

Effect of Deposition Time on Optical and Solid State Properties of Chemically Deposited Iron Copper Sulphide (FeCuS) Ternary Thin Films

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Abstract

Ternary Thin films of FeCuS were grown on glass substrates by Chemical Bath Deposition (CBD) technique above room temperature of 353K at a varying time of deposition. Iron (III) trioxonitrate nanohydrate, copper chloride dihydrate and thiourea were used as sources for iron, copper and sulphur ions respectively. The optical characterization was done by 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 optical thickness, transmittance, reflectance, refractive index, extinction coefficient and optical band gap energy were calculated. These films showed high absorbance in UV region and low values in VIS – NIR region. The transmittance of the films is low in UV region and high in VIS – NIR regions. A band gap energy range between 2.50 eV and 2.80 eV were obtained. The reflectance is low in all regions of electromagnetic spectrum studied. Refractive index of the films ranged from 2.60 to 1.10. Enhanced Mini – Material Analyzer X – ray Diffractometer was used to determine the crystal structure and crystallite size. The grain size obtained was 326.50 nm – 432.29 nm for different time of depositions. Olympus Optical Microscopy was used to capture the photomicrographs of the films. These films could be applied in solar cells fabrication optoelectronic devices, anti-reflective coating of glasses and other numerous applications.

Keyword: Thin Films, Chemical Bath Method, XRD, Optical Properties, Photomicrographs.

INTRODUCTION

Thin film is a layer of material ranging from fractions of a nanometer to several micrometers in thickness (Chopra and Anil, 2010). Thin films have very interesting properties that are quite different from those of the bulk materials which they are made of. This is because of the facts that their properties depend on some interrelated parameters and also on the method of deposition employed. One of the widely used thin film deposition method is the Chemical Bath Deposition. The use of Chemical Bath Deposition (CBD) techniques for fabrication of binary and ternary transition metal chalcogenide thin films have attracted huge interests in recent years. These great interests arise due to its relatively inexpensive, simple and convenient for large area deposition. Ternary transition metal chalcogenide thin films are films of three elemental components which contain at least one transition metal and one chalcogen. These films have wide range of properties and applications. They serve as materials for solar energy conversions such as photo-electrochemical solar cells fabrication (Osuwa, Oriaku and Uko, 2010). They are suitable materials for optical elements (Cerqua-Richardson., McKinley, Lawrence, Joshi and Villeneuve, 1998), optical memory disk (Andriesh and Chumash, 1998) and infra-red fibres (Cheng, Chen and Ye, 1995), which show high flexibility and chemical durability.

LITERATURE REVIEW

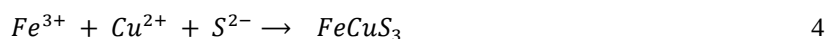
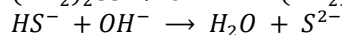
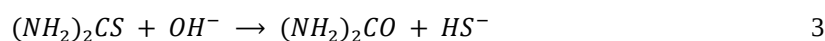
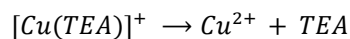
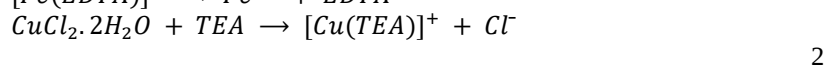
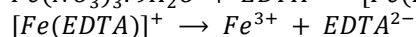
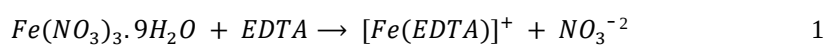
In field of thin film technology, great attention is now on deposition of ternary derivative material, due to the potential of tailoring both the lattice parameters and the band gap by controlling depositions parameters (Sankapal and Lokhande 2002). Many techniques have been successfully employed for these purposes: Chemical Vapour Deposition (CVD) (Frigo et al 1989), Successive Ionic Layer Absorption and Reaction (SILAR) (Nilolou et al., 1990), and Sol-gel Methods (Seung and Byung, 2008), Chemical Bath Deposition (Ezenwa and Okoli, 2015). Many researchers have deposited ternary transition metal chalcogenide thin films such as CuInS₂ (Tang, Yan, Zhang, Ma, Wang and Yang, 2005), PbCdS (Mohammed, Mousa, and Ponpon, 2009), ZnNiS (Ottih, 2014), Cd_{1-x}Pb_xSe (Hankare et al. 2005), Zn_xCd_(1-x)Te (Umeshkumar,

Sulakshana and Pawar, 2011) and FeCuS (Uhuegbu and Babatunde, 2012), CuZnS (Ezenwa and Okoli, 2015) for various applications.

In this paper, the effect of time of deposition on the optical and solid state properties of iron copper sulphide films above room temperature is studied. The possible applications of the films were discovered from their properties. The optical properties investigated include; 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; Jae – Hyeong, Woo–Chang, Jun–sin, and Yeong–Sik, 2003).

