Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.6 No.5, 2014

Analysis of Chemically Deposited Copper Sulphide Thin Films

Chizomam Usoh[1*]; Charity Okujagu[2] and Israel Owate[2]
1.Department of Physics, Alvan Ikoku Federal college of Education Owerri, Nigeria
2.Department of Physics, College of Natural Sciences, Faculty of Physical Sciences and Information Technology, University of Port Harcourt, Nigeria
*E-mail of the corresponding author: ihugo30@yahoo.com

Abstract
Thin films of Copper Sulphide (CuS) have been fabricated by chemical bath deposition (CBD) technique on glass substrates at room temperature .The structural, morphological and optical properties were investigated. The samples used for XRD and SEM studies were found to be amorphous for the as- deposited and annealed (573k). Film thickness was found to depend on molar concentration of complexing agent. Spectrophotometric analysis of the as- deposited films revealed peak values of 96.30%, 52.97% and 76.09% respectively for absorbance, transmittance, and reflectance respectively. Average values of refractive index (n) ranged between 1.18 and 2.47.Optical band gap values for the films are in the range 2.30eV and 2.44eV. Films could find applications in devices for photovoltaic conversion of solar energy, as window coatings and gas sensors.
Keywords: Copper sulphide, chemically deposited, band gap, thin film

1. Introduction

Copper sulphide (CuS) is among the group of II-IV chalcogenide semiconductor thin films that have attracted much attention because of their potential applications as gas sensors (Abhay et al, 2005); selective radiation filters on architectural windows for solar control in warm climates (Nair and Nair, 1989); in optoelectronic devices such as solar cells (Nair et al, 1998). Generally, thin film chalcogenide semiconductors are known to exhibit crystalline or amorphous nature depending on their deposition conditions. These amorphous films are also important in various technological areas because they exhibit some of the optical properties of their crystalline counterparts (Guneri & Kariper, 2012). As a result, intensive research has been going on during the last few decades on techniques of thin film growth of this semiconductor to ascertain their potential applications in technology. CuS has been fabricated by different techniques which include photochemical deposition (Jiban et al, 2005); electrodeposition (Thanikaikarasan et al, 2010); spray pyrolysis (Luminita et al, 2006) and chemical bath deposition (CBD) (Ezema et al, 2006; Abhay et al, 2008; Guneri and Kariper, 2012; Apolinar et al, 2013). Of these techniques, CBD method which is used for large area deposition of thin films at nano and microscale without the need for sophisticated equipment is a promising method for the deposition of optoelectronic devices. In the present study, we report the growth of thin films of CuS on glass substrates using chemical bath deposition method. Film growth was studied by varying molar concentrations of complexing agent. Deposited films were subjected to structural and optical characterizations and the observed results have been discussed in detail.

2. Materials and Methods

Chemical bath deposition technique was used in depositing CuS on glass substrates. The glass substrates were previously degreased in acqua regia (3:1 mixture of conc. HCl and conc. HNO_3) for 48hours (Okujagu, 1992), cleaned in water with detergent, rinsed in distilled water and dried in air. The degreased substrates provided nucleation centers for the growth of the films thus giving highly adhesive and uniform films.

The principle underlying the deposition of CuS as discussed by Chopra and Das (1983) is based on the slow release of Cu^{2+} and S^{2-} in basic solution and subsequent condensation of these ions on the substrate, mounted in the bath provided the ionic product of Cu^{2+} and S^{2-} is greater than the solubility product (K_{sp}) of the compound.

The chemical bath was formed in a 50mls beaker with 0.6M copper chloride as the source of Cu^{2+}, 1M thiourea as source of S^{2-}, 7.4M triethanolamine (TEA) as the complexing agent and 13.4M ammonia solution as pH adjuster. The bath solution was made up to 50mls by adding distilled water at a pH of 9. Previously cleaned microscopic glass slides were placed inside the bath and allowed to stand for different dip-times. They were later rinsed with distilled water and dried in air. Five samples were deposited at different bath conditions as shown in table1.

Table 1. Bath Constituents for the deposition of CuS thin films

Bath	Deposition time (hrs)	$CuCl_2 . 2H_2O$		TEA		NH_3		Thiourea		Vol. Of H_20 (ml)
		mol (M)	vol(ml)	mol (M)	vol(ml)	mol(M)	vol (ml)	mol (m)	vol(ml)	
G_1	8	0.6	5	2	10	13.4	5	1.0	5	30
G_2	16	0.6	5	7.4	10	13.4	5	1.0	5	30
G_3	20	0.6	5	2	10	13.4	5	1.0	5	30
G_4	24	0.6	5	7.4	10	13.4	5	1.0	5	30
G_5	24	0.6	10	7.4	10	13.4	5	1.0	5	20

