Investigation on the Optical and Solid State Properties of Copper Sulfide (CuS) Thin Films Deposited using the Solution Growth Methods

Rita A. Daniel-Umeri, Kugbere Emumejaye

Department of Science Laboratory Technology, Delta State Polytechnic P.M.B 5, Ozoro. Delta State, Nigeria

Abstract Thin films of CuS were successfully deposited on glass substrate using two simple and low cost Solution Growth Methods: chemical bath deposition (CBD) and Successive Ionic Layer Adsorption Reaction (SILAR). The chemical bath composition was made up of $CuCl_2.2H_2O$ solution, $SC(NH_2)_2$, TEA, NaOH and NH_3 solution . For the synthesis of Cu_xS thin film using the SILAR method, the cationic precursor was 0.1M $CuSO_4.5H_2O$ complexed with NH_3, while the anionic precursor was 1M $SC(NH_2)2$. All depositions were carried out under room temperature. The deposited films were characterized using 752N England UV-VIS spectrophotometer in the wavelength range, 200-1000nm. The optical and solid state properties of the as deposited films were studied. The results shows that both methods used for the deposition have similar effect on the aforementioned properties of CuS thin films deposited. However films deposited using the chemical bath method was found to posses higher values of these properties, except for the transmittance. The values of direct bandgap for films deposited using chemical bath deposition (CBD) is in the range, 2.2-2.5eV. While the values for films deposited using Successive Ionic Layer Adsorption Reaction (SILAR) is in the range of 2.5-2.8eV. The properties exhibited by these thin films show that they can possibly be used in solar energy conversions and in some opto-electronic devices.

Keywords CuS ,CBD, SILAR, Solar energy conversions

1. Introduction

In recent years, transition metal chalcogenides (TMCs) semiconductor materials have attracted much attention due to their excellent physical and chemical properties [1]. Among all semiconductor materials, Copper sulfide (Cu_xS) thin films are one of the potentially useful metal chalcogenides with significant variation in properties because of the effect of the 3*d* electrons and thus have the ability to form various stoichiometries. Copper sulphide (Cu_xS) is a binary chemical compound of the elements, copper and sulphur. It occurs in nature as the dark indigo blue mineral with different crystal structures depending upon the value of X, such as hexagonal, orthorhombic, pseudo cubic and tetragonal.

In the bulk form, five stable phases of Cu_xS are known to exist at room temperature: CuS (covellite), $Cu_{1.75}S$ (anilite), $Cu_{1.8}S$ (digenite), $Cu_{1.96}S$ (djurleite) and Cu_2S (chalcocite) [2-3].

Amongst these phases, CuS (covellite) has hexagonal primitive crystal structure, and exhibits metal-like electrical conductivity and also possesses near-ideal solar control characteristics as well as easy current-conduction and charge-transfer mechanism [4-5]. The direct band gap of this material reported in the literature lies between 1.2 to 3.8 eV [6-8].

In nanometer scale, copper sulfide (CuS) exhibits various forms such as nanocomposite [9], nanocones [10], nanobelts, [11] , nanoslice [11], nanofluids, [12] nanocages [13], nanocrystals [14] e.t.c

Chalcogenide thin films of copper sulfide have received particular attention since the discovery of the CdS/CuS hetrojunction solar cell in 1954 [15-16]. Other applications of CuS thin films include Optical filter [17], Architectural glazes[18], Solar energy conversions[19], Optically transparent light emitting diodes (LEDs) [20], Ammonia gas senso r[21], Dye-sensitized solar cell [22], Non-linear optical material [23] and Solar controller and solar radiation absorber [24].

Solution-based and gas phase techniques are used to prepare copper sulphide thin films. This includes electrodeposition [25], spray pyrolysis [26], photochemical deposition [27], successive ionic layer adsorption and reaction (SILAR) [28], chemical bath deposition (CBD) [29], microwave assisted chemical bath deposition (MA-CBD) [30], liquid-liquid interface reaction [31] Solid-Vapor Reaction sputtering [32], chemical vapor deposition (CVD) [33], etc.

Deposition of CuS using solution method is based on the slow release of Cu^{2+} ions and S^{2-} ions in an aqueous alkaline bath and the subsequent condensation of these ions on substrates suitably mounted in the bath. The slow release of Cu^{2+} ions is achieved by adding a complexing agent (ligand) to the Cu salt to form some copper complex species which, upon dissociation, results in the release of small concentrations of Cu^{2+}ions.

Copper sulphide (CuS) thin films were deposited using chemical bath deposition method by Kassim et al., (2010) [7]. The deposition was carried out at various pH values and electrolyte concentrations. The band gap was found to be 2.6 eV with p-type behavior.

Ajaya , Swati and Gautam (2013) [34] deposited CuS thin films on glass substrates using the chemical bath deposition technique at 65 °C from aqueous solutions of copper sulphate and thiourea in which tartaric acid solution were employed as the complexing agent. Absorbance of the thin film was reported in the range 300-350 nm. The highest transmittance of the as-grown film was recorded as 50 % throughout the regions.

Abdul- Hussein , Hayder and Ausama (2013) [35] prepared thin films of CuS by Successive Ionic Layer Adsorption And Reaction (SILAR) method from solutions of $CuCl_2$ and Na_2S at two different molarities (0.03 M and 0.06 M) on glass substrates at room temperature. They reported that the energy gap of CuS varies from 2.4eV to 2.8eV for thickness of 0.55μm and 0.82μm respectively.

In this study, we report the optical and solid state properties of as-prepared CuS thin films deposited on microscope glass slides at room temperature using two low cost simple techniques - chemical bath deposition (CBD) and Successive Ionic Layer Adsorption and Reaction (SILAR) Method.

2. Materials and Methods

All the chemicals used for the deposition were analytical grade reagents and all the solutions were prepared in distilled water. Microscope glass slides were used as the substrate for the deposition. Before deposition, the glass slides were degreased by soaking them in concentrated HCl for 24 hrs. It was thereafter washed with detergent, rinsed with distilled water and dried in air.

