy facilities generally require less maintenance than traditional generators. Their fuel being derived from natural and available resources reduces the costs of operation. Even more importantly, renewable energy produces little or no waste products such as carbon dioxide or other chemical pollutants, so has minimal impact on the environment. In fact, the nuclear disasters of Chernobyl and Fukushima are cautioning the world dangers of nuclear plants and consequences to mankind (Kodigala, 2014). The SnS thin films were synthesized by chemical bath deposition (CBD), dip coating and successive ionic layer adsorption and reaction (SILAR) techniques. In them, the CBD thin films were deposited at two temperatures: ambient and 70°C (Sunil., et al, 2016). The tin sulphide films obtained from chemical routes normally have two or more mixed phases

(SnS, SnS_2 and Sn_2S_3). The paper reports a holistic approach to synthesize nearly stoichiometric, single phase tin sulphide (SnS) thin films by simplified (SILAR) technique without using any complexing agents (Pawan., et al, 2020). Therefore, the fields of material science and engineering community ability to conceive the novel material with extraordinary combination of chemical, physical and mechanical properties have changed the modern society. Modern technology requires thin films for different applications. The usefulness of the optical properties of metal films and scientific curiosity about behaviour of two dimensional solids has been responsible for immense interest in the study of science and technology of the thin films. Thin film studies have directly or indirectly advance many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristics of the thickness, geometry, and structure of the film. Phenomenal rise in thin film researches is no doubt due to their extensive application in the diverse fields of electronics, optics, space science, aircraft, defense and other industries. These investigation have led to a numerous inventions and improvement of many devices viz, piezo-electric devices, micro-miniaturization of power supply, rectification and amplification, sensor elements, storage of solar energy and its conversion to other form, magnetic memories, super conduction films, interference filters, reflecting and antireflection coating and many others (Rao, 2013). Nanostructured materials and in particular semiconductor nanostructures and thin films may be exploited for their novel electronic and optical properties. These structures are of great interest since they have potential applications in future quantum and photoinic devices. Chalcogenides such as CuS, ZnS, NiS, CoS, CdS, MnS, etc. from transitional metal group have been extensively studied due to their excellent physical and chemical properties. Out of these chalcogenides, copper Sulphide is an important material from the point of view of fundamental research as it is economic and low resistance. CuS has a wide range of well-established and prospective application such as photothermal conversion application, photovoltaic application, electroconductive electrode, microwave shielding coating and solar control coating. In addition, it is a promising material with potential application in Lithium-ion rechargeable batteries, gas sensor and catalyst. SnS thin films with different thicknesses have been deposited on glass substrates at a substrate temperature of 300°C. The influence of thickness on structural, morphological, optical and electrical properties of the thin film has been investigated. X-ray diffraction (XRD) analysis and micro-Raman studies confirm the formation of single phase SnS films. The optical energy band gap decreases from 1.51 eV to 1.24eV with increase of film thickness (Devarajan., et al, 2022).

II. MATERIALS AND METHOD

2.5mI of 0.3M solution of ethylenediaminetetraacetic acid, $C_{10}H_{16}N_2O_8$ (EDTA) which is the complexing agent was extracted with a syringe added to the 50ml beaker containing 1.4M solution of copper Sulphate. It is observed that a light blue precipitate was formed when the complexing agent was added to the aqueous solution of copper sulphate forming copper complex ion. De-ionized water is added to make up the beaker to 50ml and was stirred to have a uniform solution. 10ml of Sodium thiosulphate ($Na_2S_2O_3$) as the anion precursor was prepared in a separate beaker of 50ml for completion of reaction process..

2.1 SILAR Processes

The glass substrates were first immersed into copper complex ion $[Cu(C_{10}H_{16}N_2O_8)]^{2+}$ which is the cation and then rinsed in a distilled water in order to remove some unadsorbed substances and to control the thickness of the deposition [4]. The substrates were transferred into the 50ml beaker containing the solution of sodium thiosulphate ($Na_2S_2O_3$) which is the anion precursor and then rinsed in a de-ionized water, thus completing the SILAR cycles which involves – adsorption, rinsing, reaction and rinsing as depicts on the experimental set-up in Figure 2.1. Each dip-time lasted for 10 seconds and the entire process was repeated for 10 cycles in each beaker. The substrates were dried in air.

