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PREPARATION AND OPTICAL ANALYSIS OF COPPER SULPHIDE THIN FILM USING CHEMICAL BATH DEPOSITION METHOD

***Nwaba Abraham Atta, Sulayman Muhammad kabeer and Matthew David Femi**

Department of Physics, Kogi State College of Education Ankpa, Kogi State, Nigeria

*Corresponding authors' email: nwabaattah@yahoo.com

ABSTRACT

Copper Sulphide thin films is a metal usually found in superconducting films, diamond films, among others Solution growth method was used for the preparation of CuS thin films on glass substrates at various temperatures and deposition times. In this research, optical properties of these films were investigated. It is used in ultra violet range and microwave shielding. Best deposition was obtained at 600C. The corresponding 14950 Å film showed 3.7% transmittance at 300 nm and the band gap of the films was within 1.35 – 2.35 eV.

Keywords: Bandgap, Deposition, Film, Transmittance

INTRODUCTION

Copper Sulphide thin films is a metal usually found in superconducting films, diamond films, magnetic films, microelectronic devices, surface modification, hard coatings, photoconductors, IR detectors, solar control, solar selective coatings, optical imaging, solar cells, optical mass memories, sensors, fabrication of large area photodiode arrays catalyst etc. (Ajaya et al., 2013; Ghosh & Verma, 1979; Nayak et al., 1982). A very thin layer of a substance on a supporting material, especially a coating (as of a semiconductor) that is deposited in a layer one atom or one molecule thick is referring to as thin film (Merriam-webster Dictionary, 2016). Different methods are been used for deposition of thin films, like vacuum evaporation, electro deposition, electro conversion, dip growth, spray pyrolysis, successive ionic adsorption and reaction, chemical bath deposition, solution-gas interface technique, sol gel method, sputtering, thermal oxidation, molecular beam epitaxy etc. Copper sulphides (CuxS) are important materials for applications in p-type semiconductors and optoelectronics (Partain et al., 1983). This is very useful in photo thermal conversion applications, photovoltaic applications, solar control coatings and other electronic devices (Mattox and Sowel, 1974; Agnihotri and Gupta 1981; Grozdanov et al., 1995; Pathan and Lokhande 2004). In addition, it can also be applied in fabrication of microelectronic devices, optical filters as well as in low temperature gas sensor. Special attention is now given to the study of copper sulphide thin films probably due to the discovery of heterojunction solar cell (Pathan and Lokhande 2004). At least five stable phases of the copper sulphur system are naturally known to exist. Among these include, CuxS phases for $1 \leq x \leq 2$ covellite (Cu1.00S), anilite (Cu1.75S), digenite (Cu1.80S), djurleite (Cu1.97S), and chalcocite (Cu2.00S) (Pathan & Lokhande, 2004; Evans, 1981) as cited in Ajaya et al., (2013). Other phases that exists include yarowite (Cu1.12S) and spionkopite (Cu1.14S). The structure of chalcocite and djulerite is hexagonal with alternate layers of copper and sulphur ions. The covellite contains six formula units in the unit cell with four copper ions tetrahedrally coordinated and two triangular coordinates with exagonal crystal structure (Wyckoff , 1965), also in Evans (1981) the direct band gap of this material reported in the literature lies in the range from 1.2 to 3 eV. (Popovici, 2009; Nducwe, 1996) and it is one of the source of renewable energy.

The conventional sources of energy are petroleum, coal, firewood, natural gas etc. are non-renewable and fast depleting due to excessive domestic and industrial usage. This leads to a quest for alternative, the solar energy which is unconventional sources of energy, and a renewable source, which prompt this work (Agbogu, 1995; Hayes, 1978). In this case, chemical bath deposition method (solution method) was used for the deposition of copper sulphide thin films based on the controlled precipitation from a reaction mixture; the ionic product (IP) has to be greater than the solubility products (SP) and some advantages such as low material cost, low temperature and convenient for larger area deposition of thin films. The films are uniformly deposited and above all have comparable optical properties with those obtained by other techniques. So far, a number of thin films such as CdSe, ZnS, PbS, NiS, BiS, ZnIn2Se, Pb-xFexS, CdS-xSex and ZnxCd-xS prepared using chemical bath deposition method have been reported by many researchers (Garcia et al., 1999; Arome et al., 2007; Anyika, 1988; Turner, 1976).

