Fabrication and Characterization of pH Optimized Copper Zinc Sulphide ($CuZnS_2$) Ternary Thin Films by Chemical Bath Method

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ABSTRACT

Chemically synthesized thin films of Copper Zinc Sulphide were successfully fabricated and characterized. The fabrication of the films were done under room temperature of about 300 ± 0.2 K from aqueous solution of copper chloride dehydrate, zinc chloride, thiourea, ammonium solution, Ethylenediaminetetraacetate (EDTA) and Triethanolamine (TEA). Zinc chloride, copper chloride and thiourea served as precusors for Zn^{2+}, Cu^{2+} and S^{2-} ions needed for the formation of the desired film from the solution containing these compounds. Ammonium solution was used to achieve variation in the pH of the reacting medium while EDTA and TEA were used as complexing agents for slow precipitation of cations from their parent compound. Optical characterization of the films was done using UV – VIS – NIR spectrophotometer in the wavelength range of 300 nm – 1100 nm. Optical properties such as absorbance, transmittance, reflectance, refractive index and band gap value of range (2.50 eV – 2.70 eV) were determined. XRD analysis of the films was carried out using Enhanced Mini – Material Analyzer (EMMA) X – ray Diffractometer machine. The grain sizes obtained from the XRD result range from 19.07 nm – 28.79 nm. Surface structures of the films were studied using Olympus Microscope. Micrographs obtained were analyzed using imageJ software for image analysis. The average particle sizes obtained range from 17.08 nm to 24.23 nm.

Keyword: CBD, Ternary Thin Films, XRD, ImageJ, Optical Properties

INTRODUCTION

In the field of material science, thin film has elicited great attention amongs researchers because of numerous applications in various fields. Thin films can be defined as thin material layers ranging from nanometer to micrometers thickness (Smith 1995). According to Ezema (2004),
Materials are said to be thin films when they are built up as thin layers on a substrate by controlled condensation of the individual atomic, molecular or ionic species directly by a physical process or through a chemical or electrochemical reaction. Thin film deposition involves deposition of individual atoms or deals with the deposition of particles, thin film is refers to as a very thin layer of material with thickness varied between 5 nm to 100 nm. Thin films are applied in integrated circuits, electronic packages, optical sensors and devices (William, 2007). The phenomenal rise in thin film research is no doubt due to their extensive application in diverse fields such as electronics, optics, space science, aircraft, defense and other industries. These investigation have led to numerous inventions in the form of active and passive components, piezo – electric devices, micro – miniaturization of power supply, rectification and amplification, sensor elements, storage of solar energy and conversions to other forms, magnetic

memories, superconducting films, interference filters, reflection and antireflection coatings and many others (Goswami, 2008). A thin film can be binary, ternary, and quaternary, depending on the elemental compositions that make up the film.

Ternary thin films are thin films that contain three different elements (Ezenwa and Okoli, 2015a).

There is considerable interest in the deposition of ternary derivative material, due to the potential of tailoring both the lattice parameters and the band gap by controlling depositions parameters (Sankapal and Lokhande, 2002). Ternary thin films have been grown and characterized by some researchers using different deposition methods which include: $CuSbS_2$ (Rastogi and Janardhana, 2014), FeCuS (Ezenwa and Okoli, 2015a), $CuInS_2$ (Seung and Byung 2008), CuNiS (Okereke and Ezenwa, 2015), Cu_2SnS_3 (Reddy et al., 2015) and many others. Ternary thin films are found to be suitable materials for optoelectronic device applications and good material for window layer solar cells (Woon-Jo and Cye-Choon, 2003), Some of these films have been investigated for use as superionic conducting materials (Nair et al., 1990). Ternary compounds had also been studied for efficient solar energy conversion materials (Lee et al., 2003).

In this present investigation, preparation parameter such pH was optimized in order to obtain high quality and well adhesive CuZnS thin films on microscopic glass substrates at room temperature using chemical bath deposition method.