2.2 Reaction Mechanism

1.4M solution of copper sulphate ($CuSO_4.5H_2O$) reacted with 0.3M solution of EDTA forming a complex solution of copper as seen in equation (1)

$$CuSO_4.5H_2O + C_{10}H_{16}N_2O_8 \rightarrow [Cu(C_{10}H_{16}N_2O_8)]^{2+} + 5H_2O \quad (1)$$

The complex solution of copper Cu^{2+} reacting with 0.5M solution of sodium thiosulphate ($Na_2S_2O_3$) as depicts in equation (2) produces copper sulphide (CuS).

$$[Cu(C_{10}H_{16}N_2O_8)]^{2+} + Na_2S_2O_3 \longrightarrow CuS + Na_2SO_3 + C_{10}H_{16}N_2O_8 \quad (2)$$

Two samples were selected as representative samples and were annealed at varying temperatures of 319K and 373K.

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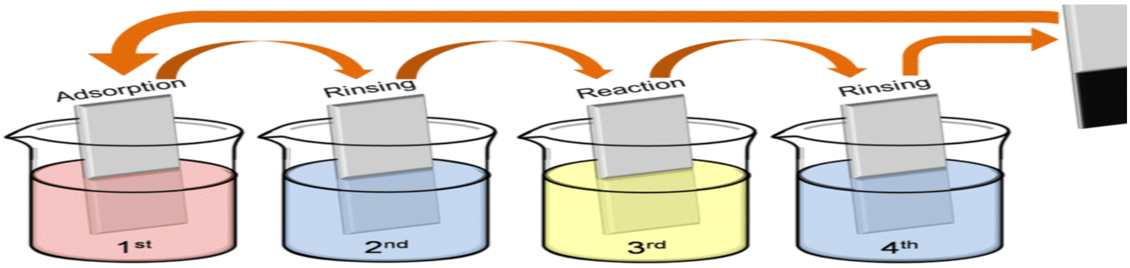

Figure 2.1 Experimental set up of Successive Ionic Layer Adsorption and Reaction (SILAR)

III. RESULTS AND DISCUSSION

3.1 Elemental Composition and Thickness measurements

The thickness measurements and elemental compositions were carried out using Rutherford Back Scattering Spectroscopy (RBS). Figure 3.1, is sample A deposited at 273K, has thickness value 150nm at annealing temperature of 319K. And compositions of Cu: 3.33% and S: 1.46%. Figure 3.2, shows sample B deposited at 273K, has thickness value 120nm at annealing temperature of 373K. It has elemental compositions of Cu: 2.90% and S: 8.36%. Tables 3.1 and 3.2 depicts the elements in the substrates before and after depositions. Layer 2, shows the elements before deposition and Layer 1 represents the elements after deposition. Other elements present are part of the substrates used

Table 3.1: Elements on sample A

Element	Layer1 (%)	Layer 2 (%)
Ca	-	1.06
Si	-	18.53
O	-	67.40
Fe	-	0.48
Na	-	8.77
Al	-	2.18
Mg	-	0.11
Ti	-	0.87
S	1.46	-
Cu	3.33	-

