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Research article

CHARACTERIZATION OF CHEMICALLY SYNTHESIZED COPPER ZINC SULPHIDE ($CuZnS_2$) THIN FILMS

Ezenwa I. A. and Okoli N. L.

Anambra State University, Uli, Anambra State, Nigeria
E.mail: amakaezenwaosie@yahoo.com

Abstract

This paper reports the deposition and characterization of Copper Zinc Sulphide (CuZnS) ternary thin films prepared by chemical bath deposition technique onto glass substrate at room temperature of 300K from aqueous solution of copper chloride dehydrate, zinc chloride and thiourea, ammonium solution, EDTA and TEA. Copper chloride dehydrate, zinc chloride and thiourea, served as precursors for copper ion, zinc ion and sulphur ion, ammonium solution acted as pH controller while EDTA and TEA served as complexing agents. The optical characterization was done using a Janway UV- VIS spectrophotometer in the wavelength range of 300 nm – 1100 nm. The optical absorbance of the films was determined directly from the spectrophotometer. Other properties such as transmittance, reflectance refractive index and absorption coefficient squared were calculated. A band gap energy range between 2.4 eV to 2.7 eV was obtained. Olympus Optical Microscopy was used to capture the photomicrographs of the films.

Keywords: Optical Characterization, Chemical Bath Deposition, Ternary Thin Films, Band Gap, Optical Microscopy.

Introduction

Substrates used in deposition of thin films maybe in form of metal, ceramics, semiconductors, glasses or plastics. The search for thin film materials for solar energy conversion and other related applications has been recently identified. In the search for novel semiconductor materials for efficient solar energy conversion, ternary thin films have been investigated extensively (Estrella et al., 2003). The preparation and study of physical properties of ternary chalcogenide compounds has increased in recent years due to their wide range of application (Ezema, 2004). Recently, some transition metal ternary compounds have been investigated for various applications such as CuAgS (Uhuegbu, 2011), FeCuS (Ezenwa and Okoli, 2015), AgAlS (Okoli et al., 2006) and$Cd_{x-1}Mg_xS$(Waleed, 2010). Ternary compounds are found to be suitable material for optoelectronic device applications and good material for window layer solar cells (Woon – Jo and Gye – Choon, 2003). Ternary chalcogenide thin films have their possible applications in solar cells, light emitting diodes (LEDs) and non – linear optical devices (Ezema, 2004 and Iacomi et al., 2006).

The process of thin film deposition involves the deposition of material atom-by-atom, molecule by molecule, ion-by-ion or cluster of species by cluster of species condensation (Chopra, and Das, 1983). Films can be deposited on a substrate either by physical or chemical methods. Of all the methods of film deposition, Chemical Bath Deposition (CBD) technique has been widely used for the deposition of both binary and ternary compounds due to its low cost and is a less sophisticated technique.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). Many techniques have been successfully employed for these purposes: Chemical Vapour Deposition (CVD), (Frigo et al 1989), Successive Ionic Layer and Reaction (SILAR) (Nilolou et al., 1990), Chemical Bath Method (Ezenwa and Okoli, 2015) and Sol-gel Methods (Seung and Byung, 2008).

The present work describes a chemical method for deposition of CuZnS thin films from alkaline bath medium on glass substrates at various time intervals. The characterization of CuZnS films was carried out by XRD and optical studies to determine their field of possible applications. The optical properties studied were; absorbance (A), transmittance (T) and reflectance (R), which were used to calculate other properties such as refractive index (n), extinction coefficient (K) and the band gap energy of the as – grown films. These properties were determined based on the equations found in the literature of some researchers on thin films like that of (Ezema and Okeke, 2003).