MATERIALS AND METHOD

Copper Zinc sulphide (CuZnS) was deposited by the reaction of solutions containing copper chloride dihydrate ($CuCl.2H_2O$), zinc chloride ($ZnCl_2$), EDTA ($Na_4(C_{10}H_{16}N_2O_8)$), TEA ($C_6H_{15}NO_3$), ammonium solution [NH_4OH], thiourea $(NH_2)_2CS$ and distilled water in a beaker. The complexing agents are EDTA and TEA. The addition of TEA and EDTA as complexing agents slowed down the precipitation of metal ions of copper and zinc in the reacting solution. Deposition of CuZnS thin films of $CZ_6,\ CZ_7,\ CZ_8,\ CZ_9\ and\ CZ_{10}$ were carried out using 100 ml glass beaker at an average room temperature of 303 K. $3\,ml$ of Zinc chloride and Copper chloride dihydrate were measured, transferred into the beaker. The mixture was stirred for 5 minutes after which $2\,ml$ of thiourea was added and stirred to have a homogeneous mixture. Addition of thiourea formed a jelly – like solution, followed by addition of $1.0\,ml$ of EDTA, and $1.0\,ml$ of TEA. Different volumes of ammonium solutions were added to each of the five baths. Volumes of ammonium solutions used were $3\,ml$, $4\,ml$, $5\,ml$, $6\,ml$ and $7ml$.The solution was stirred for 5 minutes followed with addition of $50\,ml$ of distilled water. Each of the final solutions was stirred for another 5 minutes to have a homogeneous mixture. A constant time of 36 hours and temperature of 300K were maintained throughout the deposition period. The reason of varying the volume of ammonium solution was to alter the pH of the depositing baths. pH obtained were 9.4, 9.8, 10.1, 10.4 and 10.9. Molarity and volume of reagents used are stated in table 1 below. Chemical reaction involved in the deposition processes are as follows:

$$CuCl_2.2H_2O + EDTA \longrightarrow [Cu(EDTA)] + Cl^-$$
$$[Cu(EDTA)] \longrightarrow Cu^{2+} + EDTA^{2-} \qquad 1$$
$$ZnCl_2 + TEA \longrightarrow [Zn(TEA)]^{2+} + Cl^-$$
$$[Zn(TEA)]^{2+} \longrightarrow Zn^{2+} + TEA \qquad 2$$

$(NH_2)_2CS + OH^- \longrightarrow (NH_2)_2CO + HS^-$

$HS^- + OH^- \longrightarrow H_2O + S^{2-}$ 3

$Cu^{2+} + Zn^{2+} + S^{2-} \longrightarrow CuZnS_2$ 4

The sulphide ions are released by the hydrolysis of thiourea, Cu^{2+} and Zn^{2+} ions are from complexes which the solution of their precursors formed with EDTA and TEA. The Cu^{2+}, Zn^{2+} and S^{2-} present in the solution combined to form CuZnS molecules which were deposited on the glass substrates. The films grown were characterized for optical absorbance using Janway 6405 UV – VIS spectrophotometer. From the values of absorbance obtained, other properties such as film transmittance, reflectance, thickness and band gap energy were determined through theoretical calculations. These optical properties were obtained in the wavelength range of 300 nm– 1100 nm. Surface microstructure of the films was done using optical microscope. XRD analysis of one film was carried out using Enhance Mini Material Analyzer (EMMA) X – Ray Diffractometer Machine. Crystalline nature of the films, 2 theta angles, d - spacing and grain size were determined.

Table 1: Optimization of Copper Zinc Sulphide (CuZnS) with pH at Room Temperature