2.1. Synthesis of CuS thin films using Chemical Bath Deposition (CBD)

The growth of CuS films using CBD is based on the gradual release of the metal ion Cu^{2+} and sulfide ion S^{2-} in an alkaline medium and condensation of the ions on a substrate that is suitably placed in the reaction bath. The film formation takes place when ionic product (IP) exceeds solubility product (Ksp).

The chemical bath composition was copper (II) chloride dihydrate ($CuCl_2.2H_2O$) solution, thiourea [$SC(NH_2)_2$], Triethanolamine (TEA), sodium hydroxide NaoH and ammonia solution.

Here copper (II) chloride dihydrate and thiourea are the source of Cu^{+2} and S^{-2} ions, respectively. Triethanolamine and sodium hydroxide acts as complexing agents, whereas ammonia solution was used for adjusting pH of the bath solution to achieve the alkaline medium.

In the synthesis of CuS thin films at room temperature using the CBD, the following procedure was adopted; 10 ml of 0.1M $CuCl_2.2H_2O$, 8ml of concentrated triethanolamine (TEA) and 10ml of 1M NaOH were mixed in a 100ml beaker using a glass stirrer. Thereafter, 8ml of NH_3 solution and 10ml of 1.0M thiourea [$SC(NH_2)_2$] was also added and stirred gently to ensure uniformity of the mixture . The mixture was then topped to 100ml level by the addition of 54ml of distilled water. Four glass slides were dipped vertically in the reaction bath and were allowed to stand for some hours. The slides were taken out at (4, 4:30 and 5) hrs from the reaction bath. After

the completion of deposition, the films were rinsed with distilled water dried in air and kept in an air tight container to avoid contamination.

2.2. Synthesis of CuS thin films using successive ionic layer adsorption reaction (SILAR) method

For the synthesis of Cu_xS thin film using the SILAR method, the cationic precursor was 0.1M copper sulphate pentahydrate ($CuSO_4.5H_2O$) complexed with 4ml of ammonia (NH_3), while the anionic precursor was 1M thiourea [$SC(NH_2)_2$] .

To deposit Cu_xS thin film, one SILAR cycle involves the following four steps: (i) a well-cleaned glass substrate was first immersed into cationic precursor (Beaker1) that is, (0.1M copper complex solution kept at room temperature) , so the Cu^{2+} ions were adsorbed onto the substrate surface; (ii) then the substrate was rinsed with distilled water to remove loosely bonded Cu^{2+} ions from the substrate; (iii) further, the substrate was immersed into anionic precursor (vessel 3) (1M $SC(NH_2)_2$ solution), so S^{2-} ions were adsorbed and reacted with Cu^2+ ions (iv) again the substrate was rinsed with distilled water to remove unadsorbed and unreacted S^{2-} ions from the substrate. Thus, one SILAR cycle is completed. Therefore, we obtained a Cu_xS film by repeating such SILAR cycles 60 times. The anionic and cationic immersion times were 30s and the rinsing time was 10s. After deposition, the films were rinsed with copious amounts of distilled water, dried with air and kept in an air tight container to avoid contamination. The films were also prepared for (70 and 80) SILAR cycles.

After the films were deposited, they were characterized using a 752N England UV-VIS spectrophotometer in the wavelength range (200-1000nm) using blank glass slide as reference at the scan intervals of 5 nm.

The optical and solid state properties studied in this work include: Absorbance (A), Transmittance (T), Reflectance (R), Absorption coefficient (α). Others are the band gap, refractive index (n) ,extinction coefficient (k) and Optical conductivity (σ_o)

3. Results and Discussion

Data obtained from the optical characterization of the films in the wavelength range 200 to 1000 nm were used to plot the following graphs.

3.1. Absorbance

During the optical characterization of thin films, it is the spectral absorbance of the films that are obtained directly from the spectrophotometer. The absorbance (A) is the fraction of radiation absorbed from the radiation that strikes the surface of the material. Alternatively, A is the logarithm to base 10 of the transmittance, i.e,

$$A = \log_{10} I_t /I_o = \log_{10} T \tag{3.1}$$

$$T = 10^A \tag{3.2}$$

Figure 3.1(a) and (b) shows the optical absorption spectra of the CuS thin films deposited using CBD and SILAR methods respectively. It is observed that the spectral absorbance of the specimens vary with wavelength in a similar manner. It is found to have very low absorbance between 200- 280nm which increased rapidly in the remaining part of the UV region, and gently decreases with wavelength in the VIS-NIR regions.

In the chemical bath deposition synthesized thin films, the absorption peaks are centered at 380nm, 390nm and 385nm for the various samples deposited at C4hrs, C4:30hrs and C5hrs respectively. The spectra also indicate that absorbance increased with decrease in the deposition time.

While in the SILAR synthesized films the absorption peaks are centered at 350nm, 340nm and 380nm for samples deposited at S60c, S70c and S80c respectively.

The high absorbance of the films in the UV region makes the film good material for screening off UV portion of electromagnetic spectrum which is dangerous to human and animal health. It can also be used for eye glass coating for protection from sun-burn.
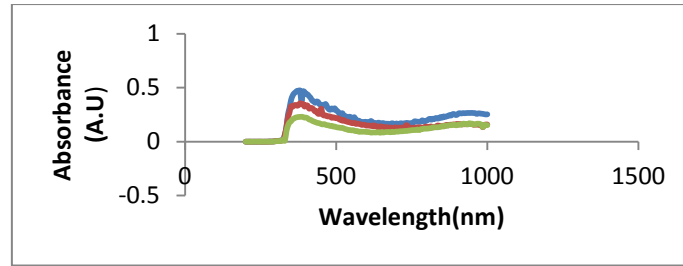
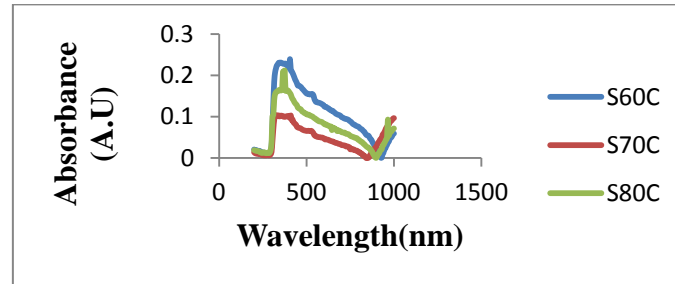*Figure 3.1(a): Plot of Absorbance versus Wavelength of CuS thin film using CBD*