The chemical reaction equations governing the reaction for the growth of CuS films are shown below:

$$CuCl_2.2H_2O + TEA \rightarrow Cu(TEA)^{2+} + 2Cl^- + 2H_2O \quad \ldots\ldots 1$$
$$Cu(TEA)^{2+} \rightarrow Cu^{2+} + TEA \quad \ldots\ldots 2$$
$$NH_4OH \rightarrow NH_4^+ + OH^- \quad \ldots\ldots 3$$
$$(NH_2)_2SC + OH^- \rightarrow CH_2N_2 + HS^- + H_2O \quad \ldots\ldots 4$$
$$Cu^{2+} + S^{2-} \rightarrow \downarrow CuS \quad \ldots\ldots 5$$

The deposited thin films were characterized using Rutherford Backscattering Spectrometry (RBS) for the elemental composition, Avantes double beam spectrophotometer, model 2048 Ava Soft 7.1, for the Absorbance-Transmittance-Reflectance spectra in the wavelength range 300-900nm, a Veeco Dektak 150 stylus surface profiler for thickness measurement. Film G_5 was used to study the structure and morphology of CuS films. To this end, an MPD X^1 Pert PRO (PAN ANALYTICAL) X-ray diffractometer with CuKα (1.54Å) radiation, operating at 40mA and 45kv, and a TM 3000 Tabletop Microscope (HITACHI) were used to study the structure and morphology of the film before and after annealing at 573k.

The absorbance, transmittance and reflectance were used to calculate the absorption, extinction coefficients α, k and the refractive index (n) from mathematical relations given by (Gumus et al, 2007; Pankove, 1971; Tanusevski, 2003). The optical conductivity, σ_{op} and the direct band gap E_g where calculated from relations given by (Pankove 1971; Stern, 1963; and Abeles, 1972).

3. Results and Discussion

The elemental composition was analyzed using Rutherford Backscattering Spectrometry (RBS). The result is shown in figure 1.

The RBS spectrum shows the number of backscattered He^+ ions as a function of their energy. The composition of CuS and substrate from RBS analysis is displayed in table 2. The proportion of constituent element measured was Cu = 50.96% and S=49.04%.The composition was near stoichiometric. RBS spectrum shows that films are free from impurities. The O_2, Si, Na, Al, Ca, Fe observed are due to substrate. Figure 2, shows a plot of thickness versus time for varying morality concentrations of complexing agent (TEA). The graph shows that the film growth sets in after an initial nucleation period of 1-4hrs. Thickness increased with deposition time and as the concentration of complexing agent increased. This shows a direct proportionality between thickness and concentration of TEA.

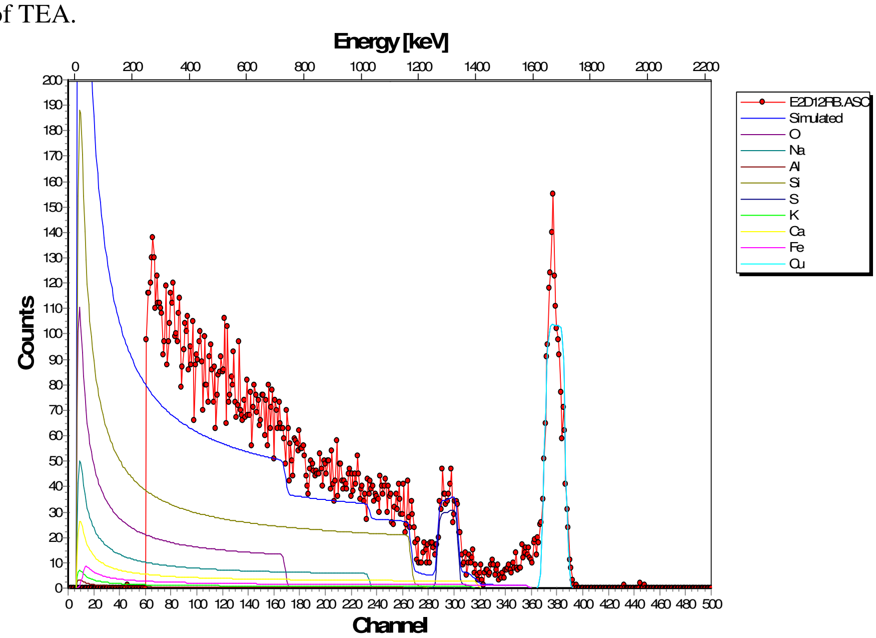

Figure 1. RBS analysis for CuS thin films

Table 2. Composition of CuS and substrate from RBS analysis

CuS	Cu	S	O	Si	Na	Fe	Al	Ca
G_5	50.96%	49.04%	-	-	-	-	-	-
Substrate	-	-	0.56%	28.00%	12.69%	0.52%	0.53%	1.83%