The optical properties of the thin film, copper sulphide (CuS) were investigated in this work. The optical properties include; absorption coefficient, transmittance and refractive index, deduction of band gap and type of transition via optical analysis.

MATERIAL AND METHOD

Thin films of CuS were deposited on glass slides (substrate) of dimension 76.2 x 25.4 x 1 mm before deposition; the substrate was treated by soaking them inside concentrated HCl acid for twenty four hours to improve the wetting of the surface of the substrate and improves the film adhesion. They were washed with detergent and raised with distilled water and dried at room temperature. The deposition of CuS thin film is based on chemical reactions of the following reagents: copper sulphate ($CuSO_4$), thiourea ($(H_2N)_2CS$), ammonia (NH_3), triethanolamine (TEA). TEA is use as complexing agent and ammonia (NH_3) is use to adjust the pH of the reaction. The film deposition was done in two sets. Each set comprising of three slides. Set 1 growth was done at fixed temperature of 30^0C and 30min, 50min and 70min. Set 2 was done at temperature range of 40 – 60^0C at fixed times 30min. The quantities of the reagents used, were 20 ml of 1M of $CuSO_45H_2O$, 20ml of 1M of $(H_2N)_2CS$, 20ml of NH_3, and 10ml of TEA. For every growth fresh reaction bath was prepared to maintain the constitution. Gentle heating and observation of thermometer achieved the required temperatures of set 2. The Absorbance of the film was taken using CAMSPEC M501 UV/visible spectrophotometer and wave length range 300 – 800 nm at 100 intervals.

RESULTS AND DISCUSSION

Thickness varies linearly with time and temperature and attains its terminal point at 55 – 65 minutes and 53^0C – 54^0C from figure 1 and 2. From table 1 and 3 of figure 3 - 8 (13400 Å, 14850 Å, 1500 Å and 14825 Å, 15075 Å, 14950 Å), absorbance generally starts to decrease after 400 nm. This is very obvious from the transmittance graphs of 13400 Å, 14850 Å, 1500 Å and 14825 Å, 15075 Å, 14950 Å (fig. 3 - 8) from table 1 and 3. The horizontal intercepts of the absorbance graphs from 13400 Å, 14850 Å, 1500 Å and 14825 Å, 15075 Å, 14950 Å (fig. 3 – 8), are used to evaluate the band gap of the films as shown in table 2. The variation of transmittance (T) of CuS thin films with wavelength (λ) in the both set are shown from table 1 and 3 and in figures 1 to 16

Table 1. Wave length, Absorbance, Absorption Coefficient, Transmittance and Photon Energy (Set 1)

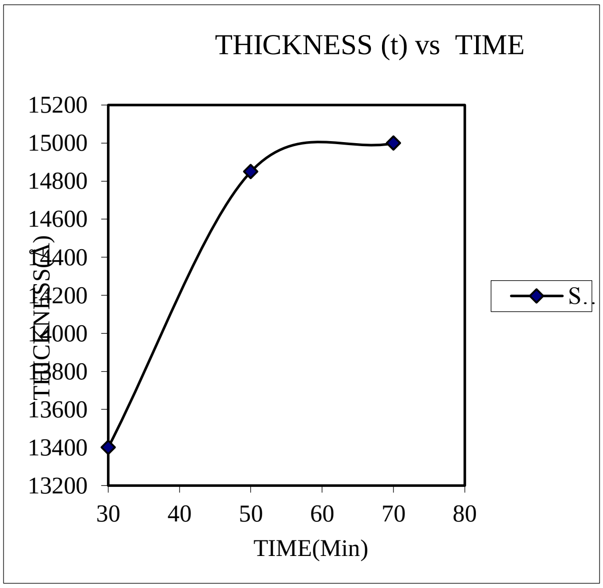
Wave length (λ) (nm)	Absorbance (Å)			Absorption Coefficient (α)			Transmittance (T %)			Photon Energy (hv) (eV)
	Slides			Slides x 10^4			Slides			
	1	2	3	1	2	3	1	2	3	
300	0.199	0.202	0.407	66.30	67.30	136.00	62.20	62.80	39.20	4.14
400	0.008	0.015	0.120	2.00	3.75	30.00	98.20	96.60	75.90	3.12
500	0.008	0.008	0.054	1.60	1.60	10.80	98.20	98.20	88.30	2.49
600	0.007	0.013	0.038	1.20	2.17	6.33	98.40	97.10	91.60	2.07
700	0.010	0.015	0.042	1.42	2.14	6.00	97.70	96.60	90.70	1.78
800	0.012	0.012	0.052	1.50	1.50	6.50	97.30	97.30	88.70	1.55