MATERIALS AND METHODS

The growth of FeCuS thin films on glass slides was carried out using chemical bath deposition technique. The glass slides used were previously degreased in trioxonitrate (V) acid for 48 hours, washed with detergent, rinsed in distilled water and dried in air. The degreased cleaned surface provides nucleation centre for the growth of the films onto the substrate surface which will help in obtaining highly adhesive and uniformly deposited films on the surface of the substrate. The slides for deposition of FeCuS were labelled FC_1 , FC_2 , FC_3 , FC_4 and FC_5 for depositions at 30 minutes, 60 minutes, 90 minutes, 120 minutes and 150 minutes respectively.. Deposition of FeCuS thin films on the slides for various minutes were carried out using 100 ml glass beaker at an average temperature of 353K above room temperature using a water bath. 3 *mls* of Iron (III) trioxonitrate nanohydrate and Copper chloride dihydrate were measured, transferred into the beaker. The mixture was stirred for 2 minutes after which 2 *ml* of thiourea was added and stirred to have a homogeneous mixture. Addition of thiourea formed a sky blue jelly – like solution. 1.0 *ml* of EDTA, 1.0 *ml* of TEA and 5.0 *mls* of 14.0M of ammonium solution were added to the solution. Addition of ammonium solution turns the mixture dark. The dark solution was stirred for 5 minutes followed by addition of 35 *ml* of distilled water. The final solution was stirred for 2 minutes to have a homogeneous mixture. The homogeneous mixtures formed in each case were immersed into a temperature regulated water bath that was set at 353K. The substrates were held vertically inside the beaker with the help of synthetic foam. The five beakers were prepared in the same manner. The varying bath parameter is the time of deposition. The films were deposited at 30 minutes intervals. At the end of each time, the substrates were removed, rinsed in distilled water, and dried in open air at room temperature of (300K). The pH values of deposition baths were obtained using a pH meter of accuracy ± 0.1 . The average value of pH obtained was 10.10 which show that the reaction bath is alkaline medium. TEA and EDTA served as complexing agents. Ammonia solution was used as a pH adjuster. The function of the complexing agent is to slow down the reaction in order to eliminate spontaneous precipitation of cations in the reacting medium. The bath composition of the five depositions made with different deposition time is shown in the Table 1 below. The chemical equation of the reaction for the deposition is given below:



The sulphide ions were released by the hydrolysis of thiourea, Fe^{3+} and Cu^{2+} ions are from complexes which the solution of $Fe(NO_3)_3 \cdot 9H_2O$ and $CuCl_2 \cdot 2H_2O$ formed with EDTA and TEA. The Fe^{3+} , Cu^{2+} and S^{2-} present in the solution combined to form FeCuS molecules which were deposited on the glass substrate. 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. The films were analysis using Enhanced Mini – Material Analyzer (EMMA) X – ray Diffractometer Machine to determine the crystal

structure and grain size. An Olympus Microscope at 100X magnification was used to examine and produce micrographs of the grown thin film samples.

Table 1: Optimization of Iron Copper sulphide (FeCuS) with pH at room temperature

Baths	Time (mins)	Fe(NO ₃) ₃ .9H ₂ O		CuCl ₂ .2H ₂ O		EDTA		TEA		H ₂ O Vol. (ml)	(NH ₂) ₂ CS		NH ₄ OH	
		Mol. (m)	Vol. (ml)	Mol. (m)	Vol. (ml)	Mol. (m)	Vol. (ml)	Mol. (m)	Vol. (ml)		Mol. (m)	Vol. (ml)	Mol. (m)	Vol. (ml)
FC1	30.0	2.0	3.0	2.0	3.0	0.5	1.0	7.4	1.0	35.0	2.0	2.0	14.0	5.0
FC2	60.0	2.0	3.0	2.0	3.0	0.5	1.0	7.4	1.0	35.0	2.0	2.0	14.0	5.0
FC3	90.0	2.0	3.0	2.0	3.0	0.5	1.0	7.4	1.0	35.0	2.0	2.0	14.0	5.0
FC4	120.0	2.0	3.0	2.0	3.0	0.5	1.0	7.4	1.0	35.0	2.0	2.0	14.0	5.0
FC5	150.0	2.0	3.0	2.0	3.0	0.5	1.0	7.4	1.0	35.0	2.0	2.0	14.0	5.0

RESULT AND DISCUSSION

Figure 1 shows the variation of film thickness with time of deposition. A critical analysis of the graph indicates that thickness increases as the time of deposition increases. The film with lowest time of deposition of 30 minutes has the lowest thickness value of 0.37µm while the film deposited at 150 minutes has the highest thickness value of 0.66µm. Figure 2 shows the variation of absorbance with wavelength. Absorbance of the films increases as time of deposition increases and decreases as wavelength increases. Highest absorbance value of 0.81 at 300nm was obtained for film grown at 150 minutes while the least absorbance value of 0.015 at 1100nm was obtained for films grown at 30 minutes. This result shows that these films have high absorbance in UV region and VIS – NIR regions. This increase in absorption of radiation by the films is due to increase in thickness of the thin film layer as time increases.