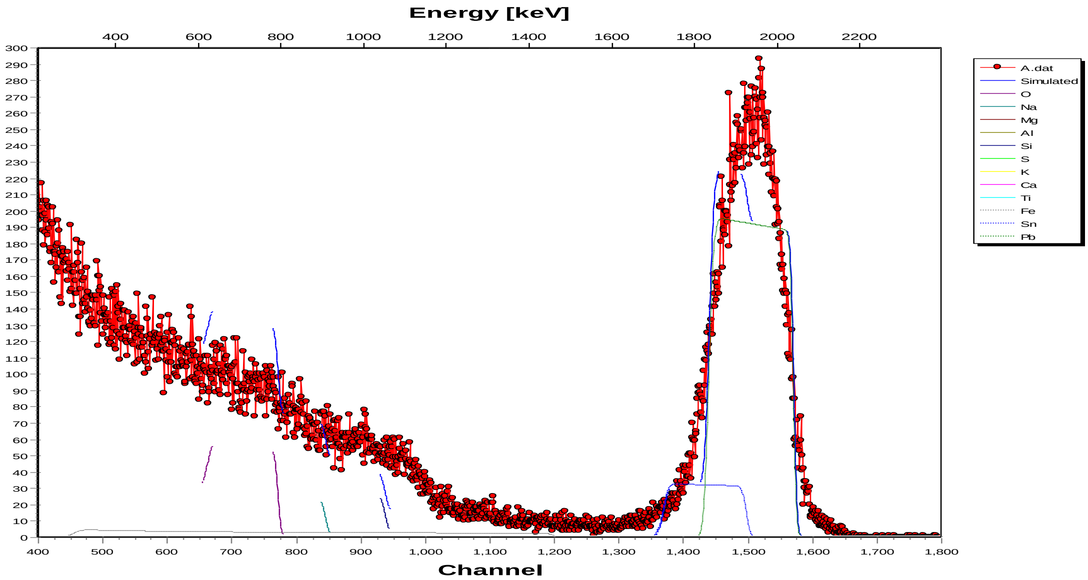

Figure 3.1.The Rutherford backscattering spectrometry (RBS) for sample A.

a. LAYER 1: THICKNESS 2781.73 (E 15 Atoms/cm^2) ; 150 nm
b. LAYER 2 (GLASS): THICKNESS 14500 (E 15 Atoms/cm^2)

Table 3.2 : Elements on sample B

ELEMENT	Layer 1 (%)	Layer 2 (%)
Ca	-	1.06
Si	-	18.53
O	-	67.40
Fe	-	0.48
Na	-	8.77
Al	-	2.18
K	-	0.49
Mg	-	0.11
Ti	-	0.87
S	8.36	-
Cu	2.90	-

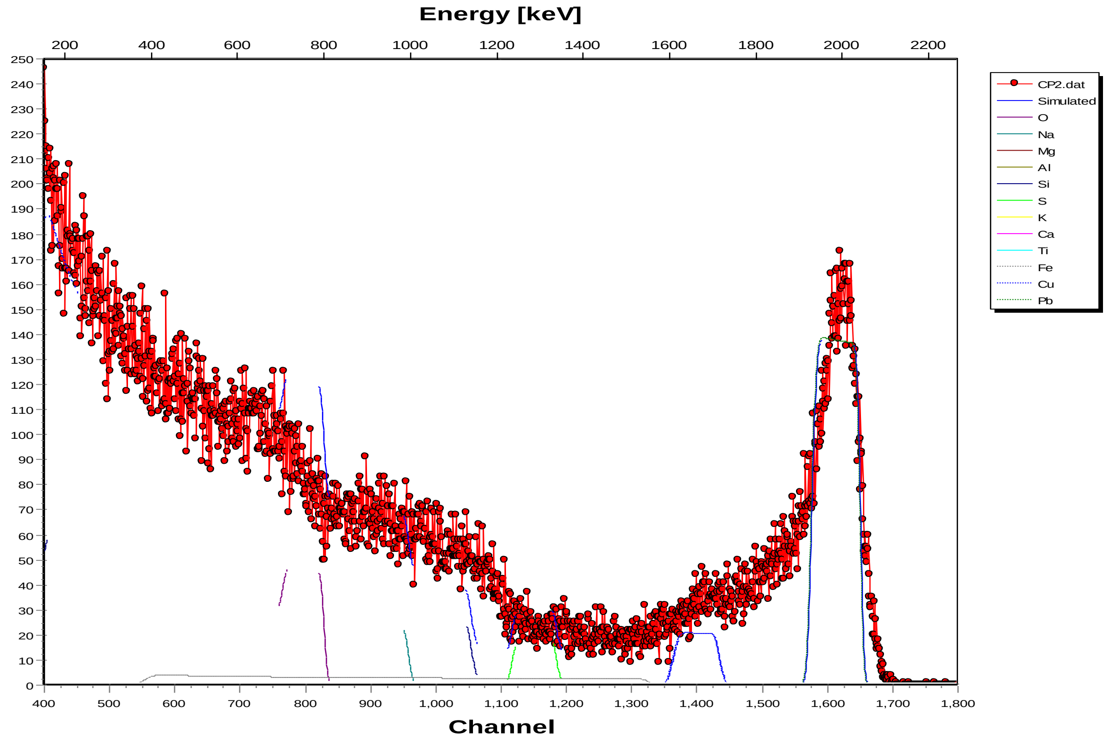

Figure 3.2 The Rutherford backscattering spectrometry (RBS) for sample B.