Figure 3.1(b): Plot of Absorbance versus Wavelength of CuS thin film using SILAR Method

3.2. Transmittance

The transmittance (T) of a specimen is defined as the ratio of the transmitted flux
 (I_t) to the incident flux (I_o) that is,

$$T = I_t/I_o \qquad\qquad\qquad (3.3)$$

Figure 3.2 (a) and (b) shows the transmittance spectra of the CuS film deposited using both methods. It is observed that the transmittance of the specimens vary in similar manner

In the chemical bath deposition synthesized thin films; they show high transmittance in the UV region and moderate transmittance in VIS / NIR region. The samples showed average transmittances greater than 50% throughout UV-VIS-NIR regions.

The CuS film deposited using the SILAR method exhibited high transmittance values throughout the UV, VIS and NIR regions with an average transmittances greater than 70% for the various numbers of cycles. This is in agreement with the findings of Vas-Umnuay and Chang (2013) [29].

The high transmittances exhibited by these films make them useful aesthetic window glaze materials. Also, the high transmittance of the film makes it suitable for solar energy collection because if coated on the surface of the collector, it will reduce reflection of solar radiation and transmits radiation to the collector fluid.
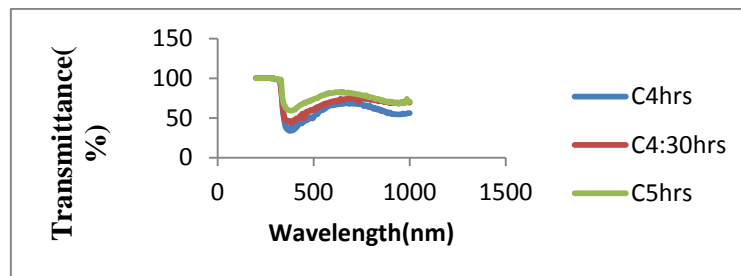

Figure 3.2(a): Plot of Transmittance versus Wavelength of CuS thin film using CBD
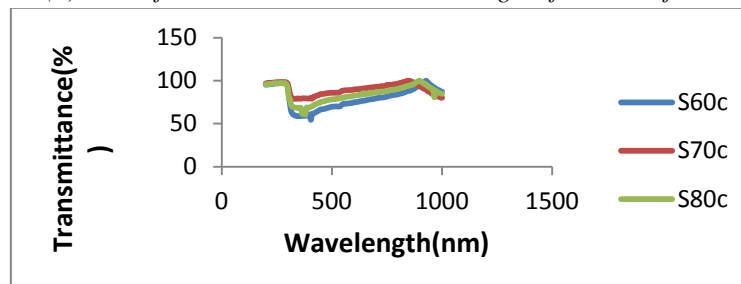

Figure 3.2(b): Plot of Transmittance versus Wavelength of CuS thin film using SILAR

3.3. Reflectance

Reflectance is the fraction of the incident radiation of a given wavelength that is reflected when it strikes a surface. A relation between transmittance (T), spectral absorbance (A) and spectral reflectance (R), according to the law of conservation of energy is given by

A + T + R = 1 (3.4)

Therefore,

R= 1-A-T (3.5)

Figure 3.3 (a) and (b) shows the plot of Reflectance versus Wavelength of the deposited CuS thin film. For films deposited using the Chemical Bath Method, all the films recorded zero reflectance between 200- 280nm which rapidly increased to an average reflectance of 19% between 340- 390nm. The films also show a low reflectance throughout the VIS/NIR regions.

For films deposited using the SILAR method, a similar trend is observed. Generally all the films show a very low reflectance between 200-300nm which increased to a maximum reflectance of 18.1%, 10.8% and 15.0% for S60c, S70c and S80c respectively at 340nm before decreasing gently with wavelength at the VIS- NIR region . The low reflectance exhibited by this material makes it useful for anti-reflection coating for consumer optics (spectacle lenses, camera objectives, and binoculars) [34].
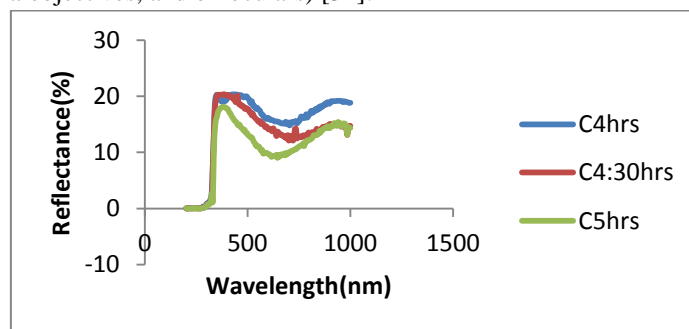

Figure 3.3(a): Plot of Reflectance versus Wavelength of CuS thin film using CBD
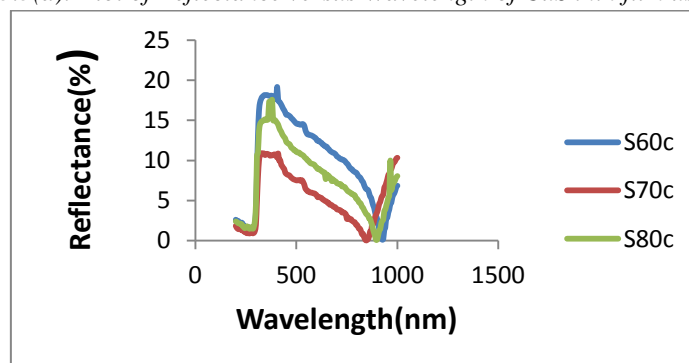

Figure 3.3(b): Plot of Reflectance versus Wavelength of CuS thin film using SILAR

3.4 Absorption Coefficient

Absorption coefficient is the decrease in the intensity of a beam of photons or particles in its passage through a particular substance or medium. When radiation of intensity Io is incident on a material of thickness d (μm) the transmitted intensity I_t is given by

$I_t = I_o \exp(-\alpha d)$ (3.6)

For pure absorption, the constant (α) is the absorption coefficient.