Baths	**pH**	**$CuCl.2H_2O$**		**$ZnCl_2$**		**EDTA**		**TEA**		**$(NH_2)_2CS$**		**NH_4OH**	
		Mol. (m)	**Vol. (ml)**	**Mol. (m)**	**Vol. (ml)**	**Mol. (m)**	**Vol. (ml)**	**Mol. (m)**	**Vol. (ml)**	**Mol. (m)**	**Vol. (ml)**	**Mol. (m)**	**Vol. (ml)**
CZ_8	**9.4**	**2.0**	**3.00**	**0.5**	**3.00**	**0.5**	**1.00**	**7.4**	**1.00**	**2.0**	**2.00**	**14.0**	**3.00**
CZ_9	**9.8**	**2.0**	**3.00**	**0.5**	**3.00**	**0.5**	**1.00**	**7.4**	**1.00**	**2.0**	**2.00**	**14.0**	**4.00**
CZ_{10}	**10.1**	**2.0**	**3.00**	**0.5**	**3.00**	**0.5**	**1.00**	**7.4**	**1.00**	**2.0**	**2.00**	**14.0**	**5.00**
CZ_{11}	**10.4**	**2.0**	**3.00**	**0.5**	**3.00**	**0.5**	**1.00**	**7.4**	**1.00**	**2.0**	**2.00**	**14.0**	**6.00**
CZ_{12}	**10.9**	**2.0**	**3.00**	**0.5**	**3.00**	**0.5**	**1.00**	**7.4**	**1.00**	**2.0**	**2.00**	**14.0**	**7.00**

RESULTS AND DISCUSSIONS

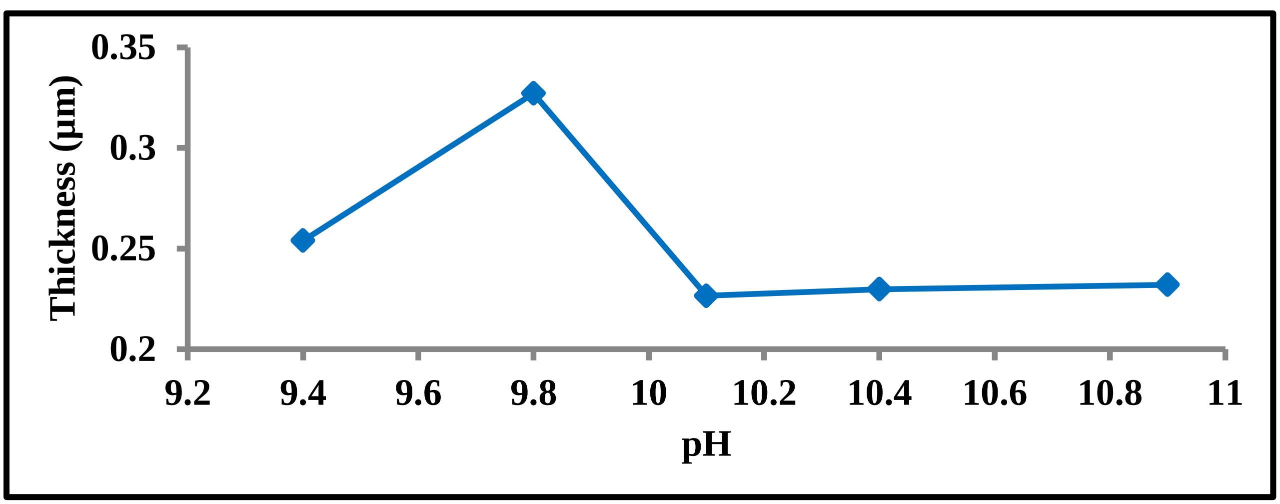

Fig. 1: Graph of Thickness (µm) versus pH for *CuZnS* Thin Films

The optical properties of as – grown Copper Zinc Sulphide under varying pH condition were studied using the absorbance values obtained in the UV region (300nm – 400nm), VIS region (400nm – 700nm) and NIR region (700nm – 1100nm). Figure 1 above shows the variation of optical thickness of the deposited films with pH of the reacting solutions. The optimal thickness of 0.327 μm was obtained at pH of 9.8 which decreased slightly to 0.23 μm at pH values of 10.1, 10.4 and 10.9 respectively.
Optical properties of the deposited films are plotted against wavelength as shown in figures 2, 3, 4 and 5 below for absorbance, transmittance, reflectance and refractive index respectively. The absorbance of the grown films is high in ultraviolet region but decreases as the wavelength increases. The films have low transmittance within the ultraviolet (UV) that increases slightly as the wavelength of electromagnetic radiation increases. Reflectance of the films is generally low. An optimal value of 0.2 was obtained for all the films at 300 nm. The reflectance decreases as wavelength increases. These results of low absorbance, high transmittance and low reflectance are in accordance with results obtained by Ezenwa and Okoli (2015b), Awoduga, and Ibiyemi (2012), Adulogu and Mukolu (2009), Uhuegbu and Babatunde (2008) for CuZnS thin films.