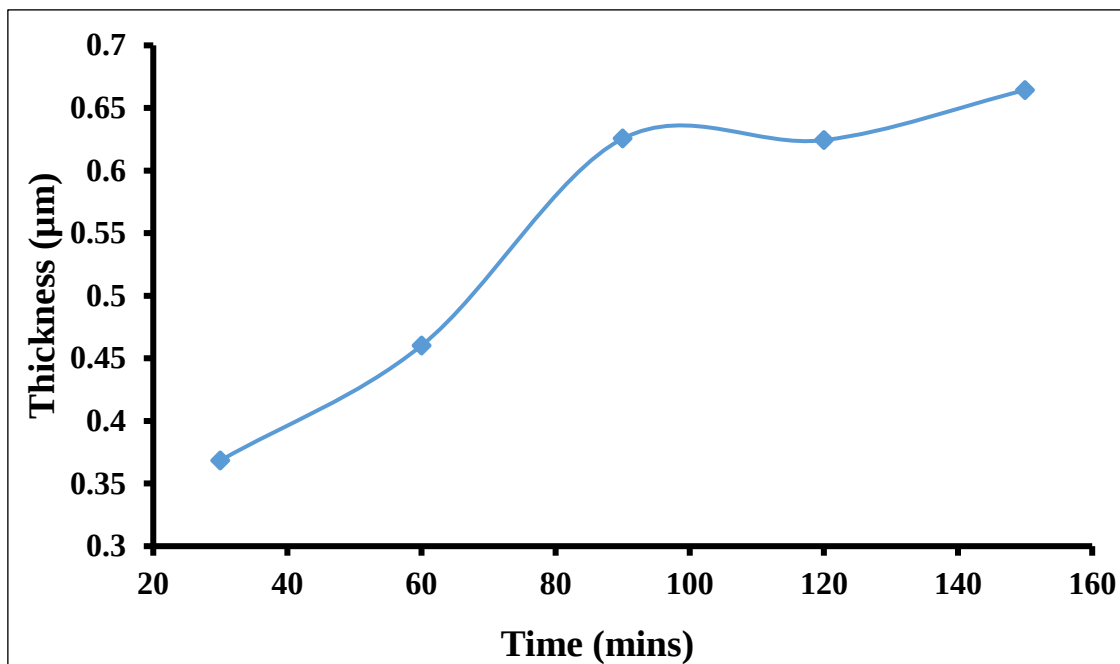


Fig. 1: Variation of Thickness (μm) versus Time of Deposition (mins)

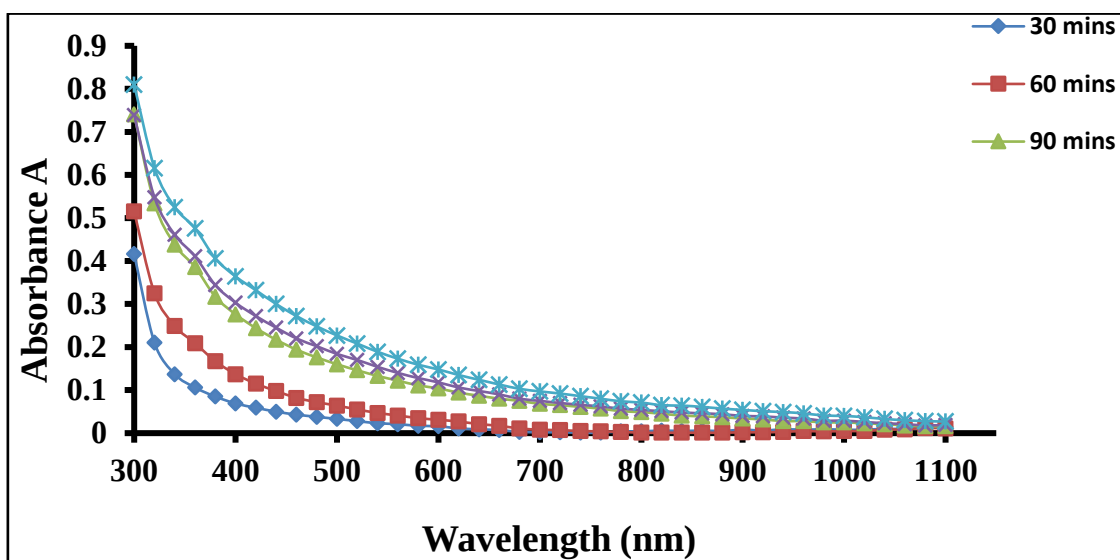


Fig. 2: Absorbance Spectra versus Wavelength of FeCuS Thin Films

Figure 3 is a plot of transmittance against wavelength. The transmittance of the films increases with increase in wavelength and decreases as time of deposition increases. The least transmittance of 15% at 300nm was obtained for films grown at 150 minutes while the highest transmittance of 97% at 1100nm was obtained for film grown at 30 minutes. This result shows that transmittance of the films is low in UV region but high in VIS – NIR regions.