Experimental Details

Copper Zinc sulphide (CuZnS) was deposited by the reaction of solution containing copper chloride dehydrate ($CuCl_2.2H_2O$), 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. Ammonia solution was used to stabilize the pH of the mixture. Deposition of CuZnS thin films of $CZ1,2,CZ3,CZ4\ andCZ5$ were carried out using 100 ml glass beaker at an average room temperature of 303K. Before the deposition of the films, the substrates used were degreased in trioxonitrate (V) acid for 48 hours, washed with detergent, rinsed in distilled water and dried in air. The degreased cleaned surface provide nucleation center for the growth of the films onto the substrate surface hence will result to highly adhesive and uniformly deposited films on the surface of the substrates. 3 ml of Zinc chloride and Copper chloride dihydrate were measured, transferred into the beaker. The mixture was stirred after which 2 ml of thiourea was added and stirred to have a homogeneous mixture. Addition of thiourea formed a jelly – like solution, 1.0 ml of EDTA, 1.0 ml of TEA and 3 ml of ammonium solution were added to the mixture. The solution was stirred for 5 minutes followed by addition of 35 ml of distilled water. The final solution was stirred to have a homogeneous mixture. The five beakers of $CZ1,2,CZ3,CZ4\ andCZ5$ were prepared in the same manner. The varying bath parameter is the deposition time. At 6 hours, the films had no deposit. They were allowed to stand for 12 hours after which deposition was noticed on the films. The remaining films were allowed to stand for 24 hours, 36 hours, 48 hours and 60 hours. The substrates were removed at the end of each time, rinsed in distilled water and dried in open air at room temperature (300K). Uniform, adherent and transparent film was noticed on the substrates. An average pH of 10.1 was obtained for the baths using a pH meter of accuracy ±0.1. Table 1 shows the detailed values of the molarity and volume of each reagent used. The chemical equation of the reaction for the deposition is given below:

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

$$ZnCl_2 + TEA \longrightarrow [Zn(TEA)]^{2+} + Cl^- \quad 3$$
$$[Zn(TEA)]^{2+} \longrightarrow Zn^{2+} + TEA \quad 4$$

$$(NH_2)_2CS + OH^- \longrightarrow (NH_2)_2CO + HS^- \quad 5$$
$$HS^- + OH^- \longrightarrow H_2O + S^{2-} \quad 6$$

$$Cu^{2+} + Zn^{2+} + S^{2-} \longrightarrow CuZnS_2 \quad 7$$

The sulphide ions are released by the hydrolysis of thiourea, copper ions and zinc ions are from complexes which the solution of their precursors formed withEDTA and TEA. The copper ions, zinc ions and sulphideions 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.

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

Reaction bath	Dip time (hrs)	$CuCl.2H_2O$		$ZnCl_2$		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_1	12	2.00	3.00	0.50	3.00	0.50	1.00	7.40	1.00	2.0	2.00	14.00	5.00
CZ_2	24	2.00	3.00	0.50	3.00	0.50	1.00	7.40	1.00	2.0	2.00	14.00	5.00
CZ_3	36	2.00	3.00	0.50	3.00	0.50	1.00	7.40	1.00	2.0	2.00	14.00	5.00
CZ_4	48	2.00	3.00	0.50	3.00	0.50	1.00	7.40	1.00	2.0	2.00	14.00	5.00
CZ_5	60	2.00	3.00	0.50	3.00	0.50	1.00	7.40	1.00	2.0	2.00	14.00	5.00

