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Optical and Structural Characterization of FeCuS Ternary Thin Films

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Abstract : **Ternary thin films of Iron Copper Sulphide (FeCuS) have been grown and characterized. Optical, compositional, surface microstructure and structural characterization of the deposited films were carried out. Absorbance spectra data of the films were obtained using a Janway 6405 UV-VIS spectrophotometer, absorbance of the films were found to be high in UV and low in VIS – NIR region, while the transmittances were low in UV region and high in VIS – NIR regions. Elemental composition of the films were done using Skyray XRF Machine, EDX Pocket III, model P530. The machine was used to determine the percentage of each transition element present in the films. The surface microstructures of the films were characterized using Olympus Microscope at 100X magnification. XRD analysis of the films was carried out using Enhance Mini Material Analyzer (EMMA) X – Ray Diffractometer Machine, the as - deposited FeCuS thin film was found to have tetragonal structure. The lattice constants obtained are $a = 10.585$ Å, $b = 10.585$ Å and $c = 5.383$ Å. The crystallite size of the film was calculated at $Cuk\alpha$ wavelength of 1.5406 Å and the calculated grain size was found to be $0.3589\ nm$ (3.589 Å). The optical absorption study reveals that FeCuS thin film has a bandgap of 2.40eV and a refractive index range of 2.00 to 2.70 at 400nm. The reflectance of the deposited films was found to be generally low.**

Keywords: **Iron copper sulphide; Chemical Bath Deposition; Optical characterization; compositional characterization; Structural characterization.**

I. INTRODUCTION

Ternary thin films are thin films that contain three different elements. The preparation and study of physical properties of ternary chalcogenide compounds have increased in recent years [1]. Ternary compounds are found to be suitable material for optoelectronic device applications and good material for window layer solar cells [2]. Some of the films are investigated for use as super-ionic conducting materials [3]. Ternary compounds had also been studied for efficient solar energy conversion materials [4]. Ternary thin film have been grown and characterized by some researchers for specific applications in solar industries, optoelectronics devices and window coating, examples include, $CuInS_2$ [5], [6], [7], $CuSbS_2$ [8], $FeCuS_2$ [9], Cu_2SnS_3 [10], PbCdS [11], CuNiS [2], CdS/CuS and CuS/CdS [13]. $FeCuS_2$ fabricated by [9], have a band gap energy of 2.4 eV to 2.8 eV and indirect band gap energy of 0.6 eV to 1.0 eV.

In this paper, FeCuS thin films were deposited using chemical bath method, time as a bath parameter was optimized. Optical and Structural Characterization of the deposited thin films were investigated. The optical properties investigated include; absorbance (A), transmittance (T) and reflectance (R), which were used to calculate other parameters such as refractive index (n), extinction coefficient (K) and the band gap energy of the as – grown films.

II. MATERIALS AND METHOD

The growth of FeCuS thin films on glass slides was carried out using chemical bath deposition technique. The glass slides used were previously inserted 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 substrate. The slides for the deposition of FeCuS were labelled FC_1, FC_2, FC_3, FC_4 *and* FC_5.

Iron Copper sulphide (FeCuS) was deposited by the reaction of solution containing iron (III) trioxonitrate nanohydrate $[Fe(NO_3)_3.9H_2O]$, copper chloride dihydrate $[CuCl.2H_2O]$, disodium ethylenediaminetetraacetate $[Na_4(C_{10}H_{16}N_2O_8)]$ commonly known as EDTA, triethanolamine $[C_6H_{15}NO_3]$ also known as TEA, ammonium solution $[NH_4OH]$, thiourea $(NH_2)_2CS$ and distilled water in a 100 ml beaker. The complexing agents used in this research are EDTA and TEA. The addition of TEA and EDTA as complexing agents slowed down the precipitation of metal ions of iron and copper. Ammonia solution stabilizes or adjusts the pH of the mixture.