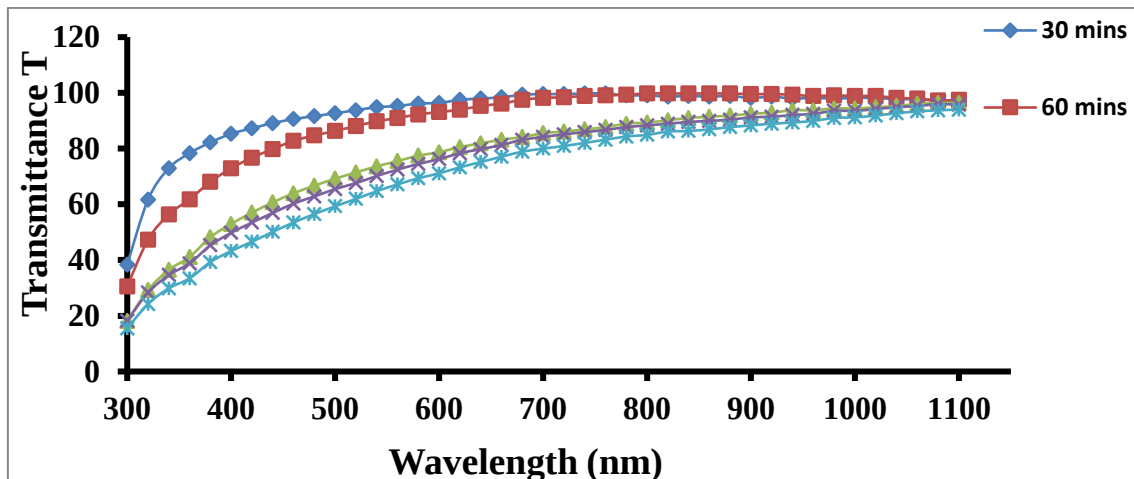


Fig. 3: Transmittance Spectra versus Wavelength of FeCuS Thin Films

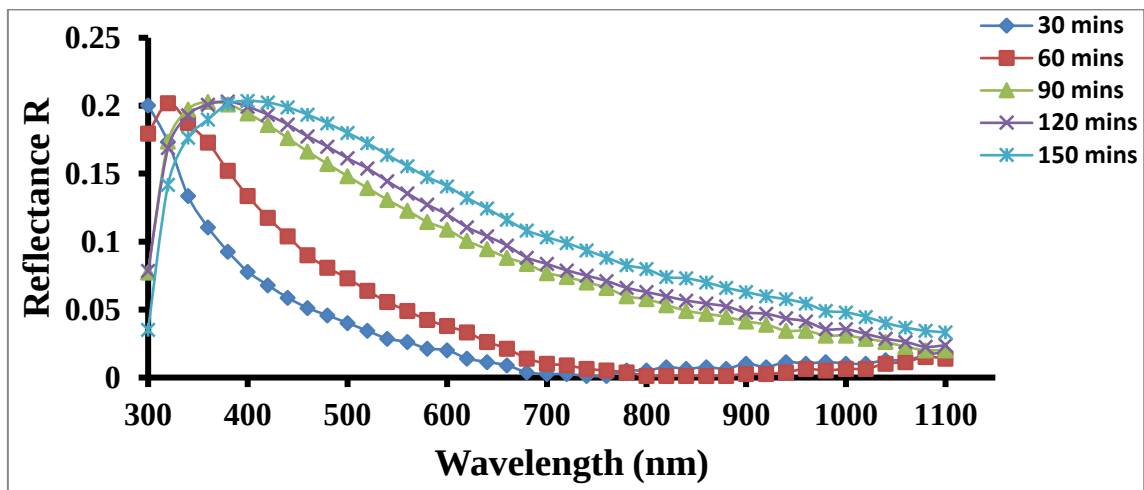


Fig. 4: Reflectance Spectra versus Wavelength of FeCuS thin films

Figure 4 shows that reflectance of the films decreases with increase in wavelength and increases as time of deposition increases. The reflectance of the films is low with peak values of 0.20 (20%) observed for all the films within UV region. The least reflectance of 0.001 was obtained within NIR region.

The plot of absorption coefficient times $(h\nu)$ squared against the photon energy is shown in figure 5. The straight nature of the plot indicates the existence of direct transition. The band gap was determined by extrapolating the straight portion to the photon energy $(h\nu)$ axis at $(\alpha h\nu)^2 = 0$. Its values was to be between 2.50 eV to 2.80 eV. This implies that FeCuS is a wide band gap energy material and can be used as an absorber layer of a solar cell.