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Result and Discussion

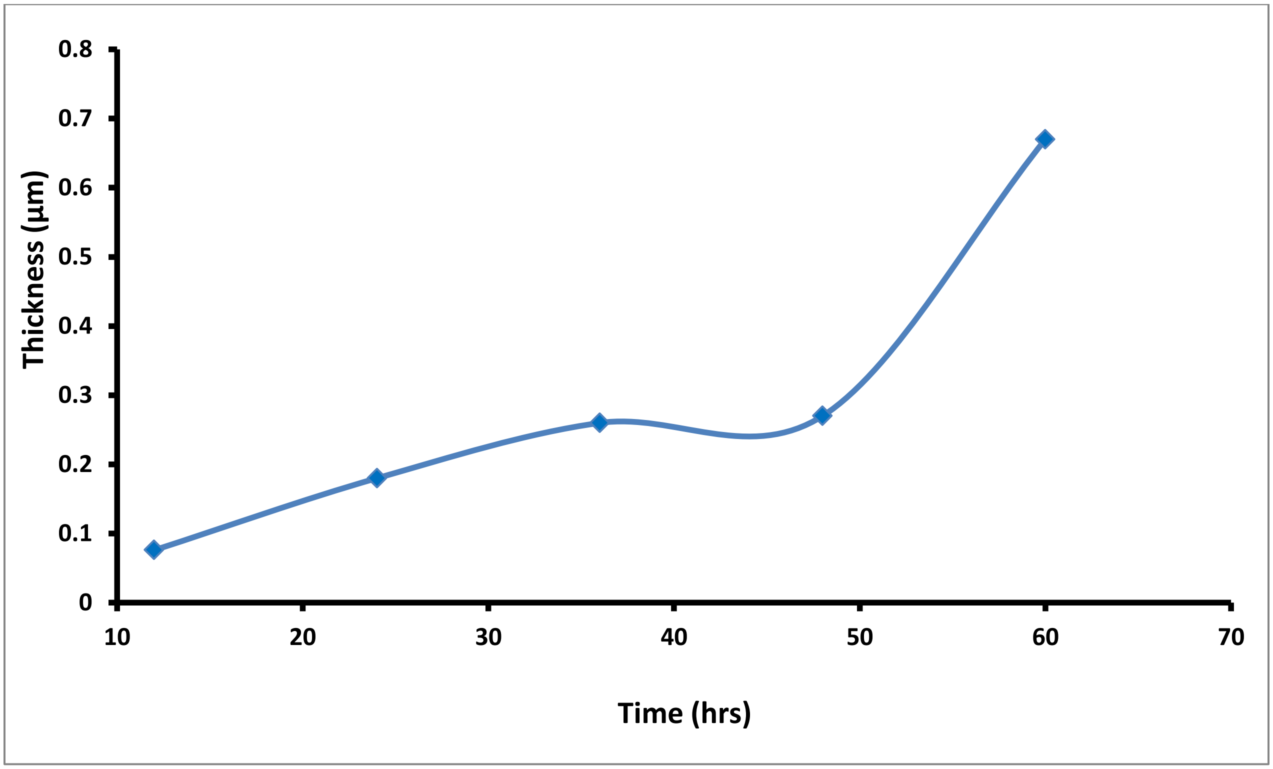

Fig. 1: Variation of Thickness (μm) versus Time of Deposition

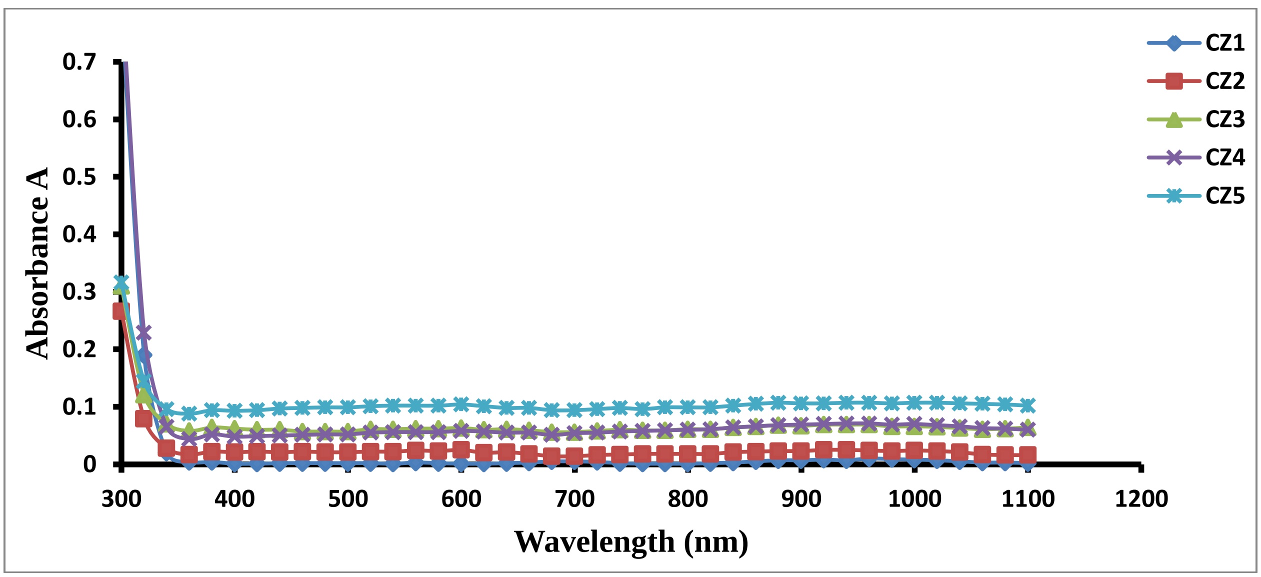

Fig. 2: Absorbance Spectra versus Wavelength of CuZnS Thin Films

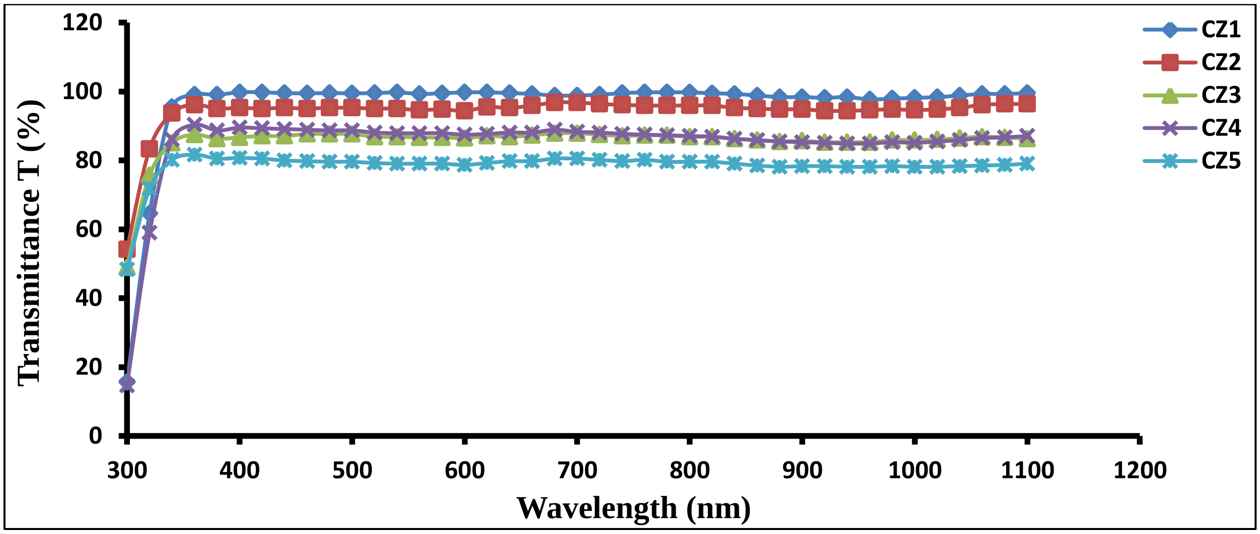

Fig. 3: Percentage Transmittance versus Wavelength of CuZnS Thin Films

Figure 1 shows the graph of thickness versus time for the deposited films. The thickness increases as deposition time increases. A peak thickness of 0.67µm was obtained at 60 hours deposition time. Figure 2 shows the plot of absorbance spectra against wavelength. The absorbance of the grown films is high in ultraviolet region but decreases within the visible and near infrared regions, and increases as time of deposition increases. Figure 3 is a plot of percentage transmittance against wavelength. The films have low transmittance within the ultraviolet (UV) that increases slightly within the visible (VIS) and near infrared (NIR) regions of electromagnetic spectrum. The transmittance decreases as time of deposition increases. Figure 4 shows a plot of reflectance of the films against wavelength. The reflectance of the films is low in all wavelength considered. A peak value of 0.2 was obtained for all the films at 300nm. Reflectance of the films increases as deposition time increases. These results of low absorbance, high transmittance and low reflectance are in accordance with results of (Awoduga, and Ibiyemi, 2012), (Adulogu and Mukolu, 2009) and (Uhuegbu and Babatunde, 2008) for CuZnS thin films.