Five reaction baths containing slides FC_1, FC_2, FC_3, FC_4 *and* FC_5 were used, average room temperature of 303 K was maintained. 3 ml of Iron (III) trioxonitrate nanohydrate and Copper chloride dehydrate were measured and 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 sky blue jelly – like solution. Followed by addition of $1.0\,ml$ of EDTA, $1.0\,ml$ of TEA and $3\,ml$ of ammonium solution. 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 with slide FC_1, FC_2, FC_3, FC_4 and FC_5 were prepared in the same manner. The varying bath parameter is the deposition time. FC_1 was allowed to stand in the bath for 12 hours after which deposition was noticed on the films. The remaining substrates, FC_2, FC_3, FC_4 and FC_5 were allowed for 24 hours, 36 hours, 48 hours and 60 hours respectively. The substrates were removed at the end of each time, rinsed in distilled water, and dried in open air at room temperature of (300K). The peak deposition time was at 48 hours. At 48 hours, a uniform and adherent film was noticed on substrates. An average pH of 8.3 was obtained for the bath using a pH meter of accuracy ± 0.1. Table 1 shows the constituents of the bath parameters.

Table 1: Optimization of Iron Copper Sulphide (FeCuS) Deposition with Time at Room Temperature

Reaction bath	Dip time (hr)	$Fe(NO_3)_3.9H_2O$		$CuCl.2H_2O$		EDTA		TEA		H_2O Vol. (ml)	$(NH_2)_2CS$		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)
FC_1	12	2.00	3.00	2.00	3.00	0.50	1.00	7.40	1.00	35.00	2.00	2.00	14.00	3.00
FC_2	24	2.00	3.00	2.00	3.00	0.50	1.00	7.40	1.00	35.00	2.00	2.00	14.00	3.00
FC_3	36	2.00	3.00	2.00	3.00	0.50	1.00	7.40	1.00	35.00	2.00	2.00	14.00	3.00
FC_4	48	2.00	3.00	2.00	3.00	0.50	1.00	7.40	1.00	35.00	2.00	2.00	14.00	3.00
FC_5	60	2.00	3.00	2.00	3.00	0.50	1.00	7.40	1.00	35.00	2.00	2.00	14.00	3.00

The stepwise reactions involved in the complex ion formation and film deposition processes for FeCuS are stated below. Sulphide ions are released by the hydrolysis of thiourea and Fe^{3+} and Cu^{2+} were released from the complex ion formed by the reaction of iron and copper compounds with EDTA and TEA respectively.

$$Fe(NO_3)_3.9H_2O + EDTA \longrightarrow [Fe(EDTA)]^+ + NO_3^-$$
$$[Fe(EDTA)]^+ \longrightarrow Fe^{3+} + EDTA^{2-}$$

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

$$(NH_2)_2CS + OH^- \longrightarrow (NH_2)_2CO + HS^-$$
$$HS^- + OH^- \longrightarrow H_2O + S^{2-}$$
$$Fe^{3+} + Cu^{2+} + S^{2-} \longrightarrow FeCuS_3$$

After the deposition of the films, optical, compositional, surface microstructure and structural characterization of the deposited films were carried out. Absorbance spectra data of the films were obtained using a Janway 6405 UV-VIS spectrophotometer. Elemental composition of the films were done using Skyray XRF Machine, EDX Pocket III, model P530. The machine was used to determine the percentage of each transition element present in the films. The surface microstructures of the films were characterized using Optical Microscopy, Olympus Microscope at 100X magnification was used to examine and produce micrographs of the grown thin film samples. XRD analysis of the films was carried out using Enhance Mini Material Analyzer (EMMA) X – Ray Diffractometer Machine. This is to determine the crystalline nature of the films, 2 theta angles, d - spacing and to calculate the grain size.

III. RESULTS AND DISCUSSION

Thicknesses of the films FC_1, FC_2, FC_3, FC_4 and FC_5 at $300\,nm$ were plotted against time of deposition of 12 hrs, 24 hrs, 36 hrs, 48 hrs and 60 hrs as shown in Figure 1. FC_2 has a peak thickness value of 0.90 μm at this wavelength. The thickness increases from 0.70 μm at 12 hrs to 0.90 μm at 24 hrs before decreasing to 0.80 μm at 36 hrs and remains constant at 48 hrs and 60 hrs.