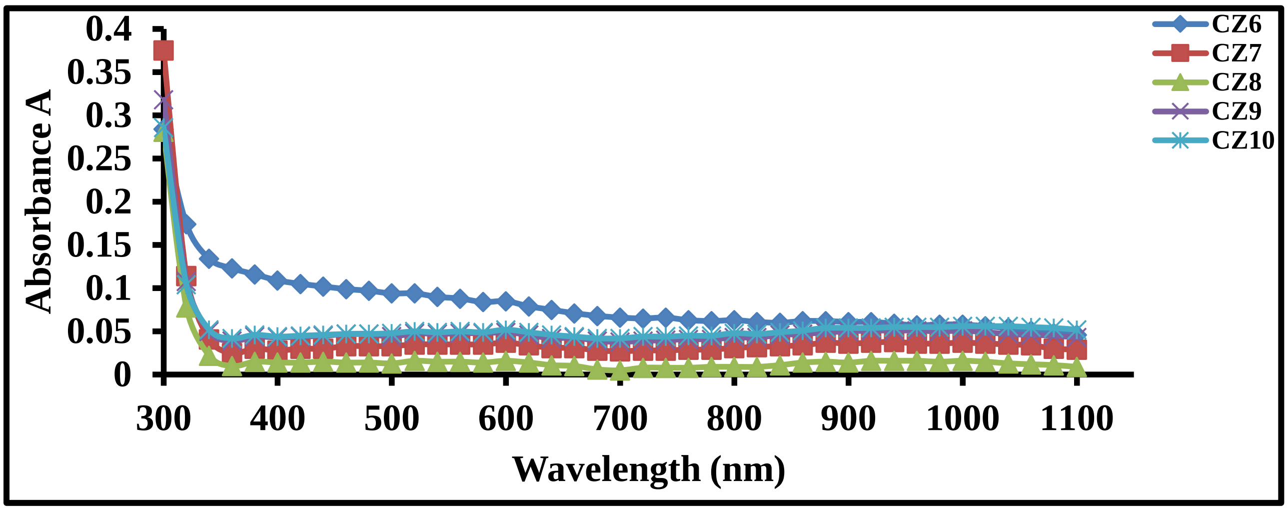

Fig. 2: Graph of Absorbance versus Wavelength (nm) for Slides CZ_6, CZ_7, CZ_8, CZ_9, CZ_{10}

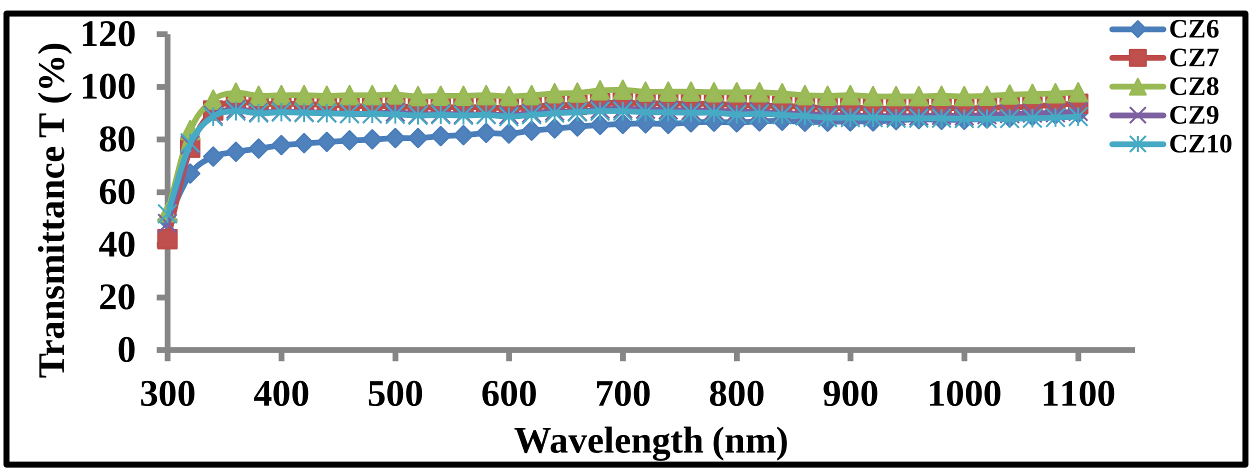

Fig. 3: Graph of Transmittance versus Wavelength (nm) for Slides CZ_6, CZ_7, CZ_8, CZ_9, CZ_{10}