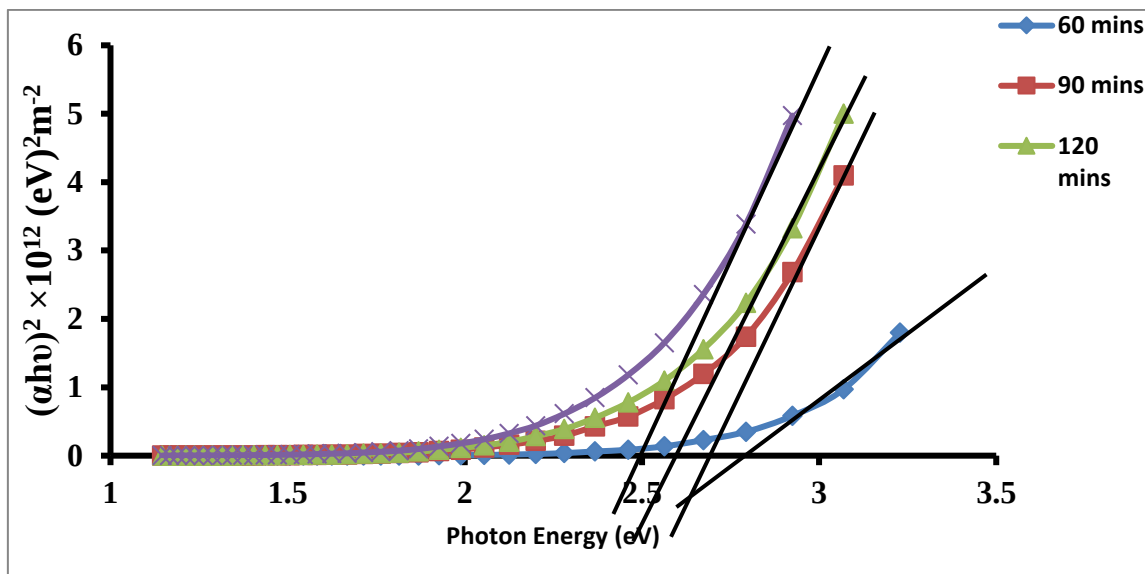


Fig 5: Graph of $(\alpha h\nu)^2$ versus Photon Energy (eV)

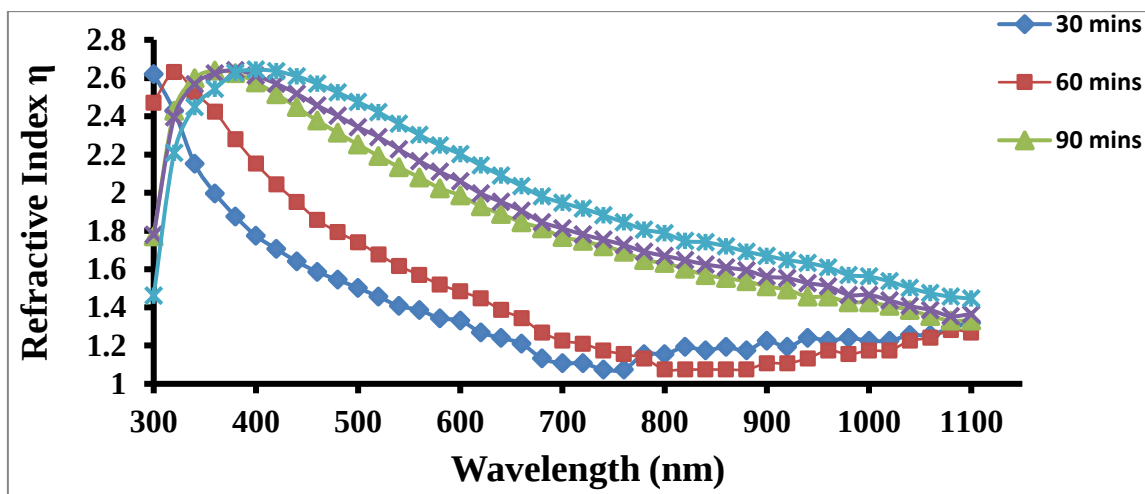


Fig. 6: Graph of Refractive Index η versus wavelength (nm) of FeCuS Thin Films

Figure 6 shows the plot of refractive index of the grown films against wavelength. Refractive index of the films decreases with increase in wavelength and increases as time of deposition increases. Peak values of 2.60 were obtained for all the films within UV regions. The least value was observed for films grown at 30 and 60 minutes within the NIR region.