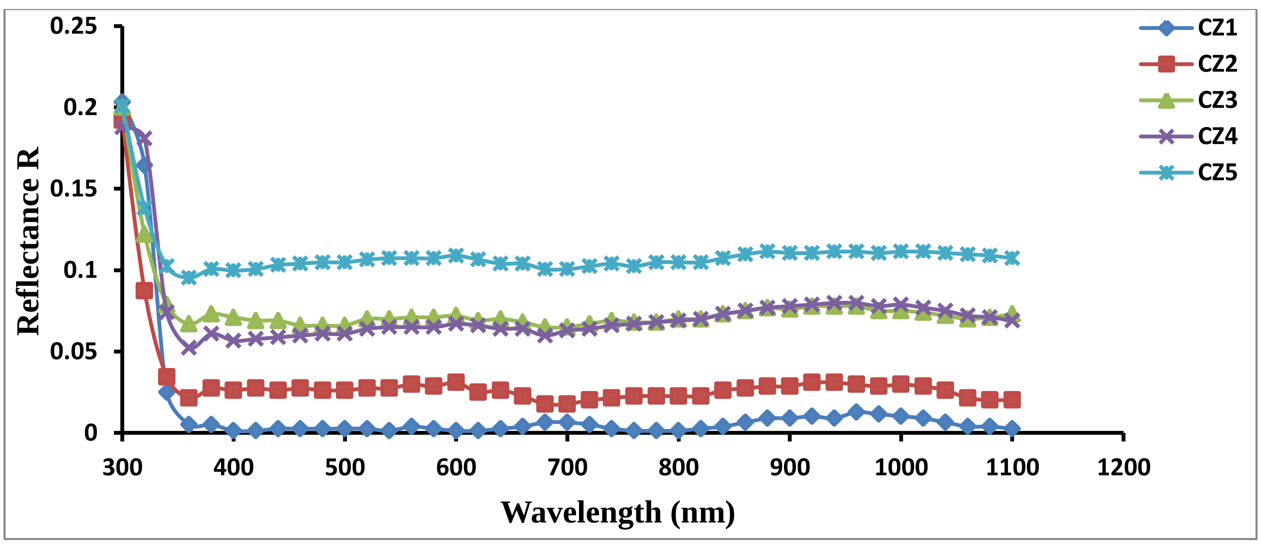

Fig. 4: Reflectance Spectra versus Wavelength of FeCuS thin films

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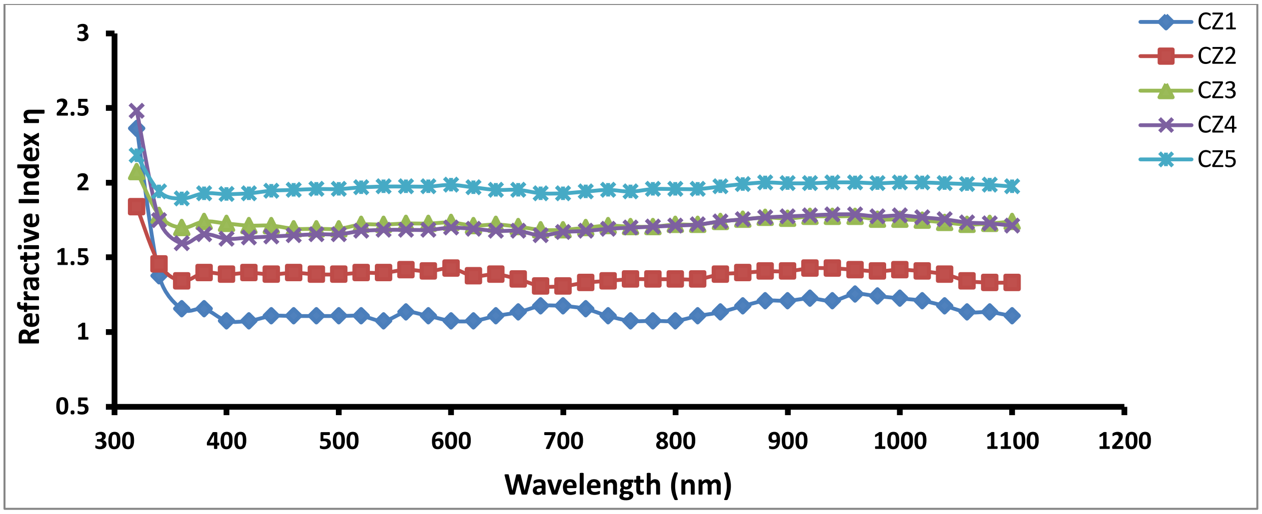