$\alpha = - [\ln T]/d \times 10^6 \text{ m}^{-1}$ (3.7)

The absorption coefficient curves for CuS thin films deposited using CBD and SILAR methods are displayed in figure 3.4(a) and (b). It is observed that there is similarity in the way absorption coefficients varied with wavelength. For films deposited using the Chemical Bath Method, it increased from $0.3983 \times 10^6 \text{ m}^{-1}$ at 1.65eV, $0.300 \times 10^6 \text{ m}^{-1}$ at 1.73 eV and $0.2026 \times 10^6 \text{ m}^{-1}$ at 1.93eV to a maximum value of $1.087971 \times 10^6 \text{ m}^{-1}$, $0.8185 \times 10^6 \text{ m}^{-1}$ and $0.5498 \times 10^6 \text{ m}^{-1}$ at 3.26eV for C4 hrs, C4:30hrs and C5 hrs before decreasing exponentially with photon energy. While for films deposited using the SILAR method the absorption coefficients increased from 0.00115

$x10^6$ m^{-1} at 1.386eV, 0.0241 $x10^6$ m^{-1} at 1.41eV and 0.0345 $x10^6$ m^{-1} at 1.41eV, to a maximum value of 0.233 $x10^6$ m^{-1} at 3.4eV, 0.4858 $x10^6$ m^{-1} at 3.3eV and 0.5318 $x10^6$ m^{-1} at 3.4eV for S60c, S70c and S80c films respectively.
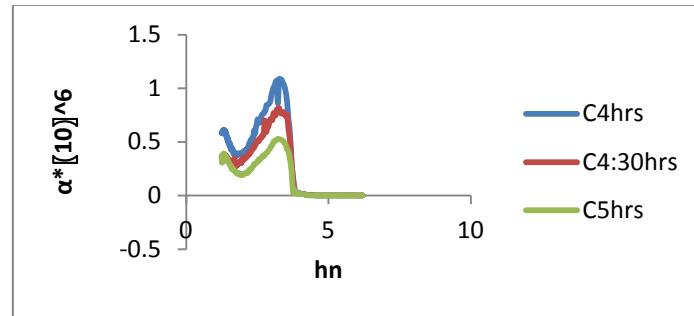
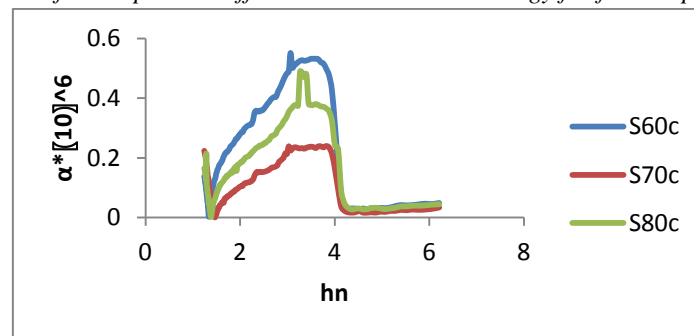*Figure 3.4(a): Plot of Absorption Coefficient versus Photon Energy for films deposited using CBD*

Figure 3.4 (b): Plot of Absorption Coefficient versus Photon Energy for films deposited using SILAR

3.5 Optical bandgap of the deposited CuS

The band gap (E_g) is the energy needed to move a valence electron into conduction band. For a semiconductor it is the energy needed to free an electron from the nucleus of the parent atom. It is defined as

$$E_g = hf = 1.241/\lambda_o \text{ eV} \tag{3.8}$$

The value of the optical band gap can be obtained from the fundamental absorption of the material which corresponds to the excitation of electrons from the valence band to the conduction band. The band gap was determined from the intersect of straight line portion of $(\alpha h\upsilon)^2$ versus $h\upsilon$.

The curves of $(\alpha h\upsilon)^2$ versus $h\upsilon$ were plotted and are shown in Figure 3.5 (a), and (b) for CBD and SILAR deposited CuS respectively. The optical bandgap of the CBD deposited CuS thin films were found to be 2.5eV, 2.3eV and 2.2eV for C4 hrs, C4:30hrs and C5 hrs respectively. It was observed that the bandgap decreases as the dip time increases. While for the SILAR deposited CuS the values obtained are 2.8eV, 2.4eV 2.5eV for S60c, S70c and S80c. These values are in agreement with the values obtained by [7], [29] and [35].
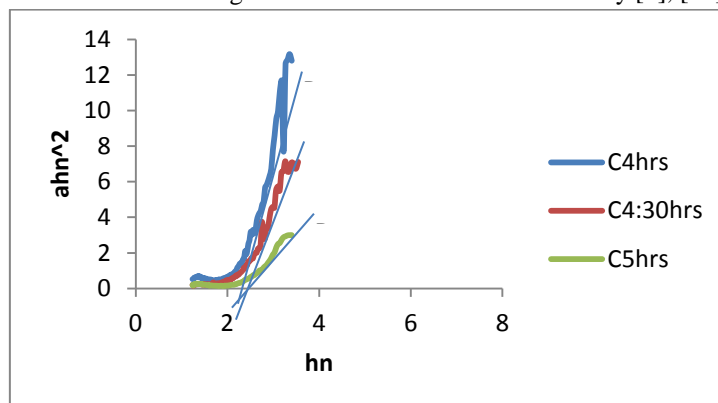
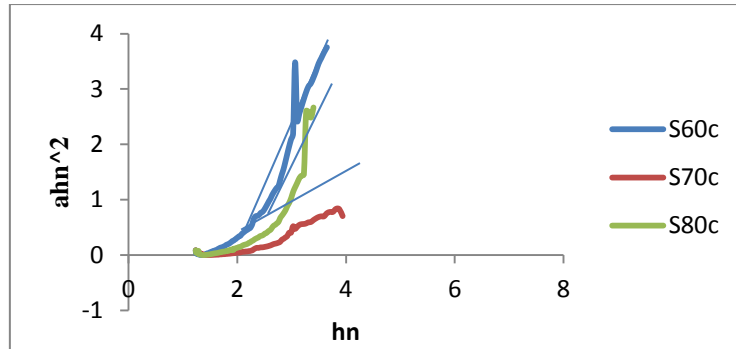*Figure 3.5(a): Plot of $(\alpha hn)^2$ versus hn for CuS film deposited using CBD*