Figure 7 shows that the extinction coefficient which is a factor that determines the extent to which radiation is absorbed in a material increases as time of deposition increases and decrease as wavelength increases. Film grown for 150 minutes has a peak value of 6.44×10^{-2} at 300nm while the least value of 1.19×10^{-3} at 1100nm was obtained for films grown for 30 minutes. These results are similar to range of values obtained by (Uhuegbu, 2010 and Uhuegbu et al, 2012) for properties of same ternary thin films studies here.

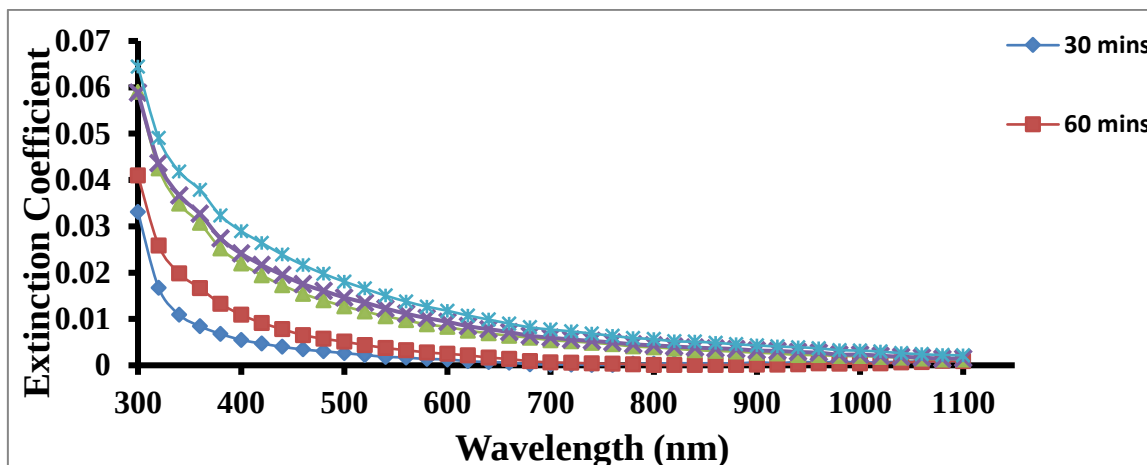


Fig. 7: Graph of Extinction Coefficient K versus wavelength (nm) of FeCuS Thin Films

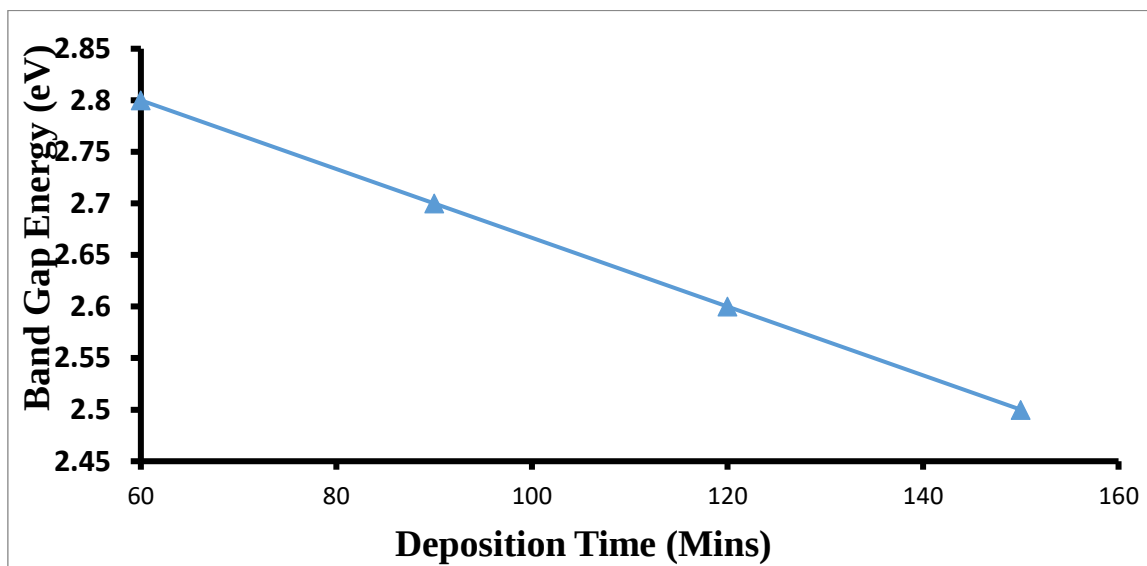


Fig. 8: Graph of Band Gap Energy versus Deposition Time of FeCuS Thin Films

Figure 8, shows the variation of band gap energy with deposition time. The result shows that energy band gap decreases linearly as time of deposition increases. Figure 9 show the X – ray diffraction spectrum of chemically deposited FeCuS thin film. According to the spectrum, the deposited thin film is crystalline with chemical formular $Cu_9Fe_9S_{16}$ which has a tetragonal structure and the mineral name is Mooihoekite (JCPDS card number 01 – 071 – 0527). The lattice constants are $a = 10.585 \text{ \AA}$, $b = 10.585 \text{ \AA}$ and $c = 5.383 \text{ \AA}$. The crystallite size of the film was calculated at $Cu - k\alpha$ wavelength of $1.5406 \text{ \AA}$ and the crystallite size was calculated using Scherrer's formula (Patterson, 1939).