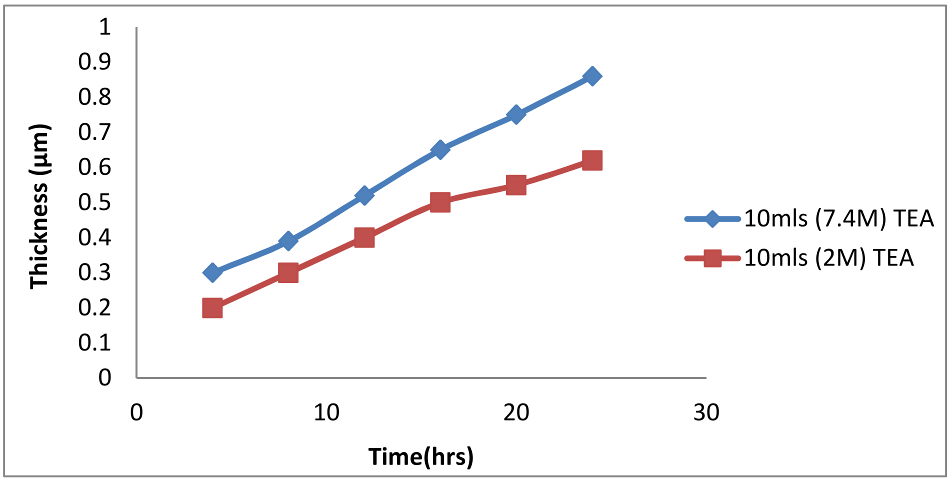

Figure 2. Plot of Thickness Vs Time for CuS fIlms for varying molarity concentrations of TEA

The spectral absorbance of the CuS thin films deposited at different bath parameters are shown in figure 3. while transmittance and reflectance spectra are displayed in figures 4 and 5.