Figure 3.5(b): Plot of (αhn)² versus hn for CuS film deposited using SILAR

3.6. Refractive index

The refractive index (η) is one of the fundamental properties of an optical material because of its close relationship to the electronic polarization of ions and the local field inside materials. Evaluation of the refractive indices of optical materials is considerably important for applications in integrated optic devices, such as switches, filters, and modulation, among others, in which η is a key parameter for the device design [36]. The value of η for thin films can be calculated from their reflectance by using simple approximations.

$$\eta = \frac{(1+\sqrt{R})}{(1-\sqrt{R})} \tag{3.9}$$

The plot for Refractive index (η) against Photon energy for CuS thin films deposited using CBD and SILAR methods are shown in Figure 3.6(a) and(b). For CBD CuS thin films, it is observed that the refractive index vary in a similar way, it increased from a minimum value of 1.85 at 1.7eV , 1.59 at 1.61eV and 1.44 at 1.89eV to a maximum value of 2.28 at 2.85eV , 2.28 at 3.26eV and 2.07 at 3.23eV for C4 hrs, C4:30 hrs, and C5 hrs respectively. Thereafter, they all decreased to a value of 1.03 at 3.93eV.

Whereas, the SILAR deposited CuS shows a maximum value of 1.5 at 3.26eV, 2.02 at 3.26eV and 1.4 at 3.30 eV for S60, S70 and S80 respectively, before decreasing to 1.04 at 5.06eV.

The high refractive index possessed by CuS films makes it suitable for use as anti-reflection coatings.
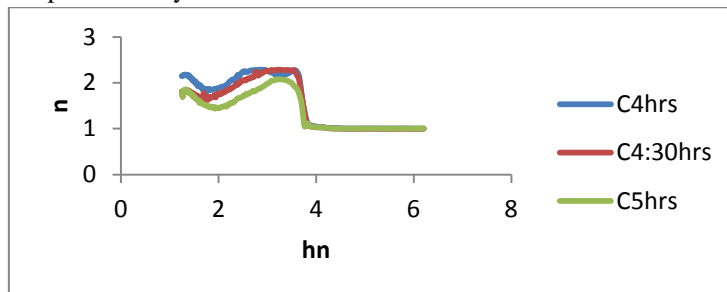

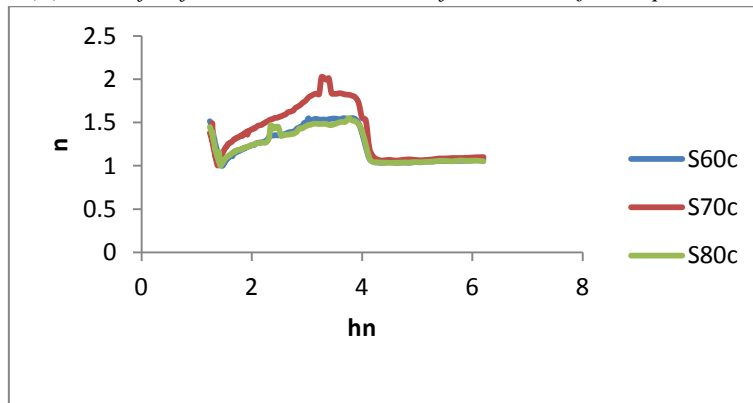*Figure 3.6(a): Plot of Refractive index versus hυ for CuS thin film deposited using CBD*

Figure 3.6(b): Plot of Refractive index versus hυ for CuS thin film deposited using SILAR method

3.7. Extinction Coefficient

The extinction coefficient or attenuation constant allows for estimation of the molar concentration of a solution from its measured absorbance. The absorption coefficient (α) can be defined with reference to extinction coefficient (k) by

$$\alpha = 4\Pi k / \lambda \tag{3.10}$$

From eqn. (3.10)

$$k = \alpha \lambda / 4\Pi \tag{3.11}$$

Where k is called the extinction coefficient (k).

The variation of extinction coefficient of the CuS film against Photon energy is shown in Figure 3.7 (a) and (b) for CBD and SILAR methods respectively.

For films deposited using CBD, the extinction coefficient of the specimens vary with photon energy in the same manner, increasing from 19.32 x10^{-3} at 1.24eV, to maximum values of 46.93 x10^{-3} at 1.27eV for C4 hrs, 28.70 x10^{-3} at 1.31eV for C4:30 hrs and 29.46 x10^{-3} at 1.27eV for C5 hrs before decreasing to 20.85 x10^{-3} at 1.92eV for C4 hrs, 15.41 x10^{-3} at 1.92eV for C4:30 hrs and 9.53 x10^{-3} at 2.01eV for C5 hrs. Thereafter it increased to 33.69 x10^{-3} at 3.18eV, 25.12 x10^{-3} at 3.14eV and 16.4 x10^{-3} at 3.1eV for C4 hrs, C4:30 hrs and C5 hrs respectively before they all decreased steadily with photon energy to zero. While films deposited using SILAR method were observed to exhibit low extinction coefficient property all through, having maximum values of 17.98 x10^{-3} at 3.06 eV , 7.86 x10^{-3} at 3.02 eV and 14.98 x10^{-3} at 3.26 eV for S60, S70 and S80 respectively.
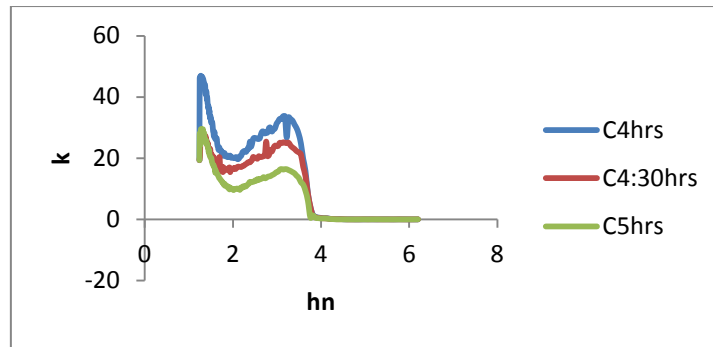