Fig. 5: Graph of Refractive Index η versus wavelength (nm) of CuZnS Thin Films

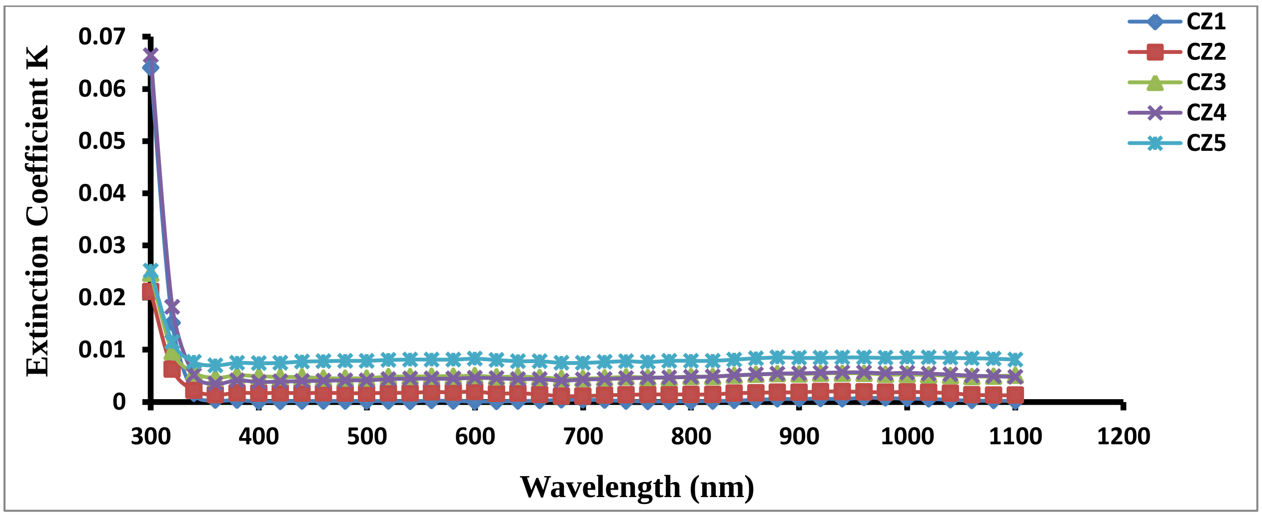

Fig. 6: Graph of Extinction Coefficient K versus wavelength (nm) of $CuZnS_2$ Thin Films