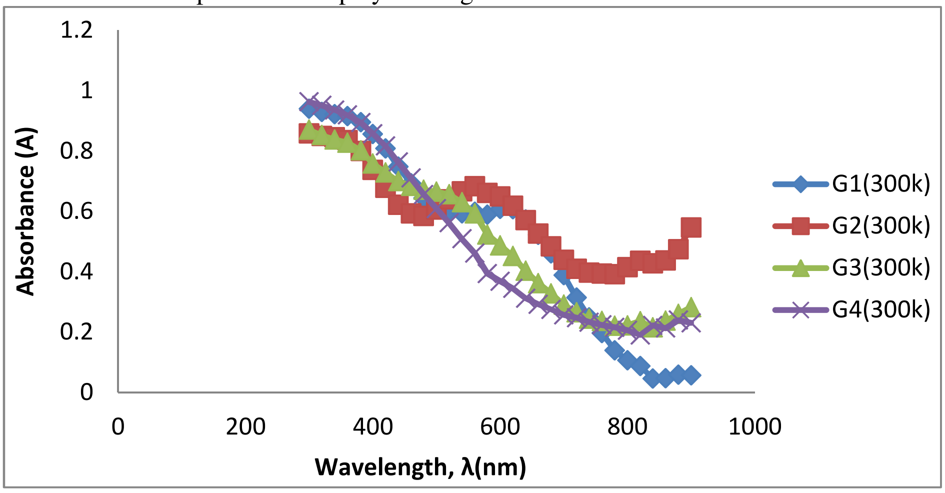

Figure 3. Spectral absorbance of Copper Sulphide (CuS) thin films

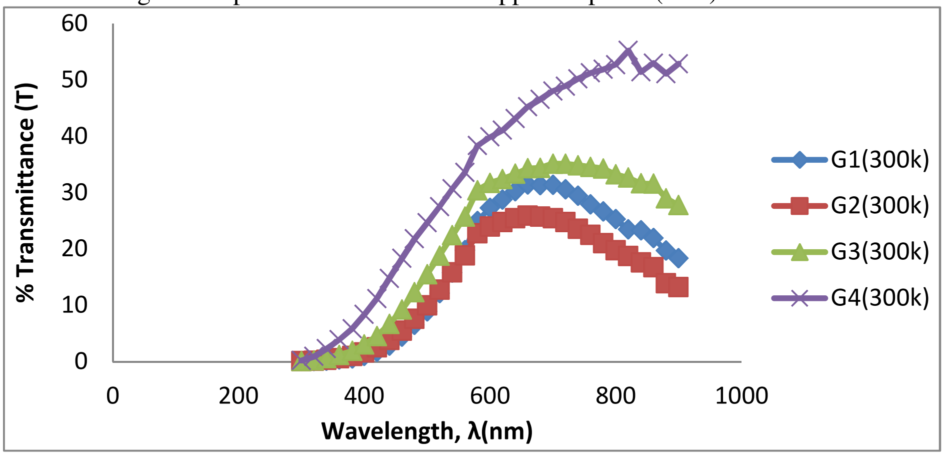

Figure 4. Spectral transmittance of Copper Sulphide (CuS) thin films

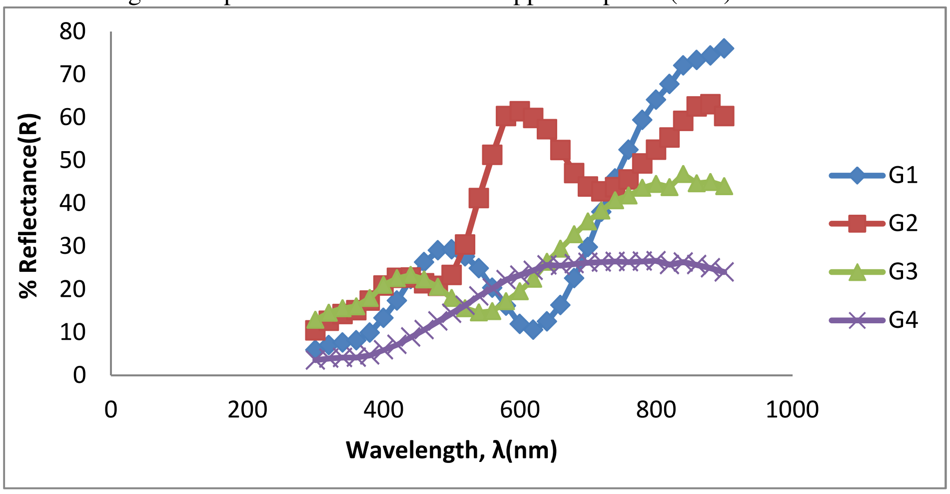

Figure 5. Spectral reflectance of Copper Sulphide (CuS) thin films

Generally, the film spectra indicate that strong absorption is obtained at shorter wavelengths (UV-VIS) while weak absorption is observed at longer wavelengths. The highest peak of 96.3% was noted for film G_4 in the Uv region. All the films showed good absorption in the range 85%-40% in the visible region. This is in line with report of Luminita et al (2007) for CuS because high absorbance makes the films potential absorber materials in devices for photovoltaic conversion of solar energy. The films showed little or no transparency in the UV region which increased between 25.97% and 52.97% in the visible and NIR regions. Film G_4 has a peak transmittance of 52.97% at 860nm. The peak reflectance of the films range between 26.66% to 76.09% in the VIS-NIR regions. The films are therefore suitable for use as thin coatings on architectural windows for warm climates since they will control the amount of light that enters a building and also reflect as much infrared radiation as possible.

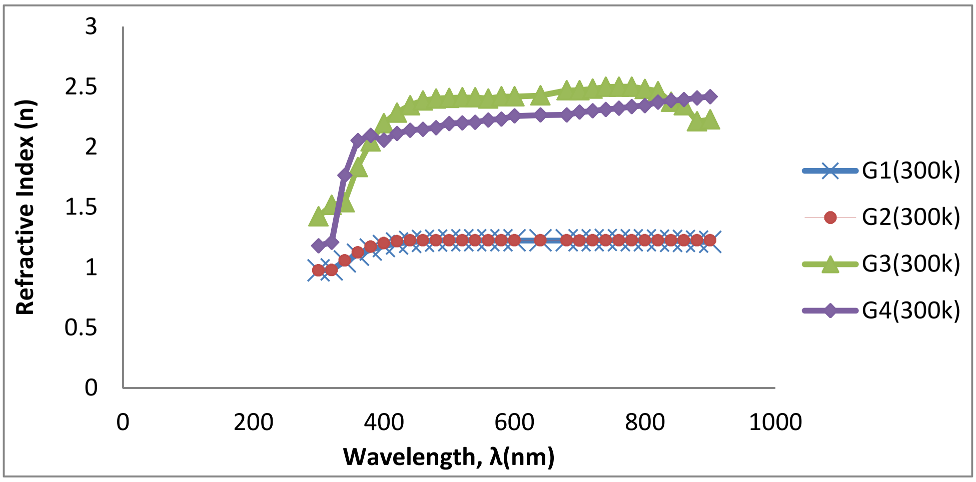

Figure 6. Plot of refractive index (n) against wavelength (λ) for CuS thin films

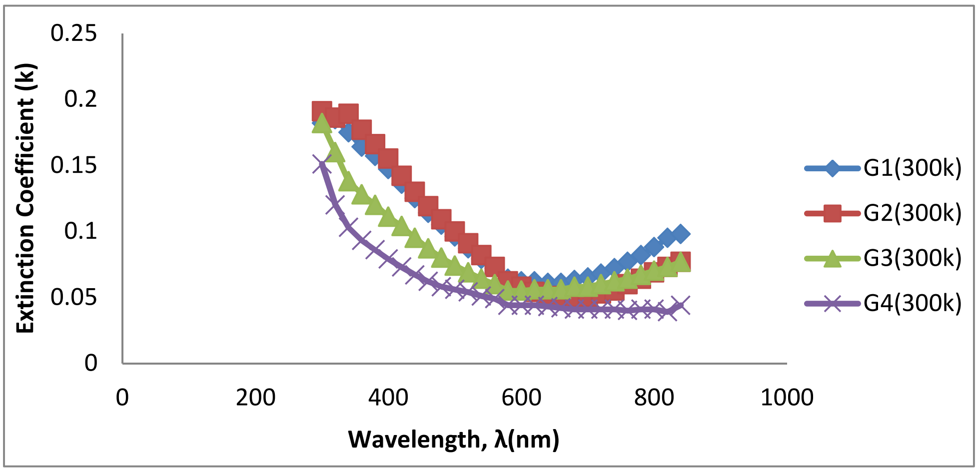

Figure7. Plot of extinction coefficient (k) against wavelength (λ) for CuS thin films

