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CHARACTERIZATION OF COPPER SULPHIDE (CUS) THIN FILMS SYNTHESIZED BY ELECTROLESS PLATING

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ABSTRACT : *In this study, metallic copper (Cu) thin film was grown on soda lime glass substrate by electroless plating method and the as-grown Cu thin films were sulfurized using direct solvothermal sulfurization and thereafter annealed at 100 ^{0}C, 200 ^{0}C, 300 ^{0}C, and 400 ^{0}C. The film thickness, elemental composition, morphology, optical and electrical properties were investigated by using stylus surface Profilometer, energy dispersive x-ray spectroscopy, scanning electron microscopy, ultraviolet-visible spectroscopy and Four-Point Probe technique respectively. The EDS spectra analysis of CuS thin films confirms the presence of copper (Cu) and sulfur (S) along oxygen as an impurity which was attributed to open air annealing. At low annealing temperature, the material showed a compact smooth surface morphology but as the temperature increased the compact smooth surface of CuS agglomerated to form a dense and rough surface then a tiny popcorn-like structure started to grow. The increase in the annealing temperature demonstrate an improvement in the crystallinity of the material. The material strongly transmit at the visible region of electromagnetic spectrum but has a poor transmittance at both UV and NIR region except the film annealed to 400 ^{0}C, which decreased towards the NIR region but later increased slowly and constantly towards far infrared (FIR) region. This indicated that the films are capable of fairly suppressing UV and IR radiations while transmitting the visible radiations which could be suitable for solar control coatings. Film annealed at 400 ^{0}C suppressed transmittance of UV radiation while fairly transmitting the VIS and IR radiations. The energy bandgap values were found to be 2.53 eV, 2.52 eV, 2.48 eV and 2.32 eV for annealing temperature at 100 ^{0}C, 200 ^{0}C, 300 ^{0}C and 400 ^{0}C respectively. As a result, the material can find application in many optoelectronic areas where low energy bandgap are desirable. The measured resistivity and evaluated conductivity were found to vary with annealing temperature. The resistivity decreased from 395.26 Ω m to 248.13 Ω m as annealing temperature increases from 100 ^{0}C to 400 ^{0}C for the CuS thin films. Therefore, the findings of the study shows that the variations in the annealing temperature alter the properties of the deposited copper sulphide thin films.*
KEY WORD: Copper Sulphide (CuS), electroless plating

INTRODUCTION

Materials science plays a vital role in this modern age of science and technology, in trying to meet the demand of various kinds of materials used in our industries, housing, agricultures, transportations, etc. This demand has encourage scientist to increase the level of investigation in semiconducting chalcogenide thin films, (Adelifard and Mohagheghi, 2012; Fayroz *et al.,* 2016). Many minerals and ores are monosulfides like CuS, ZnS, CdS, NiS, MnS, CoS, etc (Greenwood and Earnshaw, 1997). They are the members of the transition metal chalcogenides. These materials have attracted increasing attention in recent years owing to their excellent physical and chemical properties (Tafreshi and Fazli, 2012; Haynes, 2013).

Among all semiconductor materials, copper sulphide (CuS) is an important IB-VIA semiconductor material. Copper sulphide is the most extensively studied binary Cu chalcogenide nanocrystal (NC) composition and is a p-type semiconductor with a direct band gap, ranging from 1.2 to 2.0 eV (Coughlan *et al.,* 2017). Compared with its Cd- or Pb-based counterparts, it offers a benign environmental profile by using nontoxic and earth abundant materials, which makes it a promising material candidate for future technological applications. Copper sulphide (CuS) is binary chemical compound of the elements copper and sulphur. It occurs in nature as the dark indigo blue mineral. Copper sulphide vary widely in the composition with $0.5 \leq Cu/S \leq 2$, including numerous non-stoichiometric compounds with the formula Cu_xS_y such as CuS_2 (Villamanitite), CuS (Covellite), Cu_9S_8 ($Cu_{1.12}S$) (Yarrowite), $Cu_{39}S_{28}$ ($Cu_{1.39}S$) (Spionkopite), Cu_8S_5 ($Cu_{1.6}S$) (Geerite), Cu_7S_4 ($Cu_{1.75}S$) (Anilite), Cu_9S_5 ($Cu_{1.8}S$) (Dignenite), $Cu_{31}S_{16}$ ($Cu_{1.96}S$) (Djurleite), and Cu_2S (Chalcocite) (Coughlan *et al.,* 2017).

The CuS in the form of thin films has attracted a commendable attention in optoelectronics systems such as solar energy conversion, dye synthesized solar cell, Schottky barrier devices, anti-reflecting coating on solar energy collectors, among others, and ammonia gas-sensor at room temperature (Bollero *et al.,* 2012). The CuS thin films have been deposited by various methods such as, physical vapour deposition (PVC), chemical vapour deposition (CVD), electro deposition (ED), successive ionic layer adsorption and reaction (SILAR) method, chemical bath deposition (CBD), spray pyrolysis, microwave assisted chemical bath deposition (MA-CBD), liquid-liquid interface reaction, chemical vapour reaction, atomic layer deposition (ALD), spray ion layer gas reaction, solution growth technique (SGT), photochemical deposition (PCD), etc. (Coughlan *et al.,* 2017). But in this study, the electroless metallization (deposition) method was applied, this deposition method is cost-effective because it does not require vacuum equipment, such as sputtering, evaporation and chemical vapor deposition, or power supplies and seed layers, such as in electroplating (Fritz *et al.,* 2012). The electroless deposition of metal is based on the incorporation of a chemical reducing agent into the electrolyte. The electroless process is initiated by a catalyst on the insulating surface. Once the metal nuclei have been initiated, the process transitions into an autocatalytic process where the metal itself serves as the site for sulphurisation or oxidation of the reducing agent. In addition to initiating the deposition of the first metal nuclei, the catalyst sites serve as the adhesive link between the depositing metal and the insulating surface. This valuable technique could apply to not only electrically conductive materials including graphite but also insulators like glass, plastics, rubber etc. (Chen *et al.,* 2009).