Table 2. Energy Band Gap (Eg) from Absorbance and Absorption Coefficient (Set 1 & 2)

Slides	Film Thickness (t) Å	Eg from Absorbance (eV)	Eg from Absorption Coefficient (eV)
1.	13400	3.03	1.35
2.	14800	2.89	2.30
3.	15000	2.70	2.35
4.	14825	2.70	2.35
5.	15075	2.96	2.30
6.	14950	2.26	2.35

Table 3. Wave length, Absorbance, Absorption Coefficient, Transmittance and Photon Energy (Set 2)

Wave length (λ) (nm)	Absorbance (Å)			Absorption Coefficient (α)			Transmittance (T%)			Photon Energy (hv) (eV)
	Slides			Slides x 10^4			Slides			
	4	5	6	4	5	6	3	5	6	
300	0.317	0.197	1.437	106.00	65.70	480.00	48.20	63.50	3.70	4.14
400	0.087	0.016	0.838	21.80	4.00	210.00	81.80	96.40	14.50	3.12
500	0.039	0.010	0.442	7.80	2.00	88.40	91.40	97.70	36.10	2.49
600	0.031	0.010	0.329	5.17	1.67	54.80	93.10	97.70	46.10	2.07
700	0.032	0.012	0.270	4.57	1.71	38.60	92.90	97.20	53.70	1.78
800	0.039	0.013	0.283	4.88	1.63	35.40	91.40	97.10	52.10	1.55



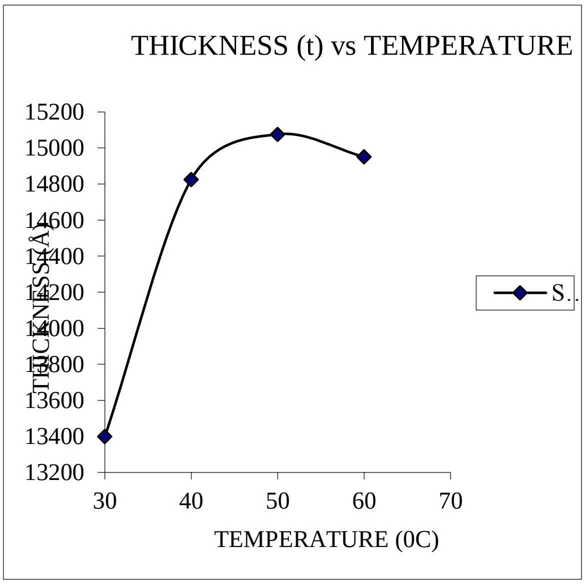
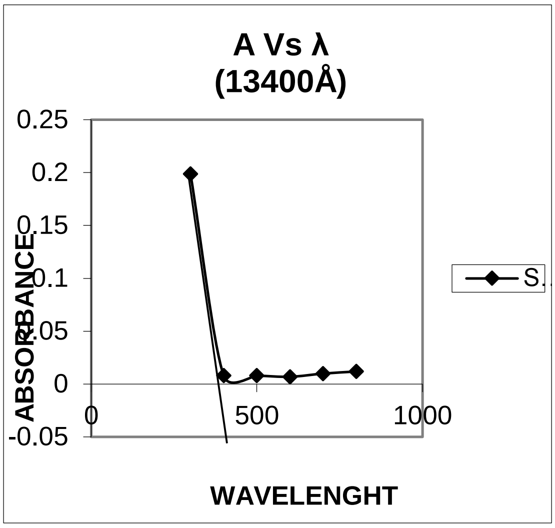