Figure 6 relates the refractive index (n) with wavelength while figure 7 shows plot of extinction coefficient (k) with wavelength. Minimum value of k for the films is 0.039 and maximum is 0.191 which occurred at 820nm (1.51eV) and 300nm (4.12eV) respectively. The average values of refractive index range between 1.18 and 2.47. These values are comparable with previous reports of 2.28 (Ezema et al, 2006), 1.78-2.63 (Ilenikena, 2008).

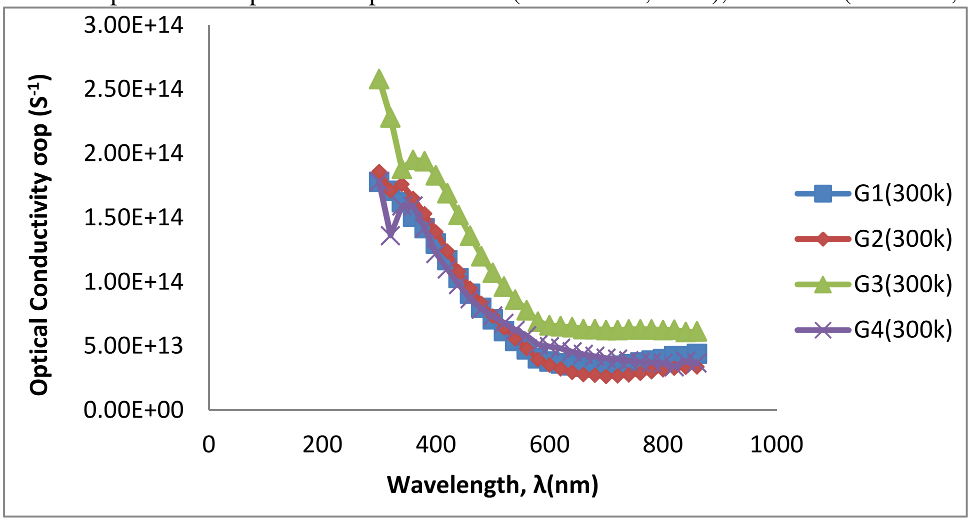

Figure 8. Plot of optical conductivity (σ_{op}) against wavelength (λ) for CuS thin films

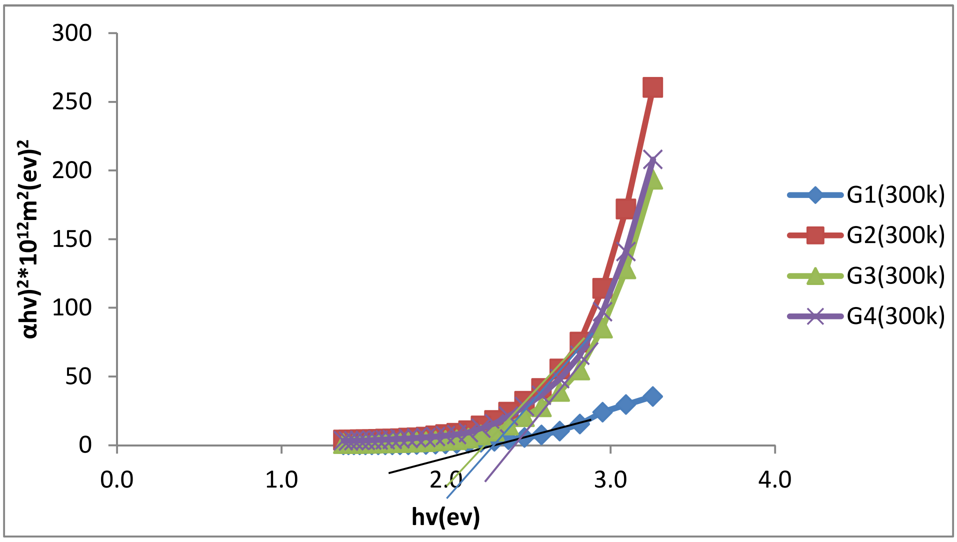

Figure 9. Variation of $(\alpha h\nu)^2$ with photon energy (hν) for CuS thin films