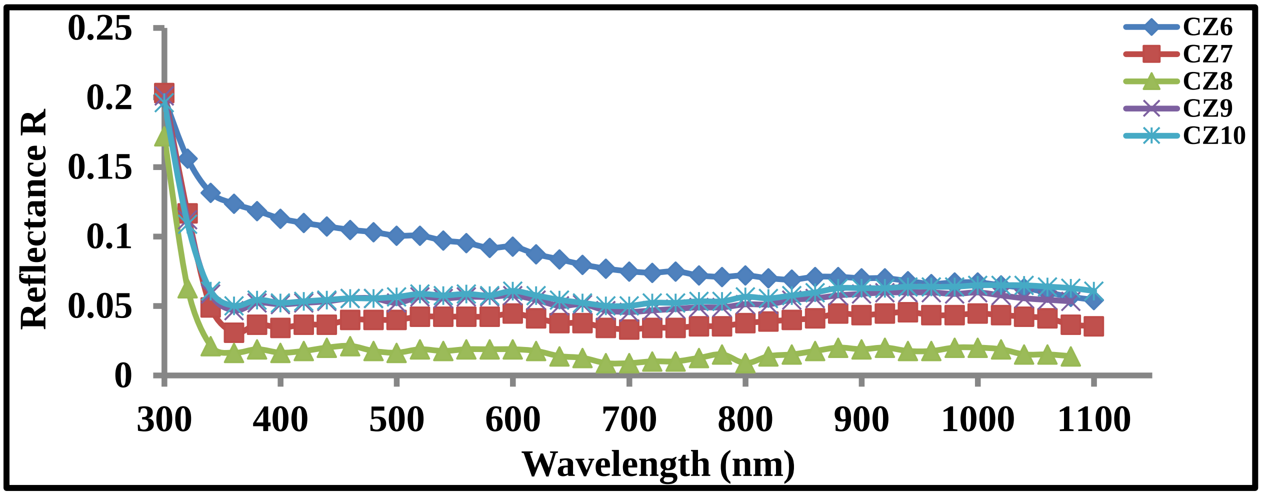

Fig. 4: Graph of Reflectance versus Wavelength (nm) for Slides CZ_6, CZ_7, CZ_8, CZ_9, CZ_{10}