a. **LAYER 1: THICKNESS 1500.0 (E 15 Atoms/cm^2) ; 120 nm**
b. **LAYER 2 (GLASS): THICKNESS 14500 (E 15 Atoms/cm^2)**

3.2 Surface Structure

The morphological studies of samples A and B were determined using Phenom Proxy by Phenom World Eindhoven, Nethertland. Sample A as revealed by scanning electron microscope (SEM) in Figure 3.3 shows that it has smooth dark surface with white spots which indicate the inter-atomic interactions between the constituent atoms that made up the emergent thin film compound, which also shows the bonding strength of the material. .

Figure 3.4 is the image of sample B as studied by scanning electron microscope; it shows that the deposited sample has a smooth surface with near uniform surface having tiny white spots. The material exhibits interactions of combining substances during chemical reactions (Bube, 1974).

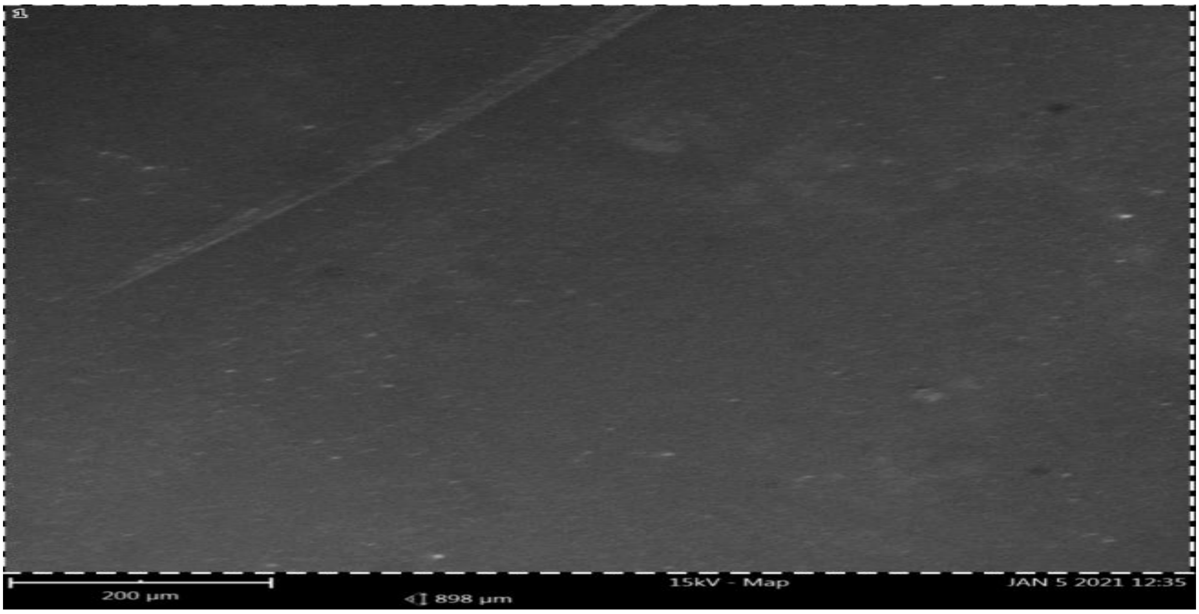

Figure 3.3. SEM image of sample A thin film at annealing temperature 319K

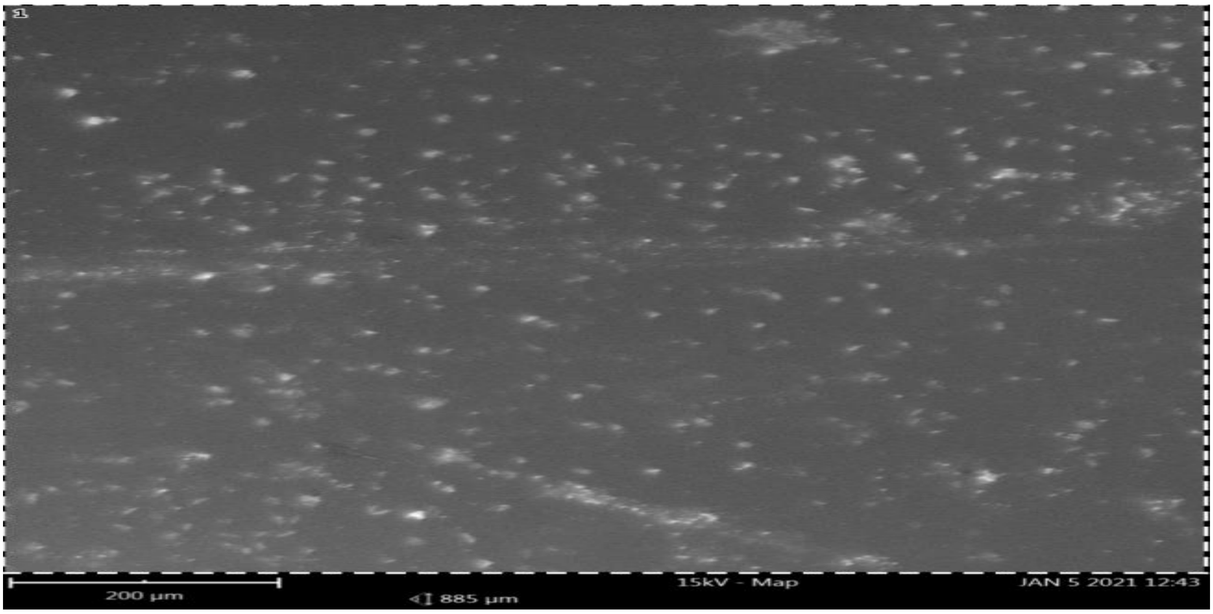

Figure 3.4. SEM image of sample B thin film at annealing temperature of 373K

3.3 Optical Properties

The transmittance of the samples were measured using UV double beam spectrophotometer 1800 series of 190-1200 nm range. The transmittance spectrum shows that the film of sample A has low transmittance in the UV (33% - 37%) at the wavelength range (350nm – 400nm). Sample B shows also low transmittance (28% - 30%) at the wavelength range (350nm – 400nm) in the UV. There is an increase in transmittance (35% - 50%) for sample A at the wavelength range from the UV through the visible region to near infrared (NIR) region (350nm–11000nm) and the transmittance range (23% - 45%) for sample B at the wavelength (350nm–1100nm) also from the UV through the visible to the near infrared (NIR) region of electromagnetic spectrum as shown in Figure 3.5. The low transmittance of these samples implies they can be applied in the areas of cold windows, smart windows, and tint in car glasses (Ohakwere, 2015). They can equally be used as flat panels for optoelectronics purposes, solar panels and LED's (Callister, 2007).