Plot of optical conductivity against wavelength is shown in figure 8. It decreased from UV towards longer wavelengths. The average values range between 7.26 x $10^{-13}S^{-1}$ and 10.80 x $10^{13}S^{-1}$.
Figure 9. shows that CuS film has direct band gap which was calculated from Stern (1963) equation

$$\alpha = \frac{[A(hv-Eg)]^{1/2}}{hv} \quad (1)$$

where; α is the absorption coefficient, hν is the incident photon energy, A is a constant and E_g is the band gap energy.
Extrapolation of the straight portion of the curves in figure 9 to the energy axis where $(\alpha h\nu)^2 = 0$ gives the value of direct band gap. The band gap is shown to vary between 2.30eV and 2.44eV as thickness varies from 0.295µm-0.506µm. The values are within the range 2.10eV-2.50eV reported by Offia et al (2012); 2.31eV obtained by Abhay et al (2008) and 2.35eV reported by Guneri and Kariper (2012) for chemically deposited CuS. A direct band gap value of 2.54eV using spray pyrolysis method was reported by Mehdi Adelifard et al (2012). Also optical band gap of 2.15-2.53eV. using photochemical deposition was reported by Jiban et al (2005) while Pathan and Lokhande (2004) reported band gap values 1.20eV-2.50eV using SILAR method. The band gap values together with high absorbance makes them good materials for fabrication of solar cells. The average values of parameters studied are displayed in table 3.

Table 3. Average values of parameters studied for as-deposited CuS films

Sample	Dip time (hrs)	Av. thickness(µm)	Band gap E_g (ev)	Av. n	Av. K*10^{-2}	Av. σ_{op}*$10^{13}(s^{-1})$
G_1	8	0.295	2.40	1.19	10.27	7.33
G_2	16	0.329	2.30	1.20	9.66	7.26
G_3	20	0.354	2.44	2.27	8.38	10.80
G_4	24	0.506	2.36	2.16	5.88	7.41