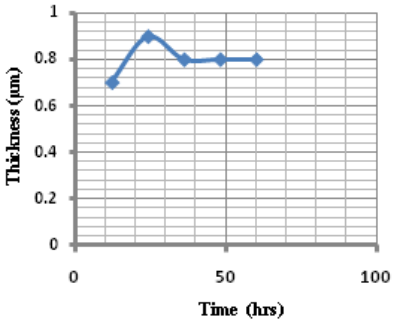


Fig. 1: Variation of Thickness (µm) versus Time (hrs) for Slides FC_1, FC_2, FC_3, FC_4 and FC_5

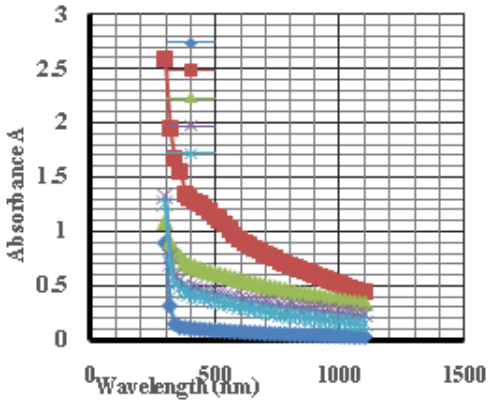


Fig. 2: Graph of Absorbance (abr. Unit) versus wavelength (nm)for Slides FC_1, FC_2, FC_3, FC_4 and FC_5

Absorbance of as – grown films were plotted against wavelength as shown in Figure 2. FC_1 has the least absorbance value followed by FC_5, FC_4, FC_3 and FC_2. Absorbance decreases as time of deposition increases except for FC_1that has least absorbance values among all samples. Generally, absorbance of the films decreases as the wavelength increases and is high in UV region but has low values in VIS and NIR regions.

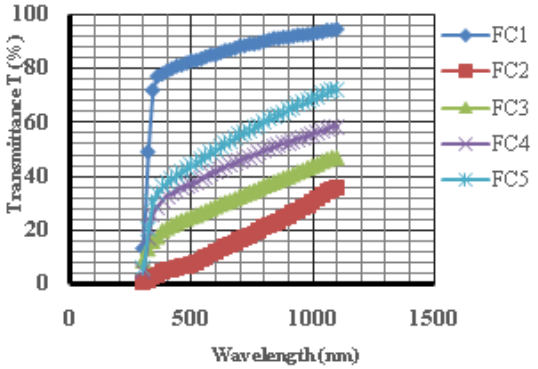


Fig 3.: Fig.3:Graph of percentage Transmittance (%) versus wavelength (nm) for Slides FC_1, FC_2, FC_3, FC_4 and FC_5

Transmittance as a function of wavelength is plotted in Figure 3, for FC_1, FC_2, FC_3, FC_4 and FC_5 respectively. Transmittance of the films increases as the wavelength increases and it increases as the time of deposition increases except for FC_1 that has highest values in all wavelength regions considered. FC_1 has transmittance values of 13 % at 300 nm and increases to 79 % at 400 nm. In VIS region, it increases from 79 % to 88 % at 700 nm, before getting to 94 % at 1100 nm in NIR region.

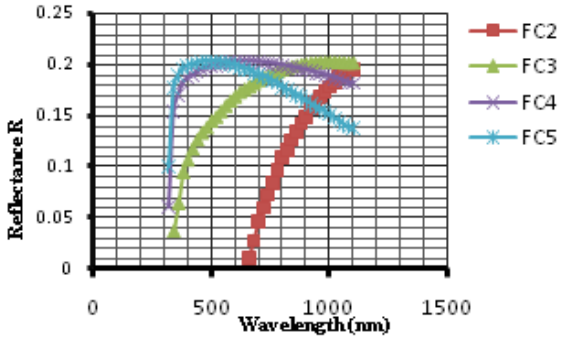


Fig 4: Graph of reflectance versus wavelength (nm) for slide FC_2, FC_3, FC_4 and FC_5

Reflectance of as – grown films for FC_2, FC_3, FC_4 and FC_5 were plotted against wavelength as shown in Figure 4. From the graph, the reflectance of the as grown thin films is very low. The grown thin films have a peak value of approximately 0.20 at different wavelengths. It remains approximately the same throughout the VIS region. Due to their low reflectance, they could be used as anti – reflective coatings materials.

Figure 5, shows the graph of refractive index of the films FC_1, FC_4 and FC_5 against wavelength. The refractive index of the films was studied within the VIS and NIR regions of electromagnetic spectrum. From the graph, it can be seen that the refractive index of the films decreases slightly as wavelength increases.