Objective of the Study

The aim of this study is to synthesize copper sulfide (CuS) thin films by direct solvothermal sulfurisation of metallic copper (Cu) thin film grown via electroless plating method in view to determining the optical and electrical properties of as-synthesized CuS thin films.

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MATERIALS AND METHODS

Synthesis of copper sulfide (CuS) thin films on glass substrate was carried out by electroless plating of copper thin films on glass substrate followed by direct solvothermal sulfurization of the copper thin films. All chemical reactants were analytical grade. The reactants used are: deionized water, $CuSO_4$, Ethylene diaminetetraacetic acid (EDTA), $K_4Fe(CN)_6.3H_2O$, Formaldehyde (CH_2O), NaOH, $SnCl_2$, HCl, $AgNO_3$ and platinum precursor were used directly without further purification. Here, $CuSO_4$ is the source of Cu^{+2}ions and the reduction of Cu was achieved using NaOHas the reducing agent. EDTA and $K_4Fe(CN)_6.3H_2O$ works as a complexing agent whereas formaldehyde was used for adjusting pH value of the bath solution to achieve the alkaline medium. Platinum precursor as catalyst spin-coated on the glass substrate to initiate the electroless process, the catalyst sites serve as the adhesive link between the Cu film and the glass surface.

In addition, $SnCl_2$, HCl, and $AgNO_3$ were used for the sensitisation of the surface by the adsorption ofSn^{2+} ions onto the surface of the glass substrate and theactivation is due to the presence of Ag. The microscope glass slides were used as substrates for deposition of CuS thin films. Spin coater for the deposition of the platinum precursor, digital thermometer for monitoring temperature, SLS as cleaning agent and magnetic stirrer to obtain a uniform solution.

Preparation of the Substrate

Glass substrates with the dimension 75 mm x 25 mm x 1.0 mm(size of a standard microscope glass slides) were used for the deposition. The optical glass substrates were degreased and washed ultrasonically in cleaning solution containing sodium lauryl sulphate (SLS) detergent, rinsed multiple distilled water wash. Finally, the glass slide was ultrasonically cleaned in methanol then dried in oven for 2 hours at 40 ^oC before using for deposition of thin film.Poor adhesion and non-uniform films are common problems when depositing films on smooth substrates by chemical deposition; the electroless process was initiated by spin-coating 1ml of platinum precursor on the glass substrate to create adhesive link between the Cu film and the glass surface, the spin-coated film was sintered at 400 $^{\mathbf{0}}C$ for 30 min to obtain platinum catalyst on the glass substrate.

Electroless Plating Synthesis of Copper (Cu) Thin films

The electrochemical activation used $SnCl_2.2H_2O$ and $AgNO_3$ solutions. The solution was prepared using 0.35g of $AgNO_3$ in 200ml of distilled water, to this, ammonia solution (NH_3OH) was added dropwise until colourless solution was observed and 0.01M concentration was obtained. The anionic (reducing agent) solution was prepared by adding 2 ml of concentrated HCl to 2g of stannous chloride ($SnCl_2.2H_2O$) in 640 ml of distilled water to obtain 0.2M concentration. The deposition was preceded by the sensitization of the surface by the adsorption of Sn^{2+} ions onto the surface of the glass slide in stannous chloride ($SnCl_2.2H_2O$) solution for 2 min. After sensitization, the substrate was placed within a bath ($AgNO_3$ solution) containing $2Ag^+$ ions in 2 min which result in the oxidation of the Sn^{2+} ions and reduction of the $2Ag^+$ ions to metallic Ag on the substrate surface creating silver nuclei through the reduction of silver ions directly on the surface that is to be plated (Ag-activation). The samples were rinsed carefully in double distilled water between each step to avoid cross-contamination of the solutions during the process.

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A solution in a beaker (bath) containing 1.8g of $CuSO_4$, 4.8 of EDTA, 5.7g of $K_4Fe(CN)_6.3H_2O$ and 2.2ml of formaldehyde in 100ml of distilled water was prepared for the deposition of the Cu thin films and thoroughly mixed with a magnetic stirrer to obtain homogenous solution. The pH value was adjusted to 12 by formaldehyde. Previously cleaned and activated glass substrates were then inserted into the beaker and the bath was warmed and kept within the temperature interval of 35 - 40 ^{0}C. No stirring was applied at this stage. At this temperature, the deposition of the films on the activated sides of the substrates started, once the precipitation began, the reaction at this temperature was completed within 4 minutes. The substrates were then taken out, rinsed with distilled water, and dried in air.

Direct Solvothermal Sulfurisation of Cu Thin Films

The synthesis of CuS thin films was done by sulfurizing the previously grown Cu thin films. The essence of the sulfurisation was to convert metallic Cu film into p-type semiconductor CuS thin film. This sulfurization was achieved by preparing a solution containing 0.32 Sulphur (S) in 100ml paraffin oil in a beaker as elevated temperature of 200 ^{0}C. At this temperature, the samples were inserted into the solution for 40 min for sulfurization. After sulfurisation process, the sulfurized Cu thin films were then taken out, dried in air and annealed at different temperatures of 100 $^{\mathbf{0}}$C, 200 $^{\mathbf{0}}$C, 300 $^{\mathbf{0}}$C, and 400 $^{\mathbf{0}}$C and preserved for characterization. It was observed that at 500 $^{\mathbf{0}}$C, the sample was destroyed.