Fig. 1: Thickness of the Films

Fig. 2: Temperatures of the Films



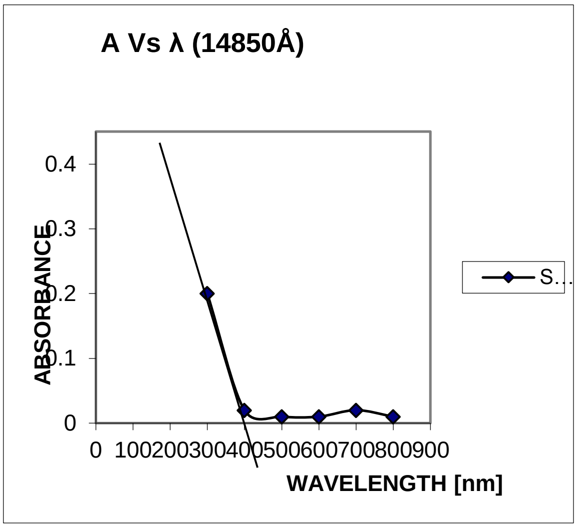
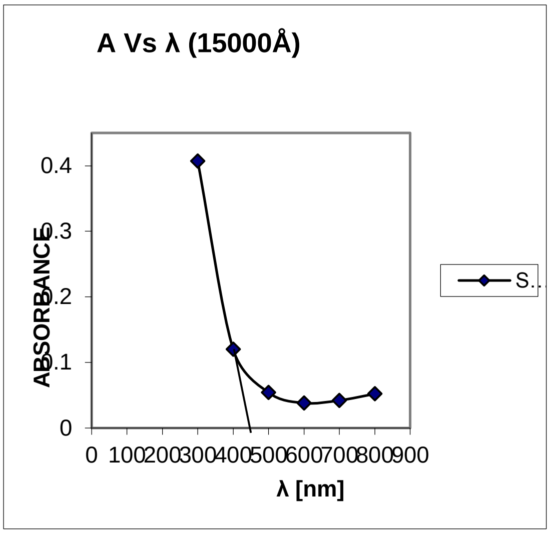


Fig. 3: Absorbance vs Wave Length

Fig.4: Absorbance vs Wave Length



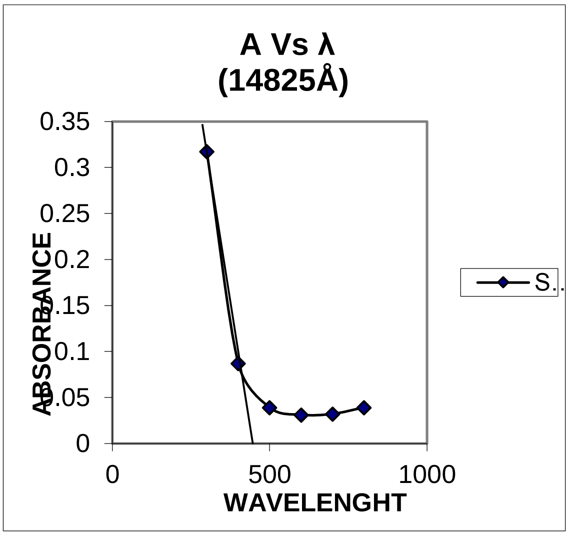
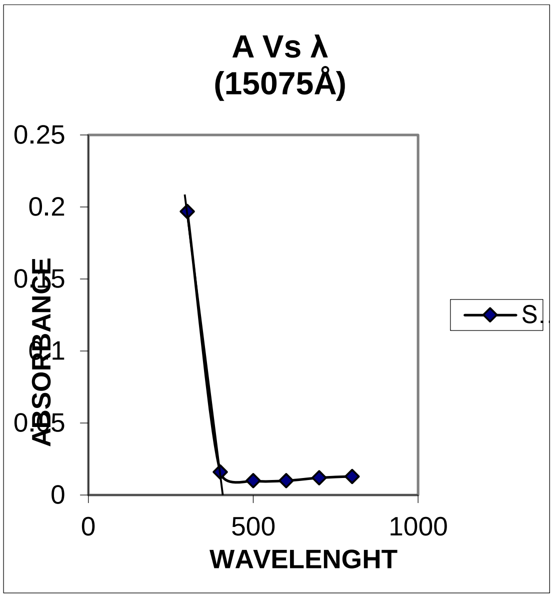