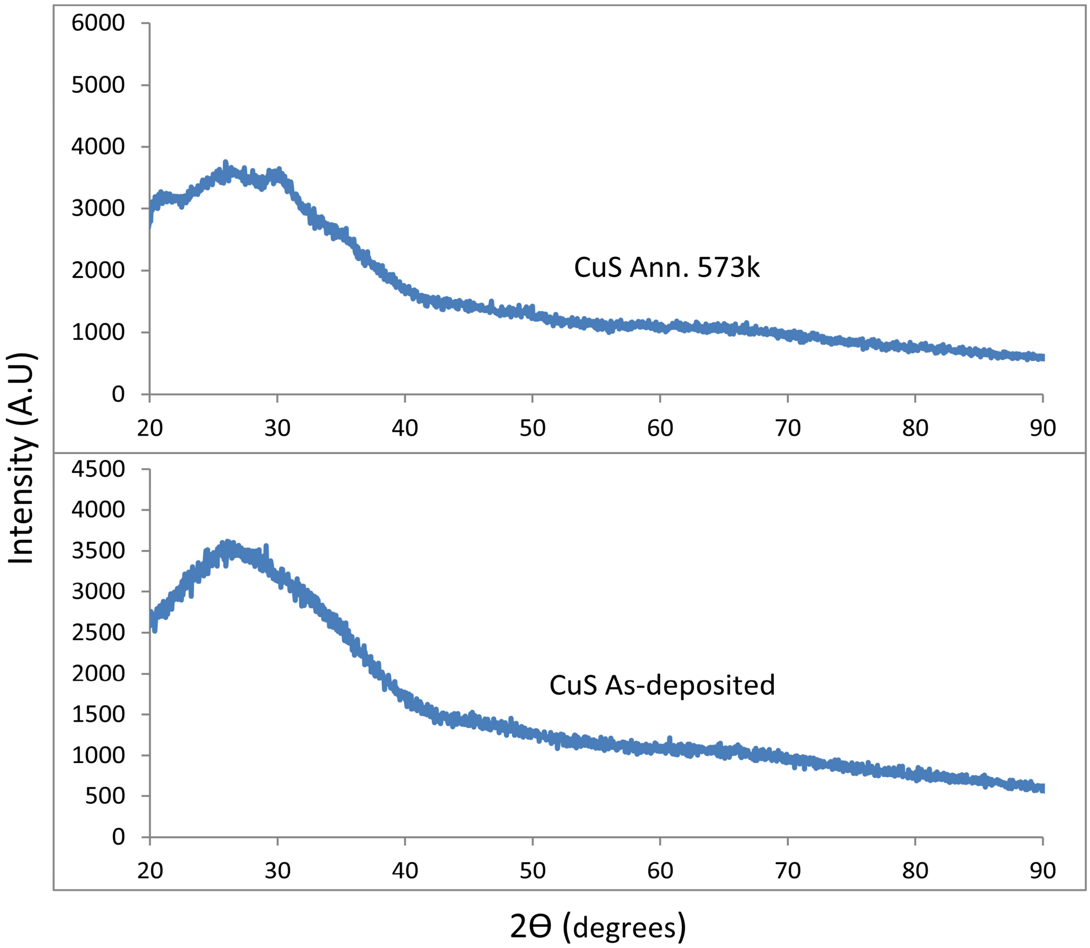

Figure 10. XRD pattern of CuS films as-deposited and annealed at 573k

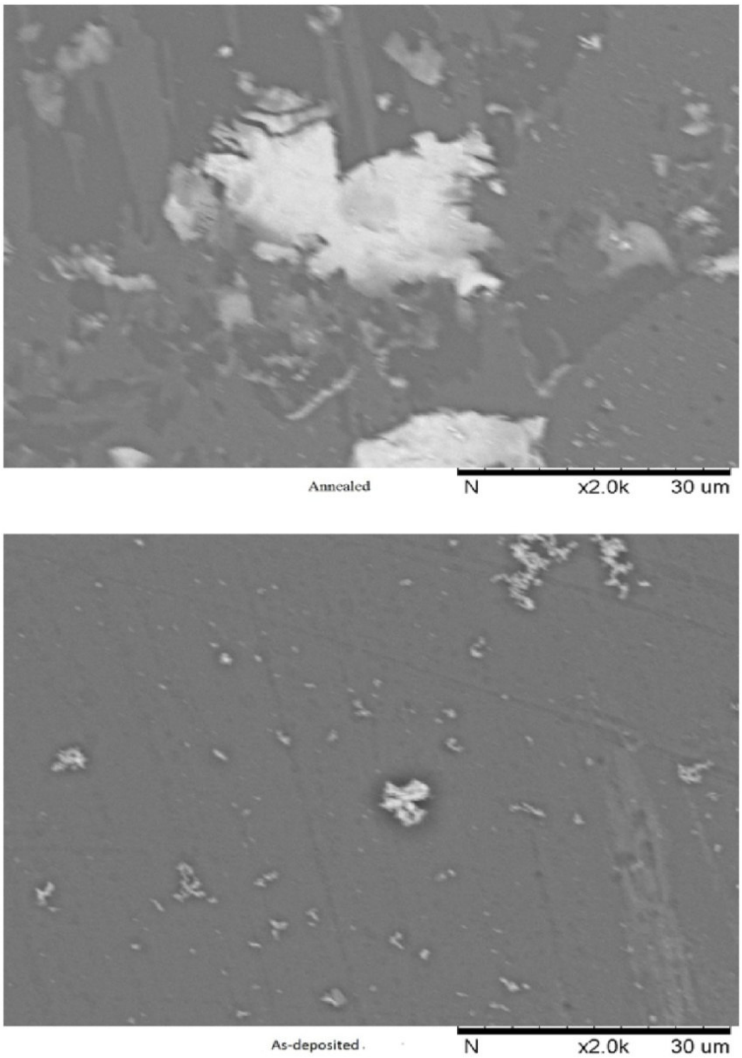

Figure 11. SEM micrographs of annealed and as-deposited CuS thin films

Figure 10 shows the X-ray diffraction pattern of as-deposited CuS films and annealed at 573k while figure 11 show the SEM micrographs of the same films. The diffraction patterns for as-deposited and annealed samples are amorphous. It is observed that the structural properties were not affected by annealing. The annealed film showed broad peaks but did not yield any information regarding its structure. This may be due to low temperature used during deposition. The as-deposited film in the SEM micrograph contains irregular features which clustered at different areas on the surface showing amorphousness. These features were highly magnified on annealing to flower-like agglomerated features which showed increase in amorphousness. CBD-derived CuS films on glass substrates, in previous work have been found to be amorphous by Guneri and Kariper (2012); Apolinar-Iribe et al (2013); Adel and Mustafa (2013).

Conclusion

CuS has been deposited from an alkaline medium by employing chemical bath deposition method. XRD and SEM studies showed that structural nature of the CuS thin films was amorphous for the as-deposited and annealed. All the films showed high absorption in the UV-VIS region with peak value of 96.30% in the UV. Some of the films showed high reflectance 76.09% in the NIR region and moderate transmittance in the visible region. The refractive index (n) of the films range between1.18-2.47 while the extinction coefficient (k) range between 0.039-0.191. Band gap values in the range of 2.30eV to 2.44eV were obtained for CuS thin films which varied as thickness varied from 0.295μm to 0.506μm. Film thickness was found to increase with time as well as molar concentration of complexing agent. The optical characterizations, within the UV-VIS-NIR regions showed that the grown amorphous CuS thin films have potential applications as absorber in devices for photovoltaic conversion of solar energy and as anti-reflection coatings; and transparent conductors in solar cells. The films are also good materials for application in thin film transistors and gas sensors.

Acknowledgements
The Authors are grateful to Prof. Obiajunwa of Energy Centre, Obafemi Amolowo University, Ile-Ife for help in the RBS analysis; Mr. Adama of Sheda Science and Technology Complex, (Shestco) Abuja for help in the XRD analysis; Mrs Unogu of Shestco, for help in the UV-Visible-NIR Studies and Mr Adurafimihan Abiona of School of Physical, Environmental and Mathematical Sciences (PEMS), University of New South Wales for help in the scanning electron microscopy.