Characterization of the CuS thin films

The surface morphology of the thin films was studied using scanning electronmicroscopy (SEM) employing at Sheda Science and Technology Complex (SHESTCO), Abuja. Optical properties of the sulfurized elctroless plating synthesized Cu thin films were studied using the absorbance spectra obtained employing UV-Vis spectrophotometer at Namiroch Laboratory, Abuja. The absorption spectra were recorded against plain glass as a reference. In this way, other optical parameters were calculated. To examine the electrical properties of the deposited materials, four-point probe technique was employed to determine the conductivity.

RESULTS AND DISCUSSION

Surface Profilometry

The film thickness was determined using stylus surface Profilometer at SHESTCO, Abuja. The average obtained thicknesses of the CuS thin films deposited by electroless plating and direct solvothermal sulfurisation method on glass substrate is tabulated in Table 4.1.

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Table 1: Thickness of the deposited films

S/No	Sample	Thickness (nm)
1	CS100	420
2	CS200	433
3	CS300	412
4	CS400	403

From Table 1, the thickness of the film increases when the annealing temperature increases, then the thickness reduces as the annealing temperature further increases.

Elemental Composition of the Material

The chemical composition of the CuS thin films were determined with the help of energy dispersive X-rays spectroscopy (EDS). The EDS spectrum of the thin films is shown in Figure 1.

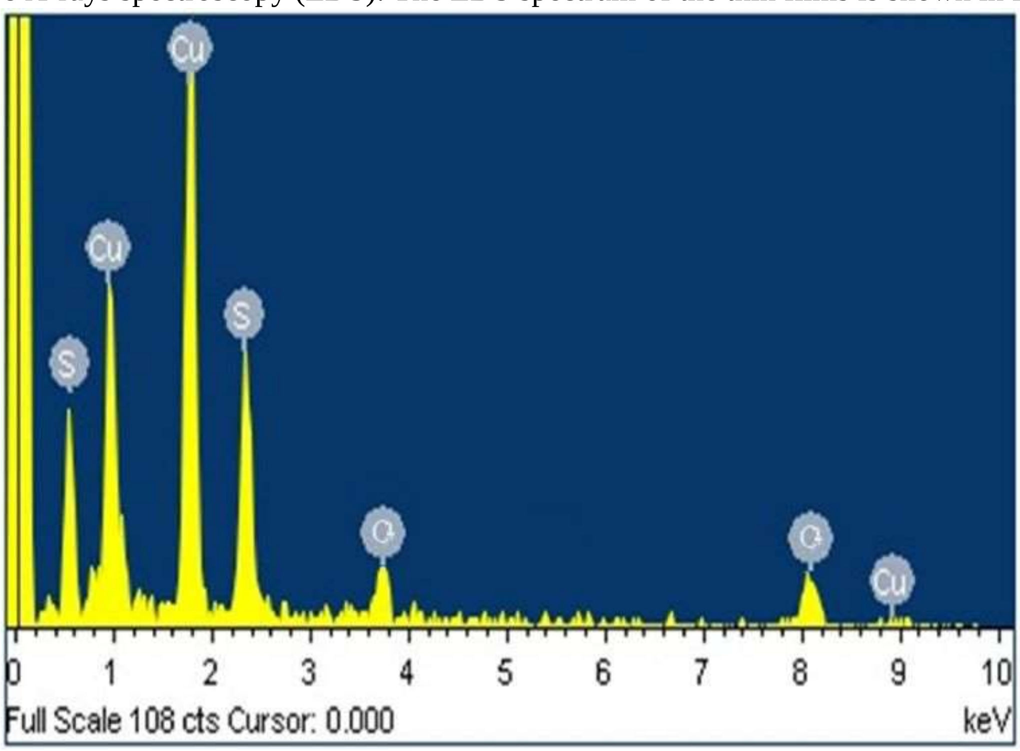

Figure 1: EDS analysis of CuS Thin films.

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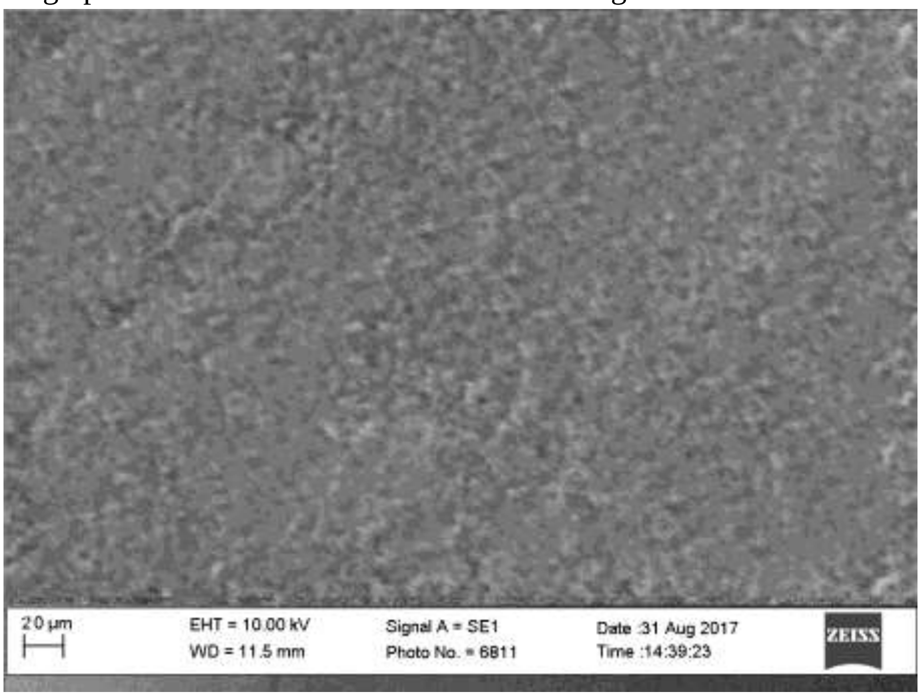
The elemental analysis confirms the presence of copper (Cu), sulfur (S) along with along oxygen (O) as an impurity. In the spectrum, O peaks observed may be due to the annealing that was carried out in open air.