The calculated crystallite size and Full Width at Half Maximum (FWHM) were determined as shown in table 2. The XRD result confirms that the film contains iron, copper and sulphur. Surface morphologies of the deposited FeCuS thin films are presented in plate 1 and plate 2 respectively. The results of the microstructure revealed that the films are polycrystalline due to varying crystallite sizes and orientation. ImageJ Microscopy Image Analysis (Abramoff, Magalhaes and Ram 2004) software was used to calculate the average particle sizes of the film. The particle size of 4.24 nm and 53.26 nm were obtained for films of 60 minutes and 90 minutes respectively.

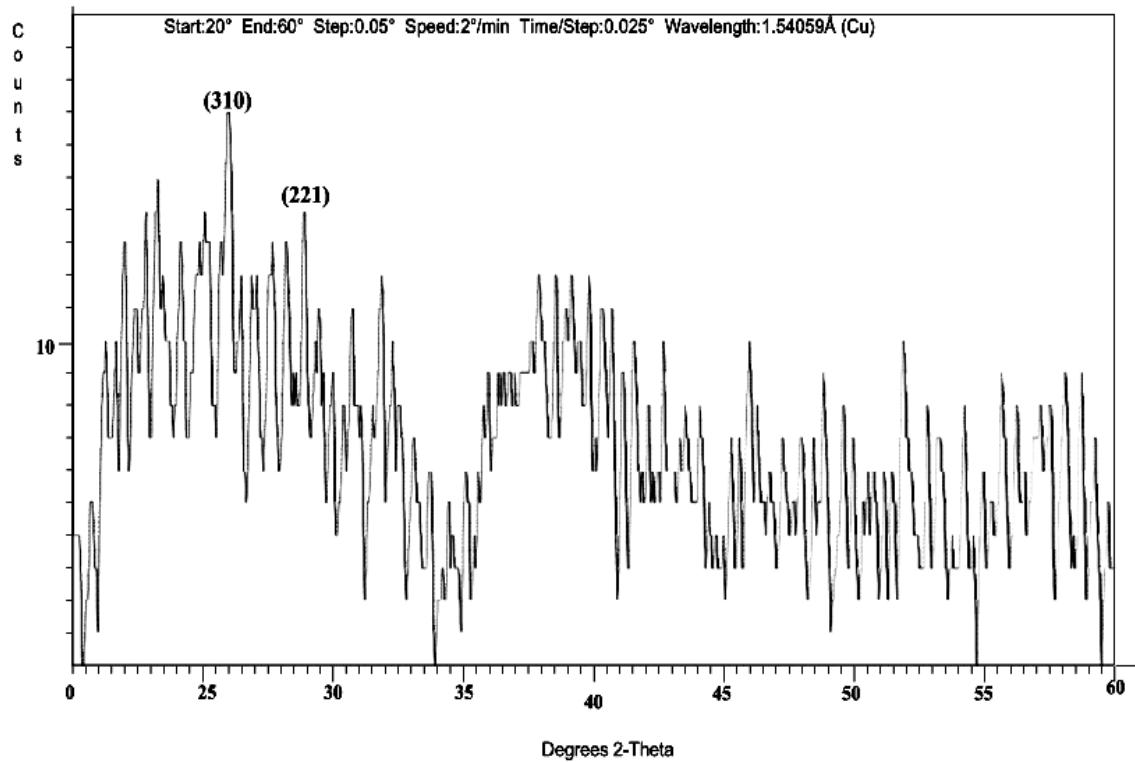


Fig. 9: X –ray Diffraction Spectral of Deposited FeCuS Thin Film for 60 Minutes Deposition Time

Table 2: XRD Analysis of Chemically Deposited FeCuS

Standard			Calculated			
2θ (°)	d – Spacing (Å)	(hkl)	2θ (°)	d – Spacing (Å)	Crystallite Size (nm)	FWHM (°)
26.61	3.347	310	26.16	3.412	326.5	0.147
29.04	3.073	221	29.06	3.425	432.29	0.141