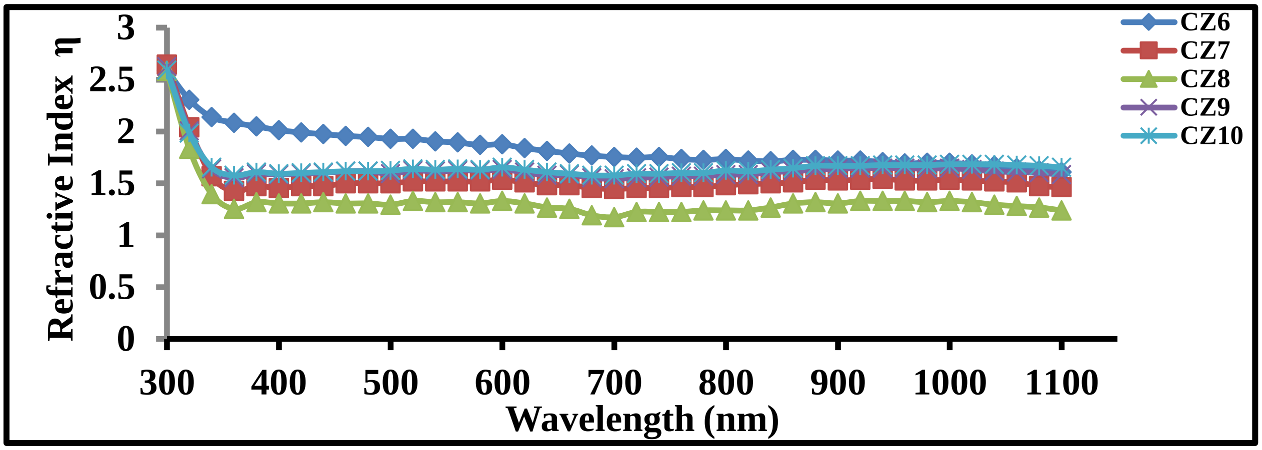

Fig. 5: Graph of Refractive Index versus Wavelength (nm) for Slides CZ_6, CZ_7, CZ_8, CZ_9, CZ_{10}