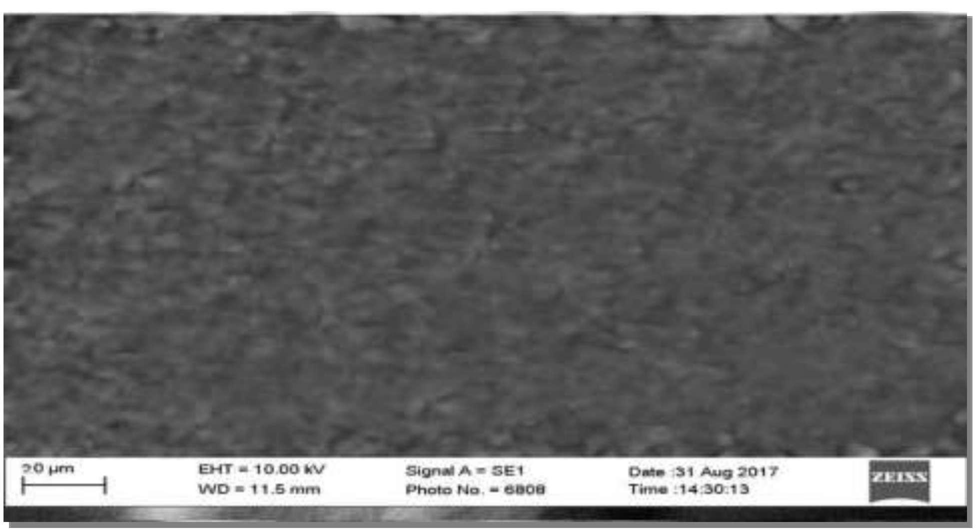
Morphological Study of the CuS

The surface morphology of thin films were studied using scanning electron microscopy (SEM). The SEM micrographs of the CuS thin films are shown in Figure 2 a-d.

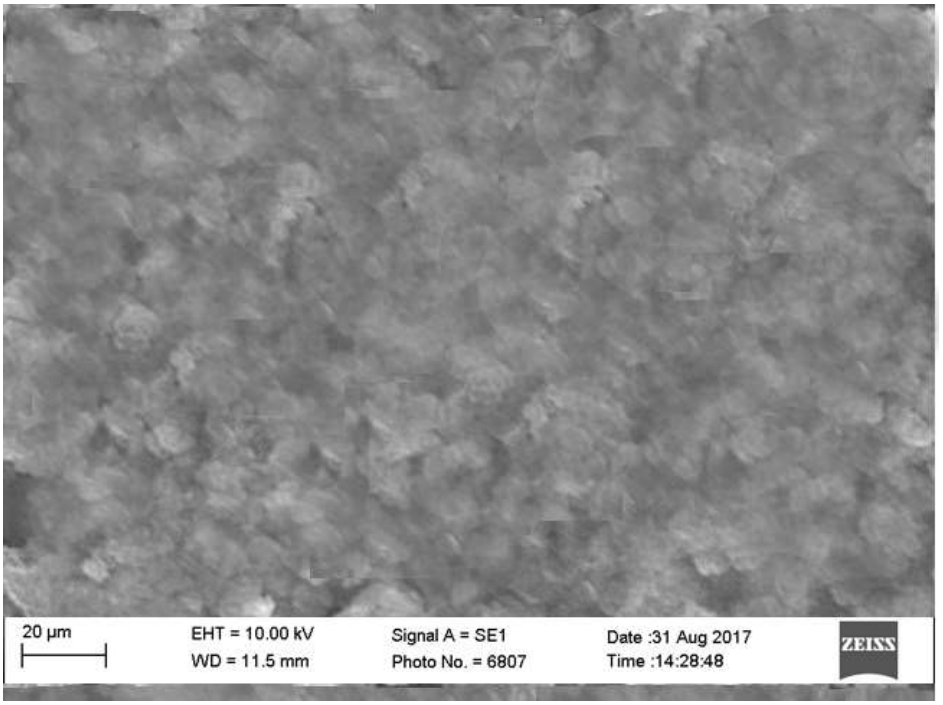
(a)



(b)



(c)



(d)

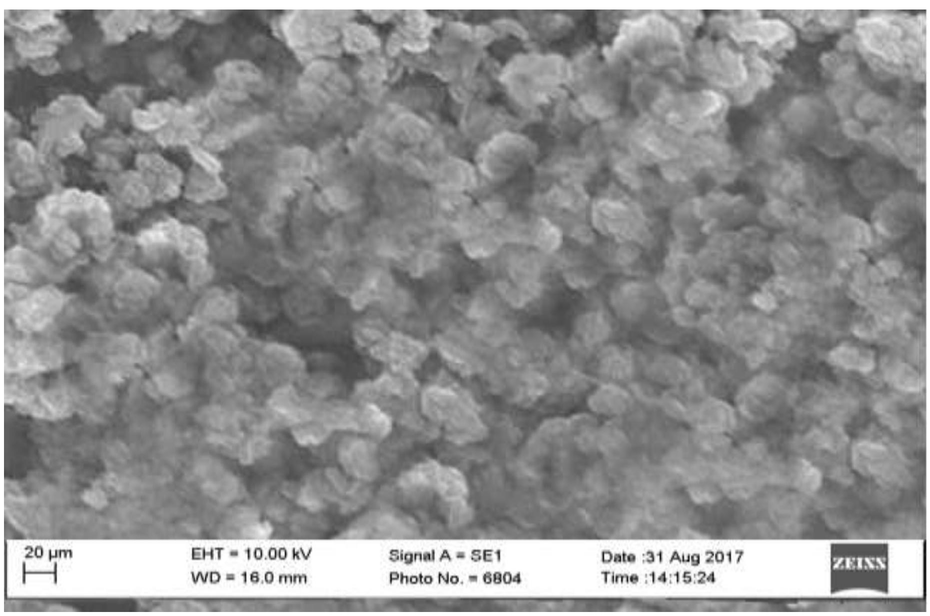


Figure 2a-d: SEM images of CuS thin films at annealing temperature of (a) 100 ^{0}C, (b) 200 ^{0}C, (c) 300 ^{0}C, and (d) 400 ^{0}C