Fig. 5: Absorbance vs Wave Length

Fig. 6: Absorbance vs Wave Length



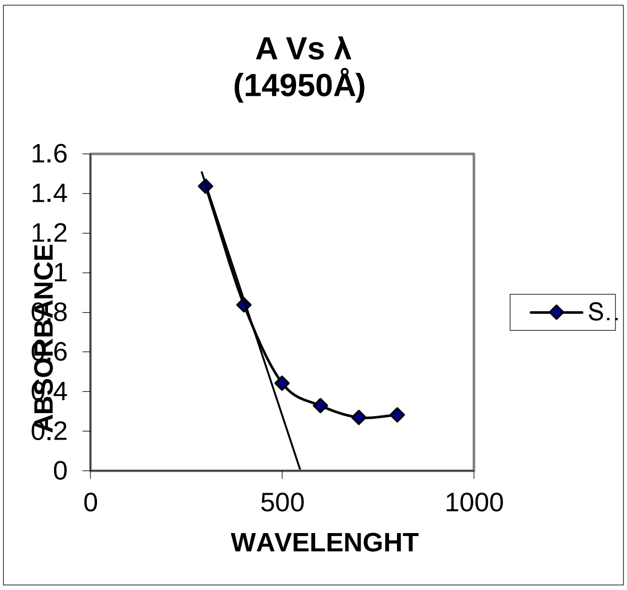
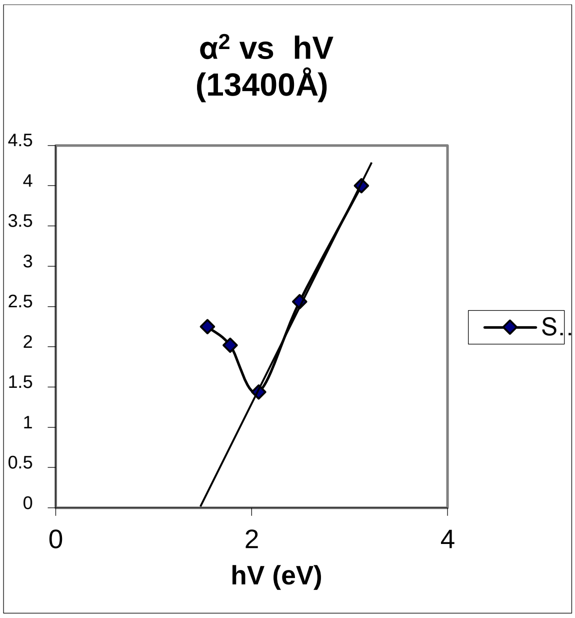


Fig. 7: Absorbance vs Wave Length

Fig. 8: Absorbance vs Wave Length



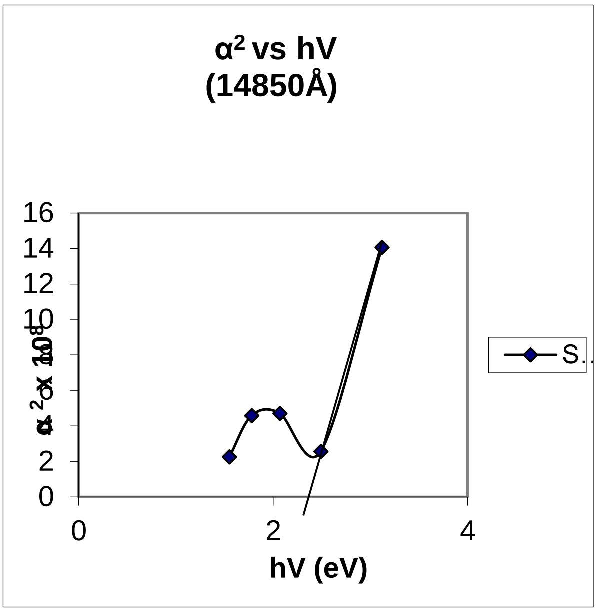
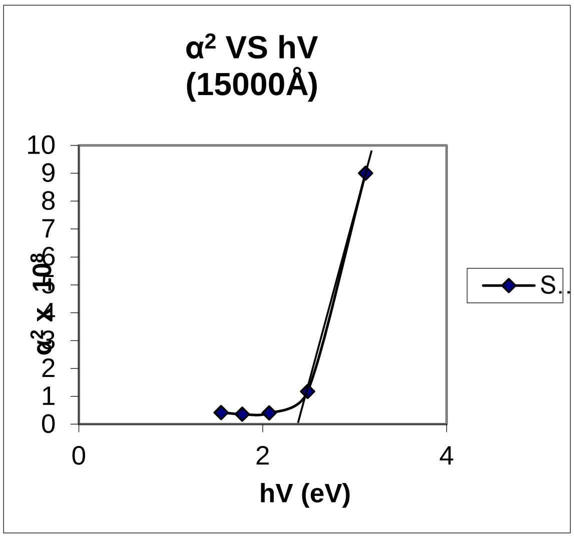