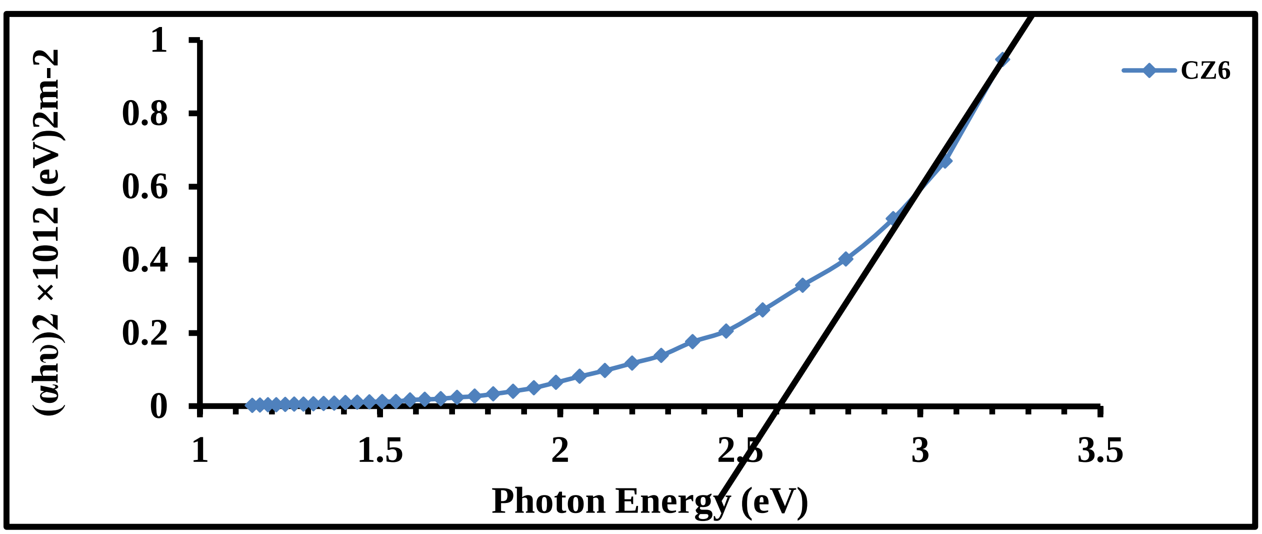

Fig. 6: Graph of $(\alpha h\upsilon)^2$ versus Photon Energy (eV) for Slide CZ_6

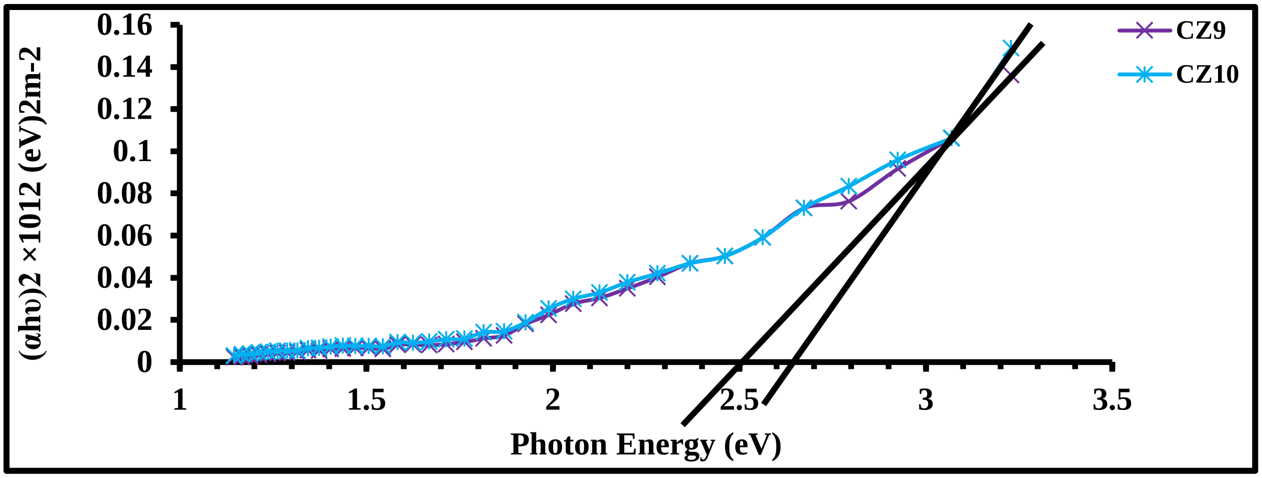

Fig. 7: Graph of (αhυ)^2 versus Photon Energy (eV) for Slide CZ_9 and CZ_{10}

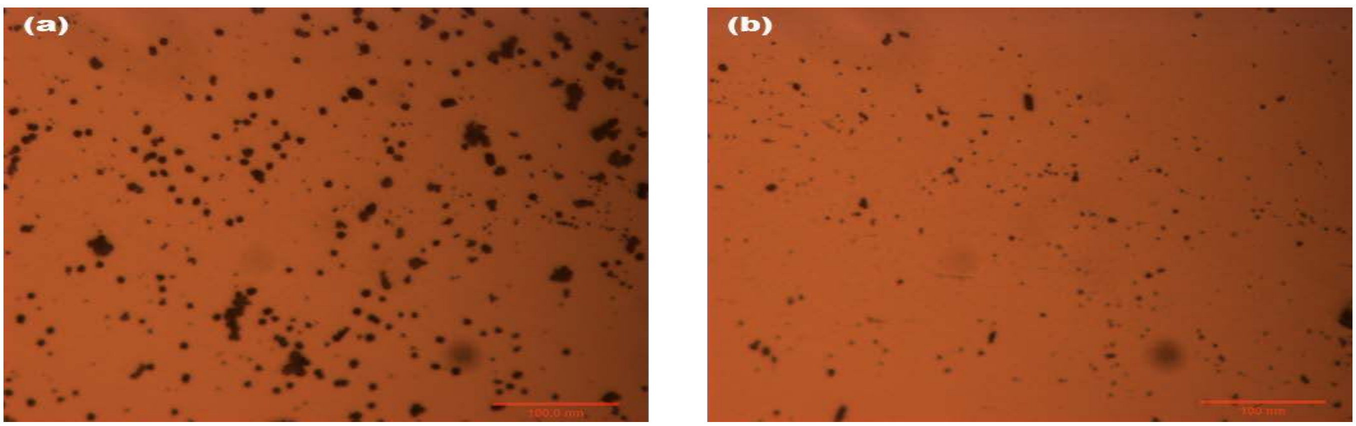

Fig. 8(a & b): Photomicrograph of $CuZnS$ for Slides CZ_6 and CZ_{10}

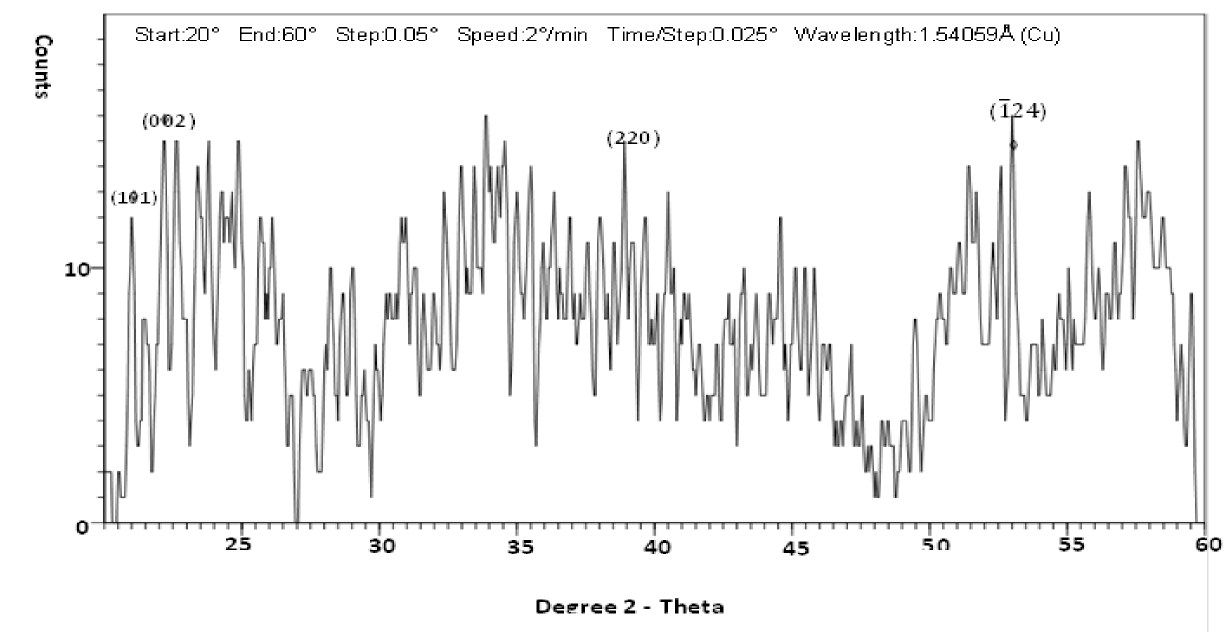

Fig. 9: X – ray Diffraction Spectra of Slide CZ_{10}

Figures 6 and 7 show the plots of $(\alpha h\upsilon)^2$ against photon energy from which the band gap was extrapolated at $(\alpha h\upsilon)^2 = 0$. The band energy obtained is between 2.5 eV and 2.7 eV which is in good agreement with results of Ezenwa and Okoli, (2015b), Uhuegbu and Babatunde (2008) for CuZnS thin films.

The micrographs of the deposited films are shown in figure 8(a & b). The micrographs obtained were analyzed using imageJ software for image analysis. The average particle sizes obtained for CuZnS thin film range from 17.08 nm to 24.23 nm. The result shows that the deposited thin films are nanoparticles of CuZnS. The X – ray diffraction spectrum of the CZ_{10} film is shown in Figure 9. Table 2 below shows the observed 2θ angles, d – spacings, the miller indices and grain sizes obtained from the x – ray spectrum analysis.

Table 2: X – Ray Analysis of the CZ_{10} film

2 theta (degree)	d - spacing	[hkl]	FWHM	Gran Size (nm)
21.08	4.211	[101]	0.544	19.07
22.20	4.001	[002]	0.453	24.33
38.89	2.316	[220]	0.480	26.35
53.05	1.725	$[\bar{1}24]$	0.429	28.76

CONCLUSION

We have successfully fabricated and characterized ternary transition metal chalcogenide thin film of Copper Zinc Sulphide by chemical bath deposition method using solution of copper chloride dehydrate, zinc chloride, EDTA, TEA, ammonium solution and thiourea. The films revealed high absorbance in ultraviolet region which decreases as wavelength shift through the visible and infrared regions. Transmittance is high in all the regions of the spectrum while reflectance is low in all wavelength studied. These optical properties confirm that the films are good materials for eye glass coating for protection, anti – reflective coating, solar cell fabrication, architectural design for cooling or heating of buildings and optoelectronics devices. Band gap energy value of the films ranges from 2.50 eV – 2.80 eV. The grain sizes obtained from the XRD result range from 19.07 nm – 28.79 nm. Micrographs obtained were analyzed using imageJ software for image analysis. The average particle sizes obtained show that the grown thin films are nanoparticles.

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