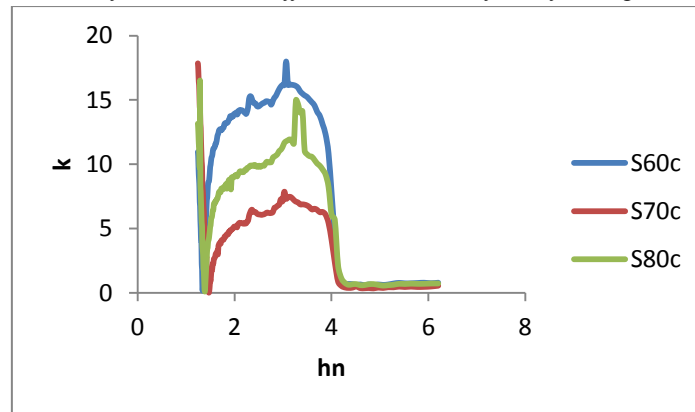*Figure 3.7(a): Plot of Extinction Coefficient versus hυ of CuS film deposited using CBD*

Figure 3.7(b): Plot of Extinction Coefficient versus hυ of CuS film deposited using SILAR

3.8. Optical Conductivity

The optical conductivity (σ) is obtained using the relation [37];

$$\sigma = \frac{\alpha \eta C}{4\pi} \tag{3.12}$$

Where c is the velocity of light in the space; η is the refractive index and α is the absorption coefficient.

Figure 3.8(a) and (b) shows the variation of optical conductivity with the incident photon energy for CuS film deposited using CBD and SILAR methods respectively. It is observed that the optical conductivity of both methods vary in similar manner. For CuS films deposited with CBD, the optical conductivity increases as the

dip time decreases, having maximum values of 0.5617 x10^{14}s^{-1} at 3.26 eV, 0.4458 x10^{14}s^{-1} at 3.26 eV and 0.2614 x10^{14}s^{-1} at 3.22eV for C4 hrs, C4:30 hrs and C5 hrs respectively. While films deposited using SILAR method were observed to posses' maximum values of 0.264481 x10^{14}s^{-1} at 3.49eV, 0.230 x10^{14}s^{-1} at 3.4eV and 0.0868 x10^{14}s^{-1} at 3.44eV for S60, S70 and S80 respectively.
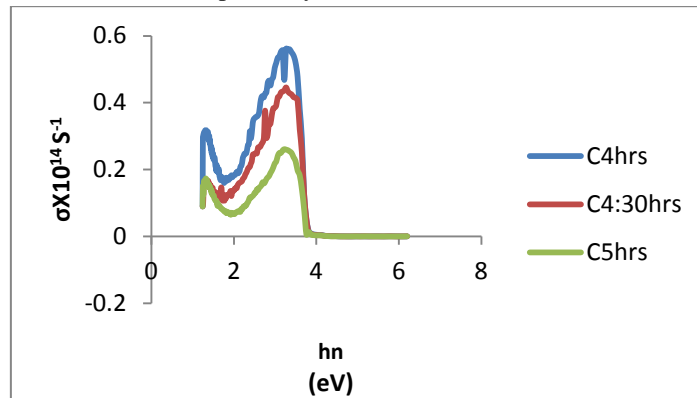
Figure 3.8(a): Plot of Optical Conductivity against Wavelength for CuS film deposited using CBD
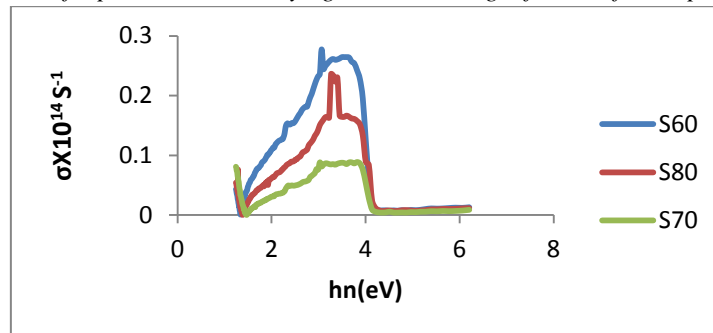
Figure 3.8(b): Plot of Optical Conductivity against photon Energy for CuS film deposited using SILAR

3.9. Dielectric Constant

A dielectric is actually an insulator (or poor conductor of electricity). This affects how light moves, through materials. A high value of dielectric constant makes the distance inside the material looks longer so that the light travels slowly. It also 'scrunches up' the waves to behave as if the signal had a shorter wavelength. For use in capacitor, it must be high and must be low semiconductors for high speed signal to take place. The dielectric constant is given by

$$\varepsilon = \varepsilon_r + \varepsilon_i \quad \varepsilon = (n + ik)^2 \tag{3.13}$$

where ε_r and ε_i are the real and imaginary parts respectively of ε and (n+ik) is the complex refractive index. Hence,

$$\varepsilon_r = n^2 - k^2 \tag{3.14}$$
$$\varepsilon_i = 2ink \tag{3.15}$$

where n is the refractive index and k is extinction coefficient.