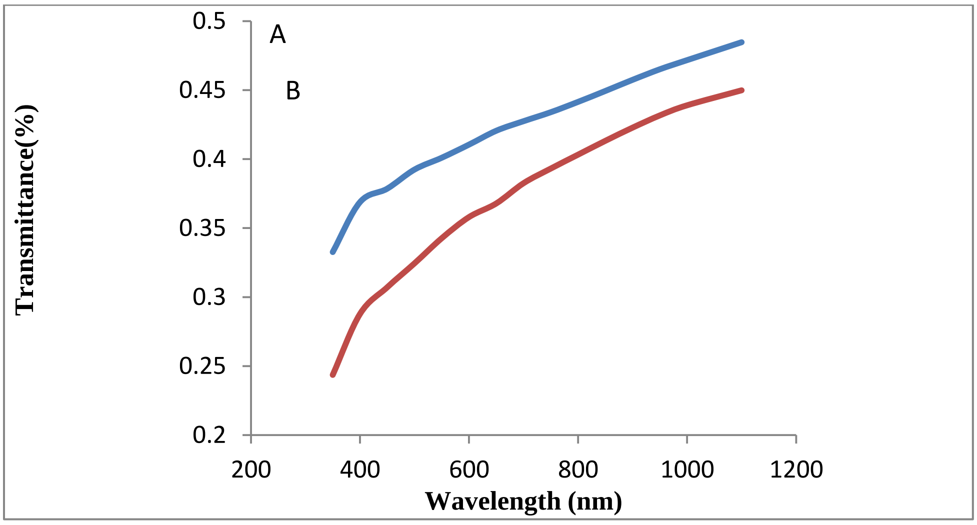

Figure 3.5.Graph of transmittance against wavelength for CuS thin film sample A and B

The graph of the absorbance in Figure 3.6, is obtained from equation

$$A = Log_{10}(^1/_T) \quad (3)$$

where A is the absorbance and T is the transmittance. The two samples A and B have decreasing absorbance from the UV, 0.55 and 0.65 respectively at wavelength 350nm which are obtained as their maximum values. The absorbance of sample A and B in the visible region decrease continually from 400nm to near infrared region of electromagnetic spectrum. This is shown in Figure 3.6 which is obtained from equation (3)

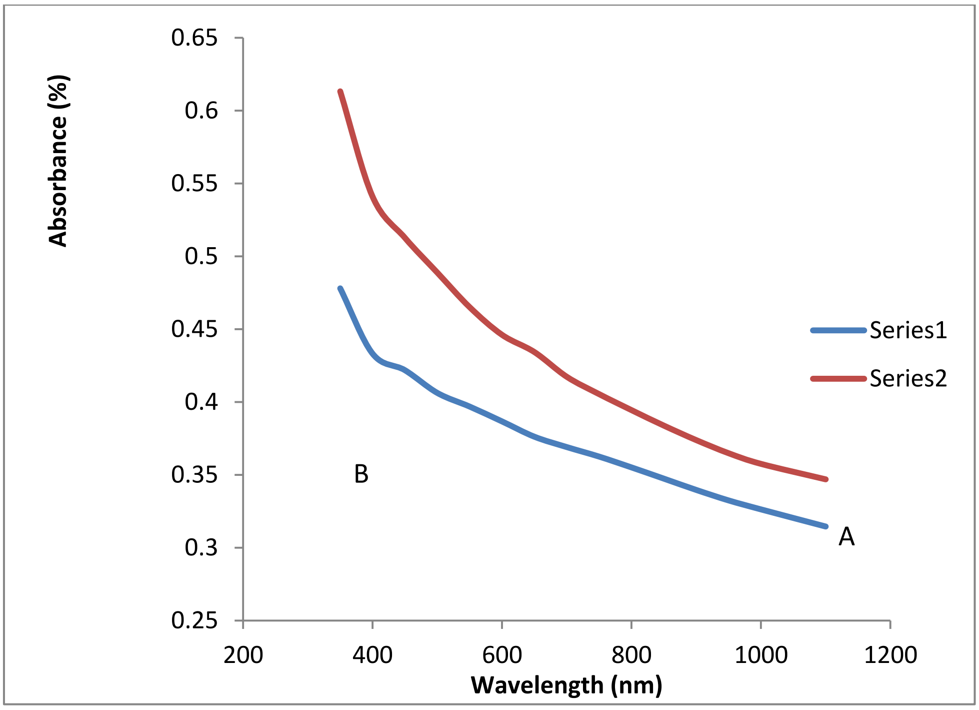

Figure 3.6 Graph of absorbance against wavelength for CuS thin film sample A and B

The graph of the reflectance in Figure 3.7, is obtained from the equation

$$R = 1 – (T + A) \quad (4)$$

where T is the transmittance, A is the absorbance and R is the reflectance. Samples A and B have low reflectance of 0.14 – 0.19 at wavelength at 350nm, 1100nm and 0.19 – 0.20 at wavelength 380nm, 400nm respectively as depicted in Figure 3.7. The reflectance increases as the wavelength increases from the UV through the visible to the near infrared regions of electromagnetic spectrum. This makes the CuS useful as anti-reflective coatings, which minimizes reflection losses to improve efficiency . This is needed in camera sensors, solar panels (Onwuemeka et al., 2014, and display screens. It is also useful in dichromic mirrors, which means they reflect light of one colour (or wavelength) while transmitting light of another colour (Ugbo et al., 2021). In solar energy they can be used to optimize light absorption and minimize reflection losses.