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SEM images of the CuS thin films clearly reveal that CuS nanoparticles are uniformly distributed. As can be seen, the sample annealed at 100 ^{0}C has a compact smooth surface morphology with only a few irregularities and there is no growth of popcorn-like structure due to the formation of the film is incomplete. The compact smooth surface of CuS agglomerate to form a dense and rough surface then a tiny popcorn-like structure started to growth caused higher annealing temperature which initiate crystallinity to improve. As can be seen in Figures 2(c) and (d), the surface structure of the samples are similar to each other which is popcorn-like structure with CS400 having a distinct formation.

Optical Characteristics

Optical Absorption and Transmission of CuS

The optical properties of the CuS thin films were studied using the absorbance spectra obtained employing spectrophotometer. The absorption spectra of the thin films are shown in Figure 3. The spectra of the thin films show strong absorption in the wavelength range of 325 nm to 550 nm with different absorption intensity. The absorption peaks were found around 427 nm, 413 nm, 405 nm, and 386 nm for 100 ^{0}C, 200 ^{0}C, 300 ^{0}C and 400 ^{0}C respectively. In contrast, the transmittance spectra (Figure 4) estimated from absorbance spectra showed that all the films have transmittance between 3 and 54 % in the UV-VIS-NIR regions.

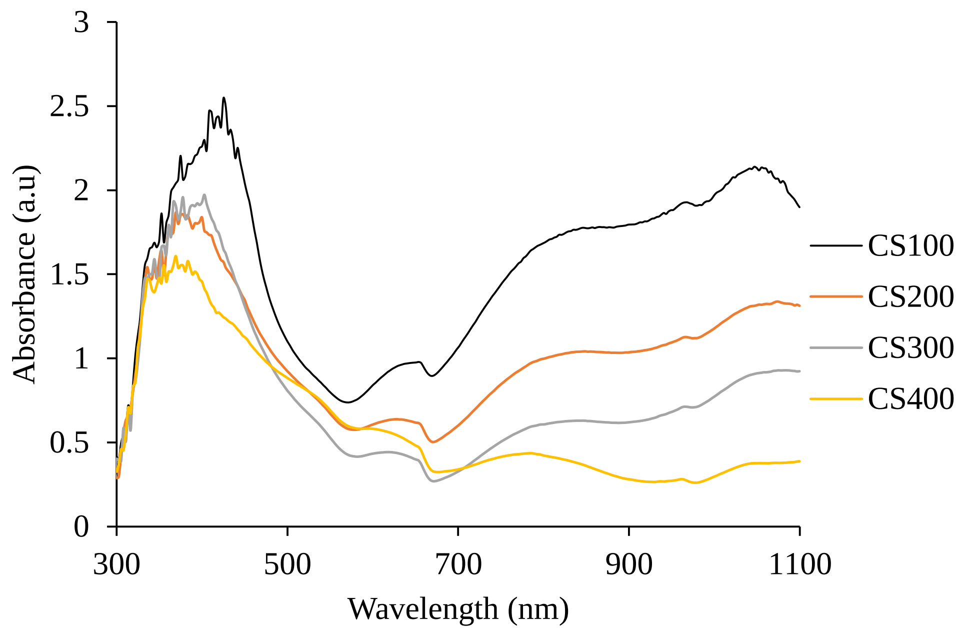


Figure 3: Absorption spectra of CuS thin films of annealing temperature at 100 ^{0}C, 200 ^{0}C, 300 ^{0}C and 400 ^{0}C.

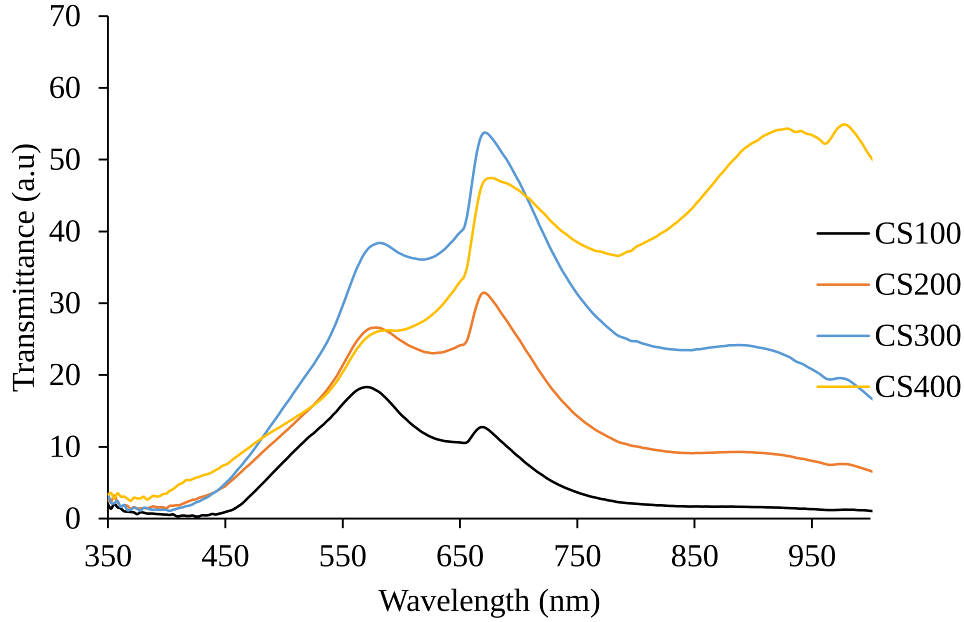


Figure 4: Transmission spectra of CuS thin films of annealing temperature at 100 ^{0}C, 200 ^{0}C, 300 ^{0}C and 400 ^{0}C.