3.9.1. Dielectric Constant (real part) (ε_r)

The graphs of dielectric constant of the real part against photon energy for both methods are shown in figure 3.9.1 (a) and (b). For CuS films deposited with CBD, the dielectric constants increases as the dip time decreases, having maximum values of 5.21 at 2.82eV, 5.20 at 3.26eV and 4.30 at 3.26eV for C4 hrs, C4:30 hrs and C5 hrs respectively. Whereas films deposited using SILAR method showed maximum values of 4.34 at 3.49eV, 2.36 at 3.18eV and 4.09 at 3.26eV for S60, S70 and S80 respectively.
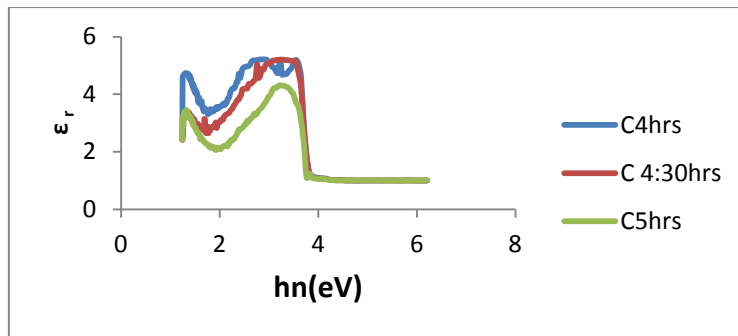
Figure 3.9.1 (a): Graph of dielectric constant of the real part against photon energy for CuS film deposited using CBD
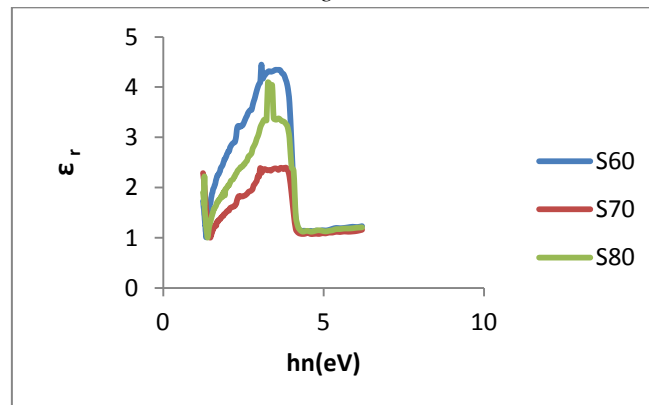

Figure 3.9.1 (b): Graph of dielectric constant of the real part against photon energy for CuS film deposited using SILAR

3.9.2. Dielectric Constant (imaginary part) (εi)

The plot of the imaginary part of the dielectric constant against the photon energy for CuS film deposited using CBD and SILAR methods are shown in figure 3.9.2 (a) and 3.9.2(b). For CuS film deposited using CBD, the imaginary dielectric constant of the specimens increased from various values of about 198×10^{-3} at 1.24eV for C4 hrs, 62.46×10^{-3} at 1.24eV for C4:30 hrs and 99.1×10^{-3} at 1.24eV for C5 hrs to maximum values of 203×10^{-3} at 1.27, 105×10^{-3} at 1.31eV and 109×10^{-3} at 1.32eV before decreasing to minimum values of 76.5 at 1.92eV, 51.8 at 1.93eV and 28.0 at 1.92eV. While for CuS deposited using SILAR method increase from 0.34×10^{-3} at 1.34eV, 0.15×10^{-3} at 1.24 eV and 0.16 at 1.38eV to maximum values of 75.8 at 3.06, 21.6 at 3.26 and 60.6 at 3.26 for S60, S70 and S80 respectively. Before decreasing sharply with photon energy, to zero.
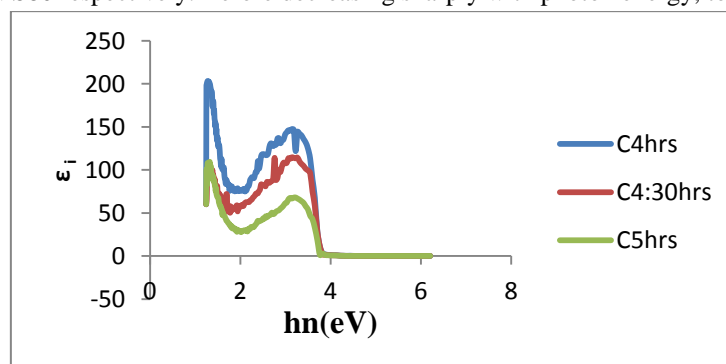

Figure 3.9.2 (a): Graph of dielectric constant of the imaginary part against photon energy for CuS film deposited using CBD.

4. Conclusion

Thin films of CuS were successfully deposited on glass substrate using two simple and low cost Solution Growth Methods: chemical bath deposition (CBD) and Successive Ionic Layer Adsorption Reaction (SILAR).

The chemical bath composition was made up of copper (II) chloride dihydrate ($CuCl_2.2H_2O$) solution, thiourea [$SC(NH_2)_2$] , Triethanolamine (TEA), sodium hydroxide NaoH and ammonia solution . For the synthesis of Cu_xS thin film using the SILAR method, the cationic precursor was 0.1M copper sulphate pentahydrate ($CuSO_4.5H_2O$) complexed with ammonia (NH_3), while the anionic precursor was 1M thiourea [$SC(NH_2)_2$. All depositions were carried out under room temperature.

The deposited films were characterized using 752N England UV-VIS spectrophotometer in the wavelength range (200-1000nm) using blank glass slide as reference at the scan intervals of 5 nm. The following properties were studied: absorbance, transmittance, reflectance, absorption coefficient, refractive index, band gap energy, extinction coefficient, optical conductivity, and dielectric constant (real and imaginary).

The results of the behavior of the film as illustrated in the graphs shows that both methods used for the deposition have similar effect on the optical and solid state properties of CuS thin films deposited. However films deposited using the chemical bath method was found to posses higher values of these properties, except for the transmittance.

The values of direct bandgap for films deposited using chemical bath deposition (CBD) is in the range, 2.2-2.5eV, while the values for films deposited using Successive Ionic Layer Adsorption Reaction (SILAR) is in the range 2.5-2.8eV.

The properties exhibited by these thin films show that they can possibly be used in solar energy conversions and in some opto-electronic devices.

Competing Interests
Authors have declared that no competing interests exist.

References

[1]. M. J. Tafreshi, B. Dibaie, M. Fazli, 2012. *Iranian J. Mater. Sci. Eng*,. 9: 51.