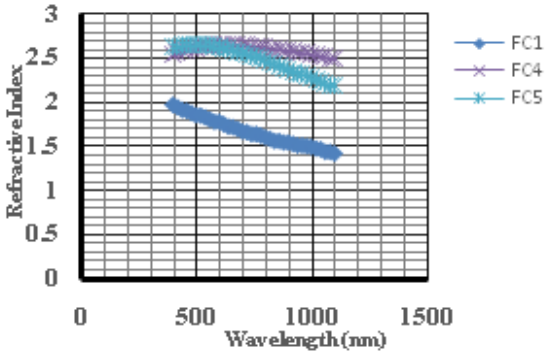


Fig 5: Graph of Refractive Index Versus Wavelength(nm) for Slide FC_1, FC_4 and FC_5

Refractive index range of 2.00 to 2.70 at 400nm is observed in the deposited films. These films are high refractive index materials. These high values of refractive index suggest that they could be used as anti – reflective coating and photonic devices such as light emitting diodes (LEDs), image sensors etc. [14].

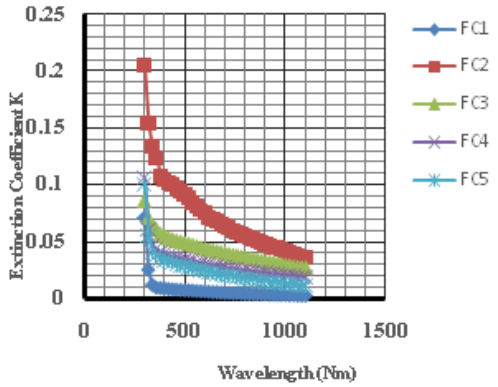


Fig. 6: Graph of Extinction Coefficient K versus wavelength (nm) for Slides FC_1, FC_2, FC_3, FC_4 and FC_5

Extinction coefficient of films FC_1, FC_2, FC_3, FC_4 and FC_5 were plotted against wavelength in Figure 6 as shown above. All the graphs show the same pattern. The Extinction coefficient decreases as wavelength increases. FC_1 has extinction coefficient values of 7.05×10^{-2} - to 8.20×10^{-3} at $300\ nm$ - $400\ nm$,. FC_5 has extinction coefficient values of 1.10×10^{-1} to 3.38×10^{-2} in UV region, 3.38×10^{-2} to 2.10×10^{-2} in VIS region and 2.10×10^{-2} to 1.11×10^{-2} in NIR region.

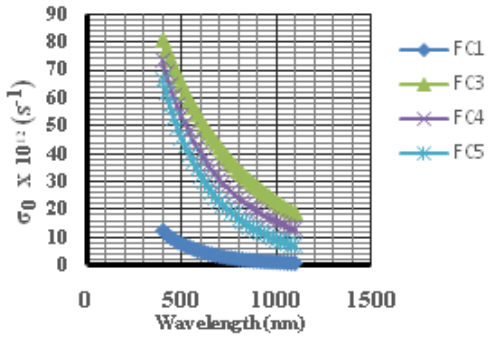


Fig 7.: Graph of Optical Conductivity versus wavelength (nm) for SlidesFC_1, FC_3, FC_4 and FC_5

Optical conductivities of slides FC_1, FC_3, FC_4 and FC_5 films were plotted against wavelength in Figure 7. FC_1 has optical conductivity values of $12.20 \times 10^{12} s^{-1}$ at 400 nm to $3.15 \times 10^{12} s^{-1}$ at 700 nm and $7.70 \times 10^{11} s^{-1}$ at 1100 nm.

Figure 8 is a plot of absorption coefficient squared (α^2) versus photon energy hυ for $FeCuS$ thin film. The optical bandgap energy of $FeCuS$ thin films were determined from this graph by extrapolating the straight portion of the graph to α^2=0. Our result shows that $FeCuS$ ($slide\ FC_1$) has band gap energy of 2.40 eV.This result is in agreement with results obtained by [9] and [13]. Due to the wide band gap of the as – grown films, they could be considered as material for absorber layer of solar cell and as effective coating material for poultry houses [13].