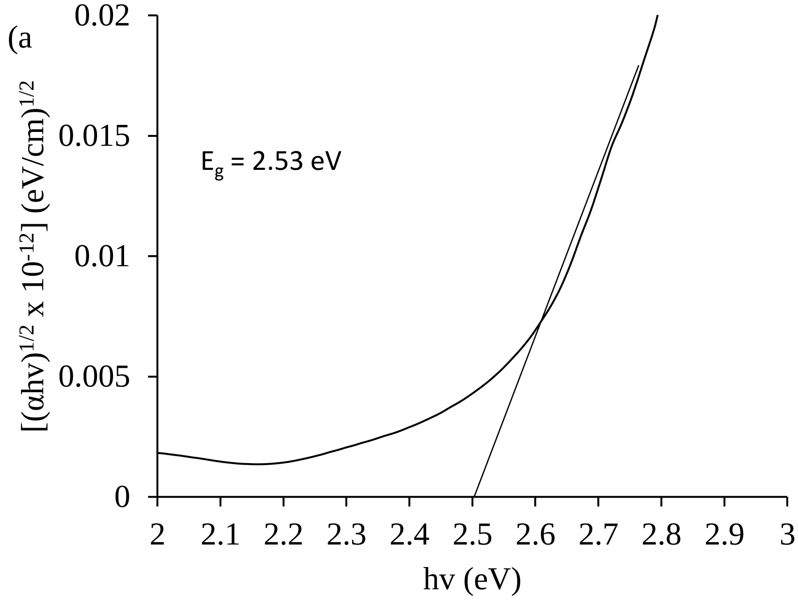
The transmittance of the films increased with wavelength from the UV regions to the visible (VIS) regions but decreased with wavelength at the near infrared (NIR) regions except the film annealed to 400 ^{0}C, which decreased towards the NIR region but later increased slowly and constantly towards far infrared (FIR) region. The samples showed average transmittances of greater than 17% throughout UV-VIS-NIR regions.

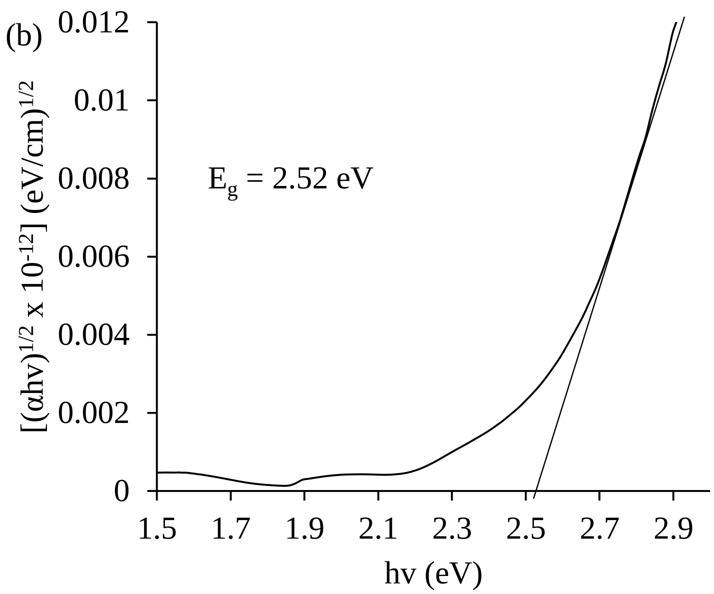
The spectral transmittances of 100 ^{0}C, 200 ^{0}C and 300 ^{0}C show that the films are capable of fairly suppressing UV and IR radiations while transmitting the VIS radiations. Films CS 100, CS 200 and CS 300 are suitable for solar control coatings. Human eye is sensitive only in the range 400-700 nm and is peaked at 500 nm (photopic vision). This is an important factor in window coatings and is fairly met in these films. This material is suitable in warm countries and saves energy spent on conventional air conditioners (Ezema *et al.*, 2006).

Film annealed at 400 ^{0}C suppressed transmittance of UV radiation while fairly transmitting the VIS and IR radiations. This property make the film annealed to 400 ^{0}C a good material for thermal control coatings and for screening off UV portion of electromagnetic radiation, which is dangerous to human health and as well harmful to domestic animals. The film can be used for coating eyeglasses for protection from sunburn caused by UV radiations. Since it shows moderately high transmittance of VIS and NIR radiations it can be used for coating of poultry roofs and walls. This will ensure that young chicks, which have not developed protective thick feather, are protected from UV radiations while the heating portion of the electromagnetic spectrum maintains the heating of the poultry house and as well there is admittance of VIS light in the house.

Optical Bandgap

The optical bandgap of the CuS thin films were determined from the absorption spectra using Tauc's relation $\propto hv \approx B\left(hv - E_g\right)^{1/2}$ (Mahato and Kar, 2017). Figure 5 a-d shows the optical bandgaps of the CuS thin films with different annealing temperature of 100 ^{0}C, 200 ^{0}C, 300 ^{0}C and 400 ^{0}C.