[2]. K. D. Yuan, J. J. Wu, M. L. Liu, L. L. Zhang, F. F. Xu, L. D. Chen, and F. Q. Huang, 2008. *Appl. Phys. Lett.*, 93: 132106

[3]. H. M Pathan and C. D Lokhande, 2004. *Bull. Mater. Sci.,*. 27(2): 85–111.

[4]. A. K Singh, S Mehra, G. S Thool, 2013. *European Chemical Bulletin*, *2(8):*518-523

[5]. M., Froment, H Cachet, H Essaaidi, G. Maurin, and R. Cortes, 1997. *Pure and Applied Chemistry*, 69, 77-82.

[6]. I. Popovici, L, Isac, A, Duta, 2009. *Bull. Transilv. Univ., 2*, (5):19-20

[7]. A. Kassim, S. Nagalingam, T. W. Tee1, K. L. Koon, H. Soon, 2010. *Gazi University Journal of Science* GU J Sci 23(4):435-443.

[8]. P.E. Agbo, F.U. Nweke, P.A. Nwofe and C. N. Ukwu, 2014. International Journal of Advanced Research 2, (10): 353-358

[9]. R. V. Kumar, O. Palchik, Y. Koltypin, Y. Diamant, A. Gedanken, 2002. Ultrason. Sonochem. 9: 65

[10]. C. Jiang, W. Zhang, G. Zou, L. Xu, W. Yu, Y. Qian, 2005. Mater. Lett. 59: 1008.

[11]. S. Xu, Q. Wang, J.Cheng, Q. Meng, Y. Jiao, 2010. Powder Technol. 199:139,

[12]. X. Wei, T. Kong, H. Zhu, L. Wang, 2010. Int. J. Heat Mass Transfer 53: 1841.

[13]. H. Xu, W. Wang, W. Zhu, L. Zhou, 2006.Nanotechnology 17: 3649.

[14]. W. P. Lim, C. T. Wong, S. L. Ang, H. Y. Low, W. S. Chin, 2006. Chem. Mater 18:6170.

[15]. J. C Osuwa and E. C, Mgbaja, 2013. IOSR Journal of Environmental Science. 5(2):27-31

[16]. F. I. Ezema, D. D Hile, S. C. Ezugwu, R. U. Osuji, P. U. Asogwa, J. 2010. Ovonic. Res. 6: 99.

[17]. P. S. Khiew, S. Radiman, N. M. Huang, M. S. Ahamd, 2004. J. Cryst. Growth 268: 227.

[18]. A. Bollero, M. Grossberg, B. Asenjo, M. T. Gutierrez, 2009. Surf. Coat. Technol. 204: 593.

[19]. S. U. Offiah, P. E. Ugwoke, A. B. C. Ekwealor, S. C. Ezugwu, R. U. Osuji , F. I. Ezema, 2012. Dig. J. Nanomater. Bios. 7:165.

[20]. M. D. Irwin, B. Buchholz, A. W. Hains, 2008. Proc. Natl. Acad. Sci. U.S.A. 105:2783.

[21]. A. A. Sagade, R. Sharma, 2008. Sens. Actuators B 133:135.

[22]. K. D. Yuan, J. J. Wu, M. L. Liu, L. L. Zhang, F. F. Xu, L. D. Chen, F. Q. Huang, 2008. Appl. Phys. Lett. 93: 132106.

[23]. A. M. Malyarevich, K. V. Yumashev, N. N. Posnov, V. P. Mikhailov, V. S. Gurin, V. B. Prokopenko, A. A. Alexeenko, I. M. Melnichenko, 2000. J. Appl. Phys. 87: 212.

[24]. Y. B. He, A. Polity, I. O. Sterreicher, D. Pfisterer, R. Gregor, B. K. Meyer, M. Hardt, 2001. Physica B 308–310:1069.

[25]. Y. Chen, C. Davoisne, J. M. Tarascon, C. Guery, 2012. J. Mater. Chem. 22: 5295.

[26]. M. Adelifard, H. Eshghi, M. Mehdi, B. Mohagheghi, 2012. Appl. Surf. Sci. 258: 5733.

[27]. J. Podder, R.Kobayashi, M .Ichimura, 2005. *Thin Solid Films*, 472: 71-75.

[28]. B. Guzeldir, M. Saglam, A. Ates, 2012. Acta Phys. Pol. A 121: 33

[29]. P. Vas-Umnuay and C. Chang, 2013. *ECS Journal of Solid State Science and Technology*, 2(4):120-129

[30]. M. Xin, K. W. Li, H. Wang, 2009. Appl. Surf. Sci. 256:1436.

[31]. C. N. R. Rao, K. P. Kallyanikutty, 2008. Acc. Chem. Res. 41: 489.

[32]. H.S. Sánchez Rangel, A. Carrillo Castillo , J.F. Hernández Paz, J.R. Farias Mancilla, H. Camacho Montes, P.E. García Casillas, C.A. Martínez Pérez, C.A. Rodríguez González , 2015, Chalcogenide Letters 12(6): 381 - 387

[33]. S. Saeed, N. Rashid, K. S Ahmad, 2013. Turk J Chem 37: 796 – 800

[34]. A. K. Singh, S. Mehra , G. S Thool, 2013. *European Chemical Bulletin*, *2(8),* 518-523

[35]. Abdul- Hussein K. Elttayef , Hayder M. Ajeel and Ausama E. Kudair, 2013. Int. J. Thin Film Sci. Tec. 2(3), 223-231.

[36]. D.E. Gray, 1982 *American Institute of Physics Handbook*. 3rd Ed. McGraw-Hill: New York, NY.

[37]. A.D. Dhondge, S.R., Gosavi, N.M. Gosavi, C.P., Sawant, A.M., Patil, A.R. Shelke, and N.G. Deshpande, 2015. *World Journal of Condensed Matter Physics*, 5: 1-9

[38]. S.A. Mahmouda, A.A Akl , S.M Al-Shomar, 2009. Physica B, 404: 2151.

[39]. R. Das and S .Pandey, 2011. *International Journal of Material Science* 1(1): 35.