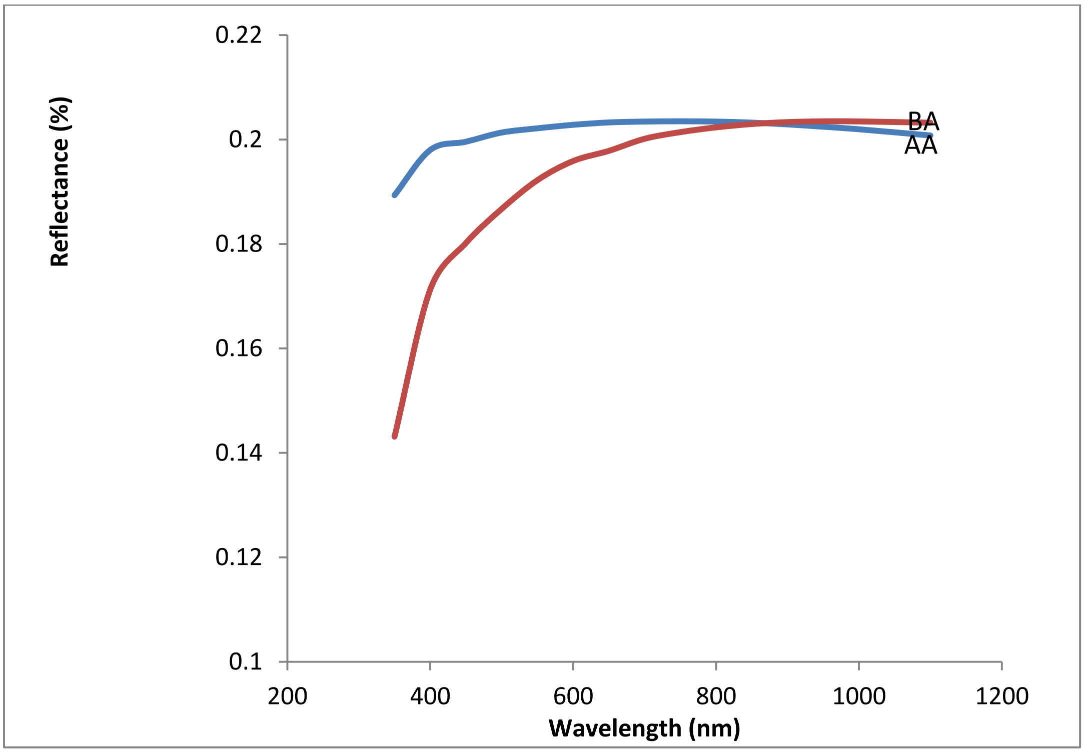

Figure 3.7 Graph of reflectance against wavelength for CuS thin film sample A and B

The optical energy gap of the material is obtained in k space from the relation $(\alpha h\upsilon)^2=A(h\upsilon-E_g)$ where A is a constant, $h\upsilon$ is the photon energy, E_g is the energy band gap and α is the absorption coefficient. The energy band gaps of sample A and B are evaluated by extrapolating the linear portion of the plot $(\alpha h\upsilon)^2$ against $h\upsilon$ at $\alpha h\upsilon=0$ (Look, 2001; Nicolau, 1985). From Figure 3.8 a direct band gap value of 2.50 $\pm$0.05eV is obtained for sample A. Sample B has direct band gap of 2.40$\pm$0.05eV. The two samples have average energy band gap of 2.45$\pm$0.05eV. The narrow band gap obtained in this work makes the CuS a good material for the production of laser diodes and light emitting diodes (LED).