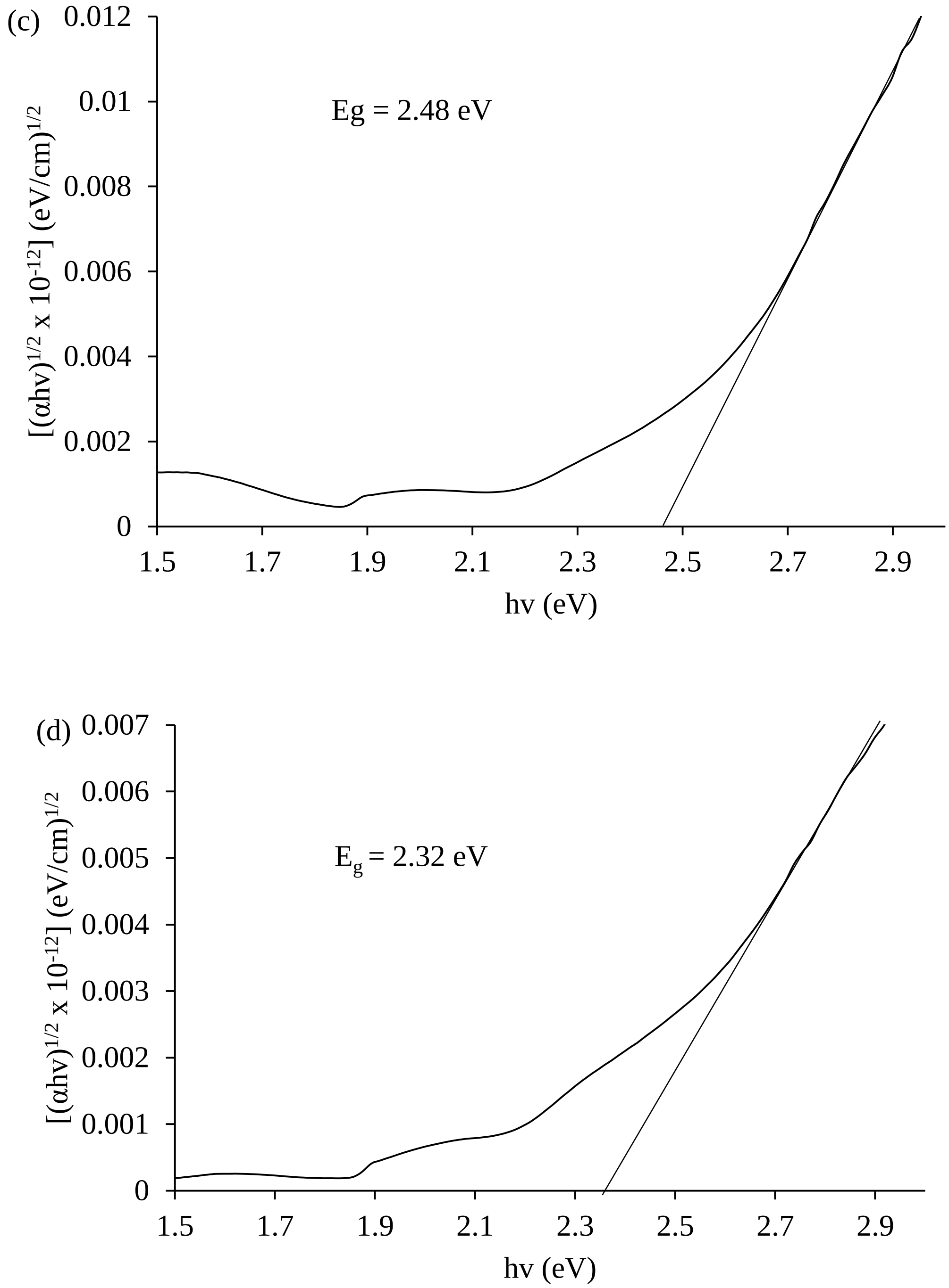


Figure 5 a-d: Bandgap of CuS thin film at annealing temperature of (a) 100 ^{0}C, (b) 200 ^{0}C, (c) 300 ^{0}C, and (d) 400 ^{0}C

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The energy gap values are 2.53, 2.52, 2.48 and 2.32 eV for CS100, CS200, CS300 and CS400 respectively. It is observed that increase in annealing temperature resulted to decrease in the energy gap values which could be attributed to improvement in the crystal and change in grain size of the film as evidenced in the SEM images presented in Figure 6. It is found that the band gap energy decreases from 2.53 to 2.32 eV as the annealing temperature of films increased from 100 ^{0}C to 400 ^{0}C.

Electrical Properties

The films resistivity (ρ) was determined with the sheet resistance obtained from 4-points probe measurements, according to $\rho = R_s t$, where t is the film thickness and R_s is the sheet resistance. The measured electrical resistivity and evaluated electrical conductivity are given in Table 2

Table 2, Effects of annealing temperature on electrical properties of CuS

Annealing Temperature (^{0}C)	Resistivity ρ (Ω m)	Conductivity σ (s) x 10^{-5}
100	395.26	253
200	340.19	294
300	331.62	301.5
400	248.13	403

The relationship between annealing temperature and resistivity is shown in Figure 6b

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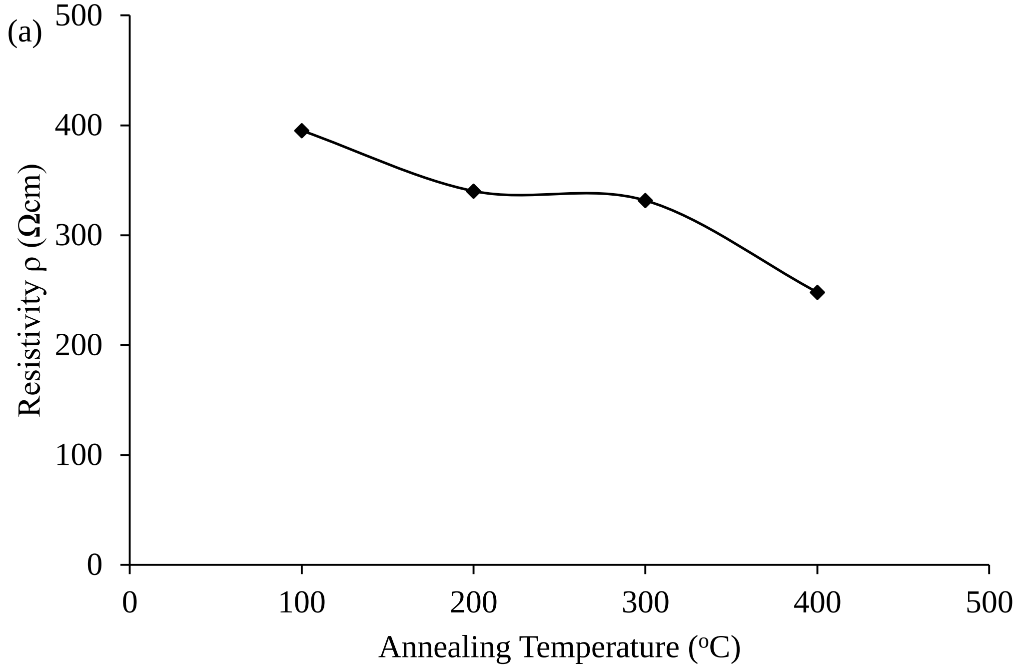