References
Abeles, F. (1972), "Optical Properties of Metals: In Optical Properties of Solids", Abeles (Edn). North-Holand Pub. Co. Amsterdam p.97.
Abhay, A., Sagade Ramphal, Sharma (2008), "Copper Sulphide as An Ammonia Gas Sensor Working At Room Temperature", *Sensor and Actuators B. Chemical* 133, 135.
Adel, H., Omiran Al-Khayatt & Mustafa, D. Jaafer (2013), "Annealing Effect on The Structural and Optical Properties Of CuS Thin Film Prepared By Chemical Bath Deposition (CBD)", *Journal of KUFA-PHYSICS* 5(1), 79-90.
Apolinar-Iribe, A., Acosta-Enriquez, M. C., Berman-Mendoza, D., Mendivil-Reynoso, T., Larios-Rodiguez, E., Ramirez-Bon, R., & Castillo, S. J. (2013), "Effects Of The Annealing on CuS Thin Films Using Triethanolamine as Complexing Agent by CBD", *Chalcogenide Letters* 10(12), 543-553.
Ezema, F. I., Nnabuchi, M. N., & Osuji, R. U. (2006), "Optical Properties of CuS Thin Films Deposited by Chemical Bath Deposition Technique and Their Applications", *Trends In Applied Sciences Research* 1, 467-476.
Gumus,C., Ulutas,C., & Ufuktepe,Y. (2007), "Optical Properties of manganese sulphide thin films", *Optical materials* 29, 1183-1189.
Guneri, E., and Kariper, A. (2012), "Optical Properties of Amorphous CuS Thin Films Deposited Chemically at Different PH Values", *Journal of Alloys and Compounds* 516, 20-36.
Ilenikhena, P. A. (2008), "Comparative studies of improved chemical bath deposited Copper Sulphide (CuS) and Zinc Sulphide(ZnS) thin films at 320k and possible applications", *African Physical Review* 2, 59.
Jiban Podder, Ryohei Kobayashi & Masaya Ichimura (2005), "Photochemical Deposition of Cu_xS Thin Films From Aqueous Solutions", *Thin Solid Films* 472, 71-75.
Luminita Isac, Anca Duta, Angela Kriza, Simona Manolache, Marian Nanu (2007), "Copper Sulfides Obtained by Spray Pyrolysis - Possible Absorbers In Solid State Solar Cells", *Thin Solid Films* 515(15), 5755-5758.
Mehdi Adelifard, Hosen, E. Shghi, Mohamed Mehdi Mohagheghi (2012), "Comparative Studies Of Spray Pyrolysis Deposited Copper Sulphide Nanostructural Thin Films On Glass and FTO Coated Glass", *Bull. Mater. Sci.* 35(5), 739-744.
Nair, P. K., Nair, M. T. S., Garcia, V. M., Arenas, O. L., Pena, A. C., Ayala, I. T., Gomezdaza, O., Sanchez, A., Campos, J., Hu, H., Suarez, R., Rincon, M. E. (1998), "Semiconductor Thin Films By Chemical Bath Deposition For Solar Energy Related Applications Solar Energy Materials and Solar Cells" 52(3), 314-344.
Nair, M. T. S., & Nair, P. K. (1989), "Chemical Bath Deposition Of CuS Thin Films and Their Prospective Large Area Applications", *Semicond. Sci. Technol* 4, 191-199.
Okujagu, C. U. (1992), "Growth and Characterization of Thin Film Selective Surfaces and Their Applications", *Ph.D. Thesis*. University of Nigeria, Nsukka.
Pankove, J. T. (1971), "Optical Processes in Semiconductors", Prentice-Hall. New Jersey p58.
Pathan, H. M., & Lokhande, C. D. (2004), "Deposition Of Metal Chalcogenide Thin Films by Successive Ionic Layer Adsorption and Reaction (SILAR)", *Method. Bull.* Mater. Sci. 27(2), 85-111.
Stern, F. (1963), "Elementary theory of the optical properties of solids, solid state Physics" 15, 299-408.
Thanikaikarasan, S., Mahalingam, T., Kathailingam, A., Moon Hosun & Yong Deak Kim (2010), "Characterization of Electrodeposited Copper Sulphide Thin Films", *Journal of New Materials For Electrochemical Systems* 13, 29-33.

First Author
Chizomam Usoh. B.Sc physics (1979) University of Nigeria Nsukka, Nigeria; M.Sc (solid state physics and materials science) 1998 from Federal University of Technology,Owerri, Nigeria. Serves in the Department of Physics, Alvan Ikoku Federal College of Education Owerri, Nigeria. Her research interests include deposition of nanomaterials, photovoltaics and energy conversion applications.
Second Author
Prof. (Mrs) Charity Okujagu. B.Sc physics, M.Sc meteorology, Ph.D. solar energy physics. Professor of solar energy physics and materials science. She serves in the Department of physics, University of Port Harcourt, Nigeria. Her research interests include solar energy materials and material science, organic and nanomaterials for electronics, optoelectronics and energy applications.