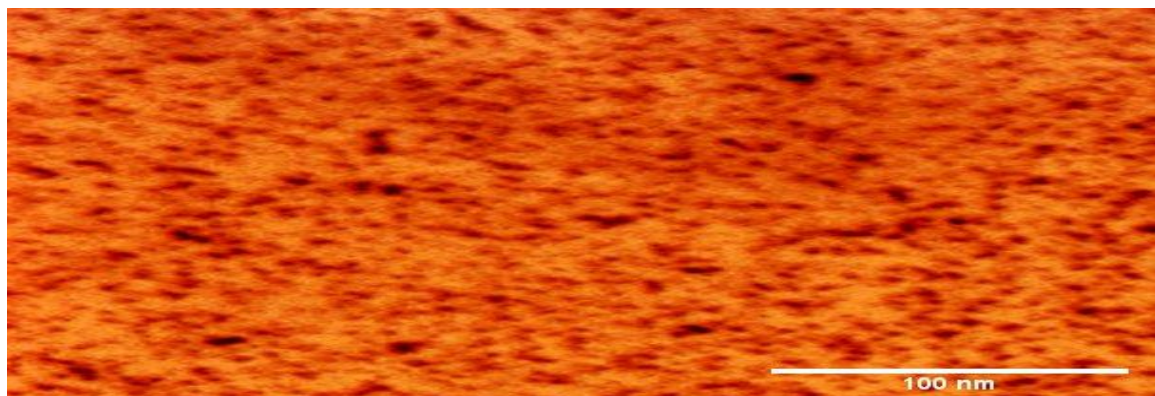


Plate 1: Micrograph of FeCuS Thin Film Deposited at 60 Minutes.

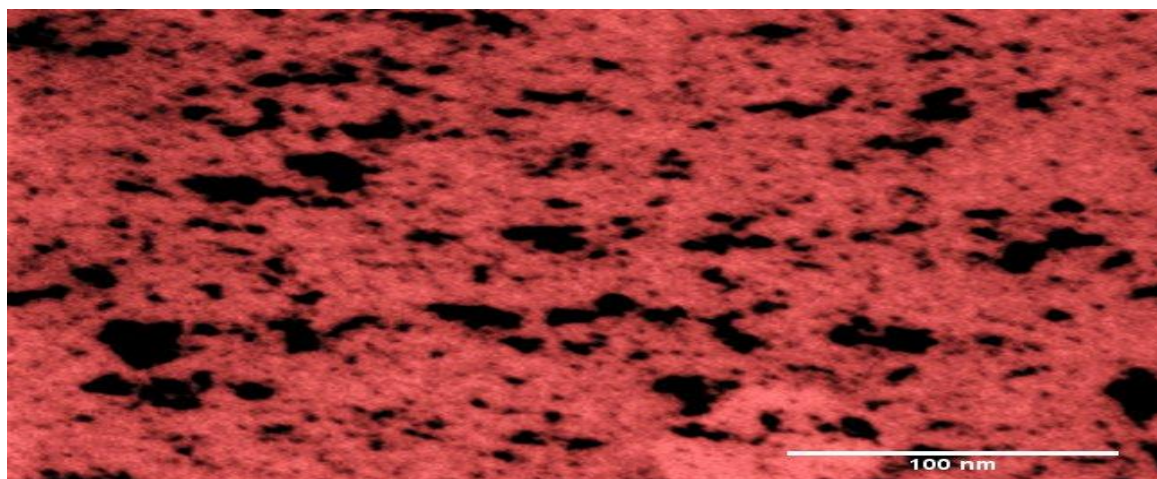


Plate 2: Micrograph of FeCuS Thin Film Deposited at 90 Minutes.

CONCLUSION

Ternary thin films of Iron Copper Sulphide have been grown on glass substrate using Chemical Bath Method at varying time above room temperature, characterized using a spectrophotometer to determine its optical properties and EMMA X – Ray Analyzer to determine the structural properties of the films. The absorbance of the films is high in UV region of electromagnetic radiation and low in VIS – NIR region while the transmittance is low in UV region and high in VIS – NIR region. Reflectance of the films is low at all wavelengths with a peak value of 0.20 in UV region. The refractive index values range from 2.60 to 1.10. Energy band gap of the films obtained is between 2.50 eV and 2.80 eV. These results above suggest that the thin films can suitably be applied in the following: (i) solar cell fabrication, (ii) for the screening off UV radiation that is harmful to human beings and animals due to its high absorbance, low transmittance and low reflectance in UV region, (iii) optoelectronic devices, (iv) architectural design for cooling or heating buildings, (v) coating of windscreen and driving mirrors to reduce the effect of dazzling of light into driver's eyes etc. These deductions agree with the findings of other researchers on similar films (Ezema, 2004 and Uhuegbu, 2010).

RECOMMENDATION

It is recommended that other types of substrates such as ITO, FTO, metals and polymers are used in the deposition of FeCuS thin films. Use of other methods of thin film deposition such as electrodeposition, Successive Ionic Layer Absorption and Reaction (SILAR), physical vapour deposition and so on, and results compared with that of this work. Use of concentrations of the precursors less than 2.0 moles should be considered. Government should provide fund for larger application of the results gotten from this work, like coating of windows and glass doors. Government institutions should fund researches that will help develop local devices for film deposition. New research should be geared into fabrication of other ternary transition metals chalcogenides apart from the one fabricated in this work.

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