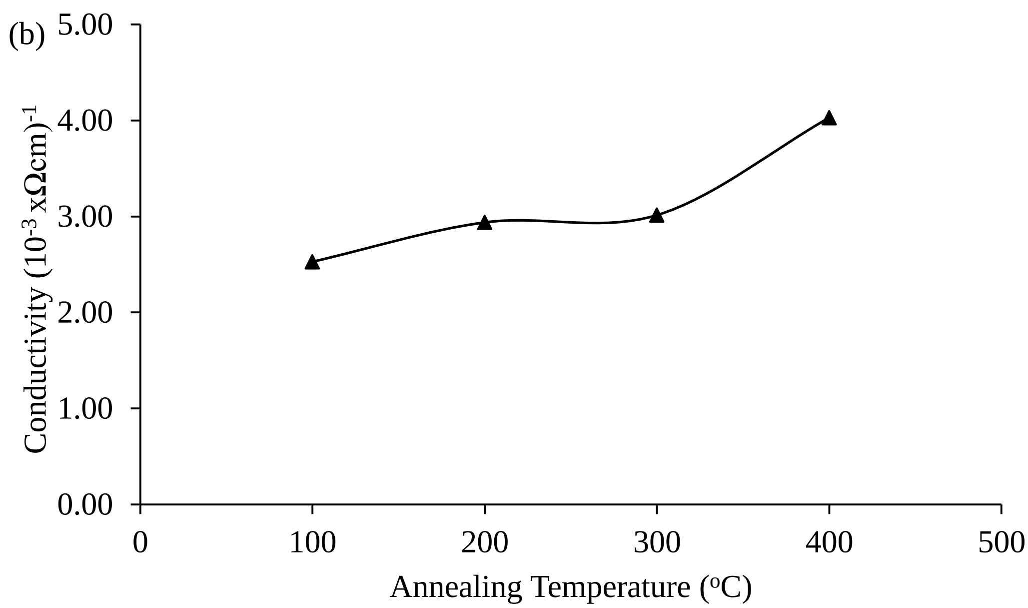

Figure 6: Variation of (a) resistivity and (b) conductivity with annealing temperature T_a

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The measured resistivity and evaluated conductivity were found to vary with varying annealing temperature. The resistivity decreases from 395.26 Ω m to 248.13 Ω m as annealing temperature, T_a, increases from 100 ^{0}C to 400 ^{0}C for the CuS thin films. This could be attributed to the formation of defects inside the material, and these majority defects could be Cu vacancies (V_{Cu}). The material tends to grow with a deficiency of copper (Cu-poor). This was also observed by Adelifard *et al.* (2012) and Cruz *et al.* (2013). V_{Cu}'s have a negative net charge, and then trap holes that can be ionized easily with temperature, which becomes the CuS films p-type. The resistivity value of CuS thin films decreases with increasing annealing temperature.

The decrease in resistivity with the annealing treatment is due to the increase in the majority carrier concentration. Conductivity depends on (i) crystallinity, (ii) both grain size and their orientation, and (iii) texture. In the electroless plating method the annealing processes affect the morphology, structural and electrical properties. It has been observed in the present study that the annealing improves the conductivity.

CONCLUSION

Metallic copper sulphide (Cu) thin film has been grown using electroless plating method. The as-grown Cu thin films were subsequently sulfurized by direct solvothermal sulfurization method. The sulfurized Cu thin films were annealed at 100 ^{0}C, 200 ^{0}C, 300 ^{0}C, and 400 ^{0}C. Morphological, optical and electrical characteristics of the films were investigated to study the effect of the annealing temperature on the film properties.

The elemental composition analysis of the materials confirmed the presence of Cu and S. The morphological study showed the variations of the film micrographs with annealing temperature. The increase in the annealing temperature demonstrates an improvement in the crystallinity of the material. The optical transmittance of the films estimated from absorbance spectra showed that the films have transmittance between 3 and 54 % in the UV-VIS-NIR regions. The study established that the films are capable of fairly suppressing UV and IR radiations while transmitting the visible radiations which could be suitable for solar control coatings. Film annealed at 400 ^{0}C suppressed transmittance of UV radiation while fairly transmitting the VIS and IR radiations. This property make the film annealed to 400 ^{0}C a good material for thermal control coatings and for screening off UV portion of electromagnetic radiation, which is dangerous to human health and as well harmful to domestic animals. The film can be used for coating eyeglasses for protection from sunburn caused by UV radiations. Since it shows moderately high transmittance of VIS and NIR radiations it can be used for coating of poultry roofs and walls.

Finally, the energy bandgap values were found to decrease as the annealing temperature of films increased. As a result, the material can find application in many optoelectronic areas where low energy bandgap p-type semiconductor are desirable. Therefore, the findings of the study show that the variations in the annealing temperature alter the properties of the material.

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