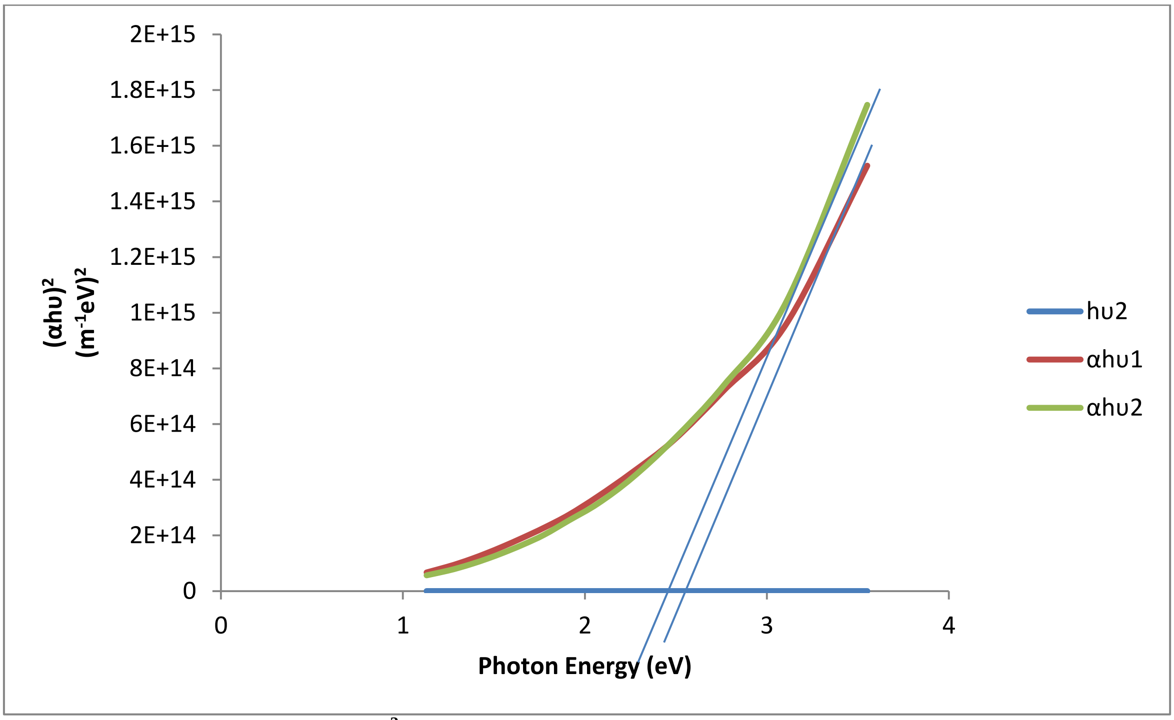

Figure 3.8 Graph of $(\alpha h\upsilon)^2$ against photon energy hυ for CuS thin film sample A and B

IV. CONCLUSION

Thin films of Copper sulphide (CuS) were successfully deposited on a glass substrate using Successive Ionic Layer Adsorption Reaction (SILAR) method. The chemical composition and thickness of the films were obtained using Rutherford backscattering spectrometry while the topography of the films was obtained by scanning electron micrograph. the optical absorbance and transmittance data were obtained using UV-1800 series.

The chemical compositions of the deposited samples were analyzed by Rutherford backscattering spectrometer. Results show the availability of Copper (Cu: 3.33%), Sulphur (S: 1.46%). The deposited films analyzed with Scanning Electron Microscopy. The structural study shows that the samples arecrystalline and are found to be non-homogeneous.The films as observed on the surface region indicate that the films were more compactable on glass substrate, as the kinetics of film formation on the substrate was not uniform.It was also observed that CuS thin films have band gap energy of 2.5eV-2.4eV respectively.CuSthin films have transmittance in the ranges of 0.3326-0.484 and, reflectance ranges from 1.893-2.007 at wavelength of 350nm-1100nm respectively. The absorbance and transmittance of the films increases as the wavelength of the films increases. These materials could be used optical coatings-heat and cold window, anticorrosion coatings, active applications in laser diodes, light emitting diodes, photovoltaic,sensors, flat panel displays,

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