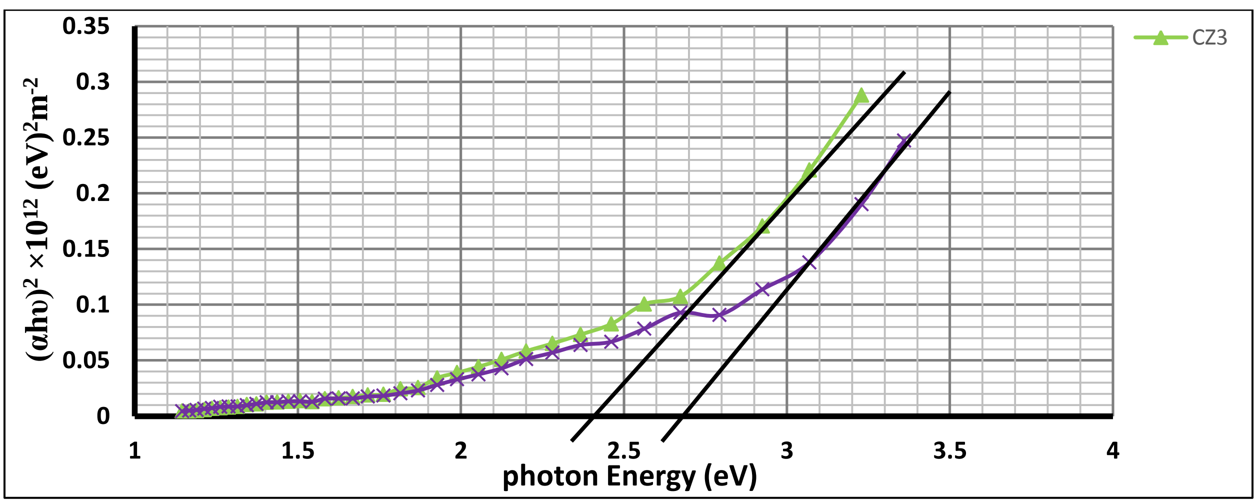

Fig 7: Graph of $(\alpha h\upsilon)^2$ versus Photon Energy (eV) for CZ_3 and CZ_4

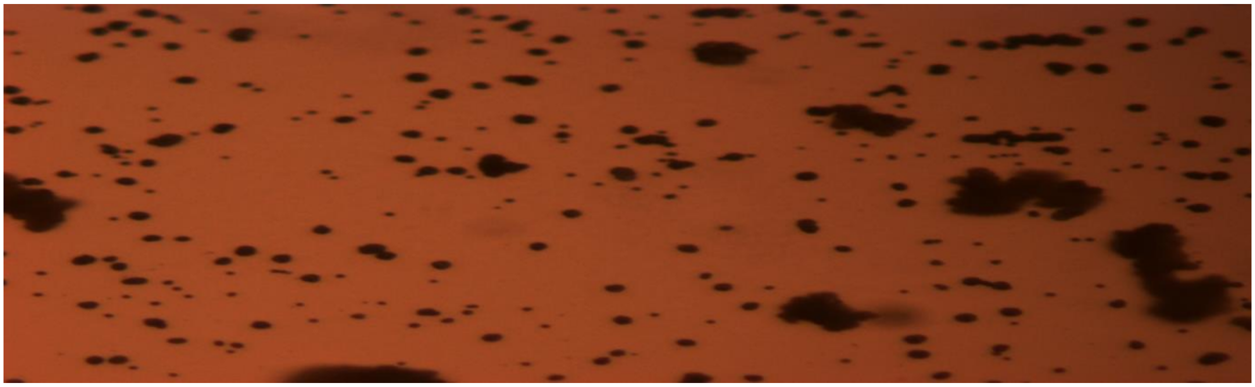

Fig. 8: Photomicrograph of for Slide

Fig. 9: Photomicrograph of for Slide

Fig. 10: Photomicrograph of for Slide

Figure 5 shows the plot of refractive index of the grown films against wavelength. The refractive index of the films ranged from 1.0 to 2.60. The films have peak values of 2.60 each at 300nm and increases as time of deposition increases.Figure 6 shows the plotted graph of extinction coefficient against wavelength. Extinction coefficient which is a measure of the amount of absorption loss when electromagnetic radiation propagates through the films has values between 6.6×10^{-2} and 8.0×10^{-5}. These values show that the grown films absorb more in UV region than in VIS and NIR region. The degree of absorption also increases as time of deposition increases. Figure 7 shows the graph of the plot of $(\alpha h\nu)^2$ against photon energy to determine the band gap of the films. Band gap was determined by extrapolating the straight portion to the photon energy axis at $(\alpha h\nu)^2 = 0$, the band gap was found to be between 2.40 eV and 2.70 eV. The values are in agreement with values of 1.8eV – 3.5eV obtained by (Noriyuki et al., 2013) and 2.4 eV obtained by (Uhuegbu and Babatunde, 2008).

Figures 8, 9, and 10 show the photomicrograph of $CuZnS_2$ thin films deposited. The photomicrograph at 100X magnification of the deposited thin films at different deposition time reveal differences in micro-surface texture and high film uniformity over significant surface area of the substrates. The variation in photomicrographs of the films show that time of deposition affects the microstructure of the films. The variation observed in the optical properties studied in this work could be attributed to changes observed in the micro-surface texture of deposited films.

Conclusion

This study reveals that ternary transition metal chalcogenide thin film of Copper Zinc Sulphide can be synthesized 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. Other 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.

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