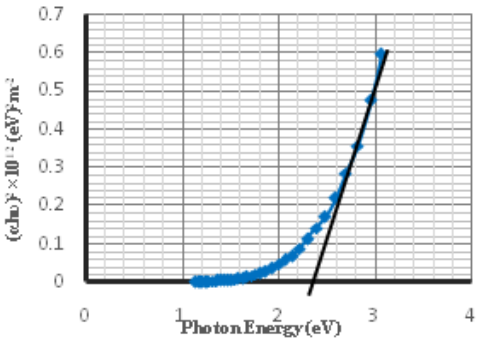


Fig.8: Graph of $(\alpha h\upsilon)2$ versus Photon Energy (eV) for FC_1

Figure 9 and 10 shows the micrograph of FeCuS thin films for slides FC_1, FC_3. Critical observations of the micrographs reveal that the films are crystalline in nature and have small grain sizes. The particle grain sizes increased as the time of deposition of the reaction bath increases.

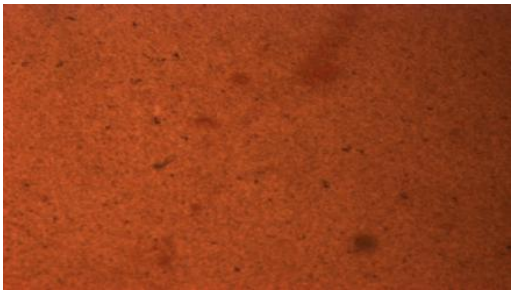


Fig. 9: Micrograph of FeCuS for FC_1 Thin Film

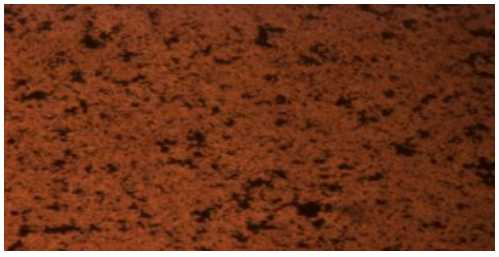
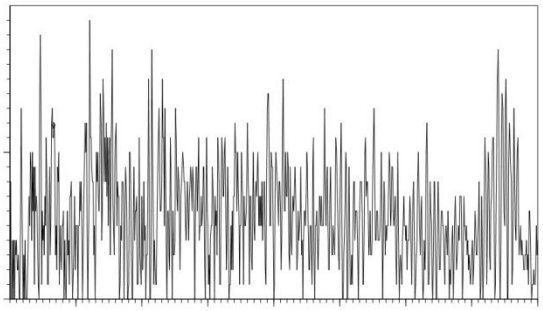


Fig. 10: Micrograph of FeCuS for FC_3 Thin Film

Figure 11 shows the X – ray diffraction spectra of chemically deposited FeCuS thin film. According to the result, 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 $a = 10.585$ Å, $b = 10.585$ Å and $c = 5.383$ Å. The crystallite size of the film was calculated at $Cu - k\alpha$ wavelength of 1.5406 Å and the grain size was calculated using Scherrer's formula. The calculated grain size was found to be 0.3589 nm (3.589 Å).

Table 2: XRD Analysis of Chemically Deposited FeCuS

Standard Peak		Calculated Peak		
2θ (°)	d –	2θ (°)	d –	(hkl)
23.554	3.774	23.300	3.815	201



Degrees 2 - Theta
Fig. 11: XRD pattern of FeCuS Thin Film

Table 3: Elemental Analysis of as – grown Thin Films

SAMP	Ti	Cr	Fe(%	Cu	Z	Pb
FC5	0.06	0.08	80.92	18.52	0	0.044

Elemental components of characterized films are shown in table 3. From the table, it can be seen that for sample FC_5, iron content is 80.9295%, copper content is 18.5298%. Other elements amount to 0.19866%.

IV. CONCLUSION

In summary, XRD result shows that we have successfully fabricated Ternary thin films of Iron Copper Sulphide (FeCuS) deposited on glass substrates through chemical bath technique. Absorbance of the films were found to be high in UV and low in VIS – NIR region, while the transmittances were low in UV region and high in VIS – NIR regions. Elemental components of the characterized films for sample FC_5 was found to be: iron content (80.9295%), copper content (18.5298%), other elements amount to 0.19866%. The as - deposited FeCuS thin film has tetragonal structure. The lattice constants are $a = 10.585$ Å, $b = 10.585$ Å and $c = 5.383$ Å. The Calculated grain size was found to be 0.3589 nm (3.589 Å). The optical absorption study reveals that FeCuS thin film has a bandgap of 2.40eV and a refractive index range of of 2.00 to *2.70* at 400nm. The reflectance of the deposited films was found to be generally low.

V. REFERENCES

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