Fig. 9: Absorption Coefficient Square vs Photon Energy

Fig. 10: Absorption Coefficient Square vs Photon Energy



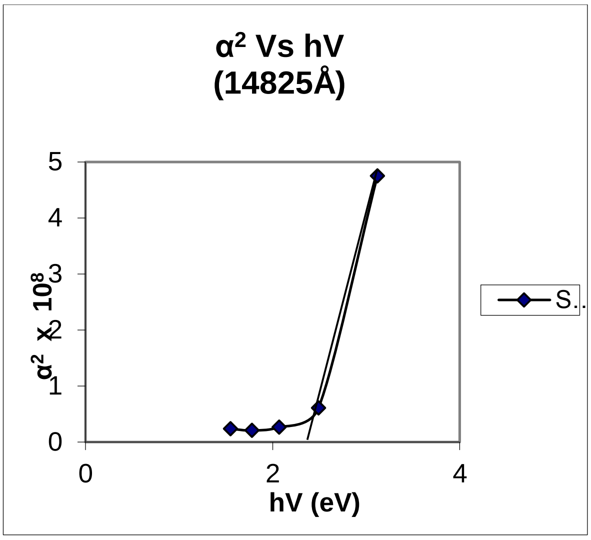
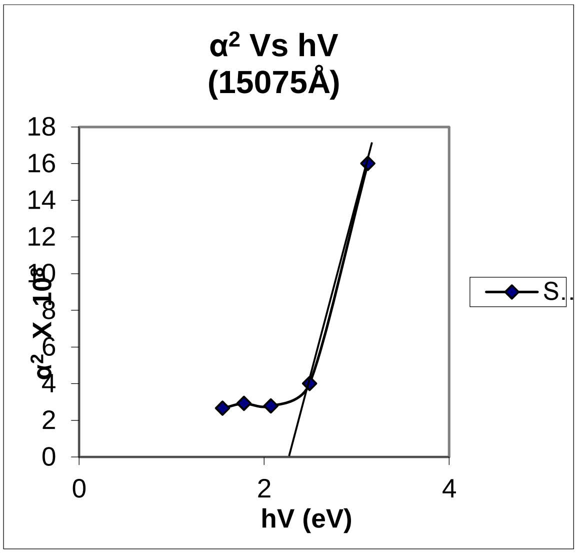


Fig. 11: Absorption Coefficient Square vs Photon Energy

Fig. 12: Absorption Coefficient Square vs Photon Energy



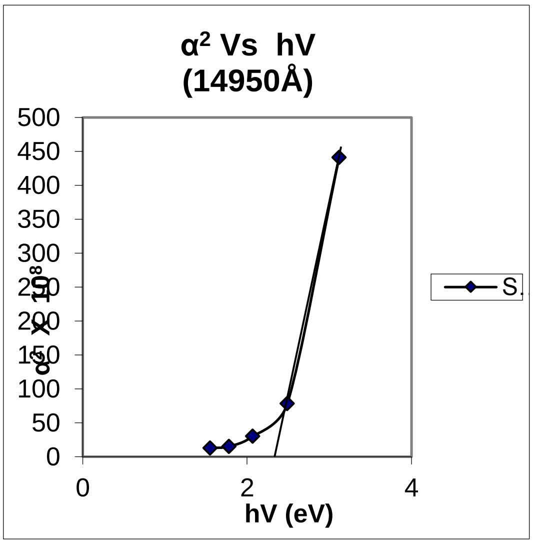


Fig. 13: Absorption Coefficient Square vs Photon Energy Fig. 14: Absorption Coefficient Square vs Photon Energy

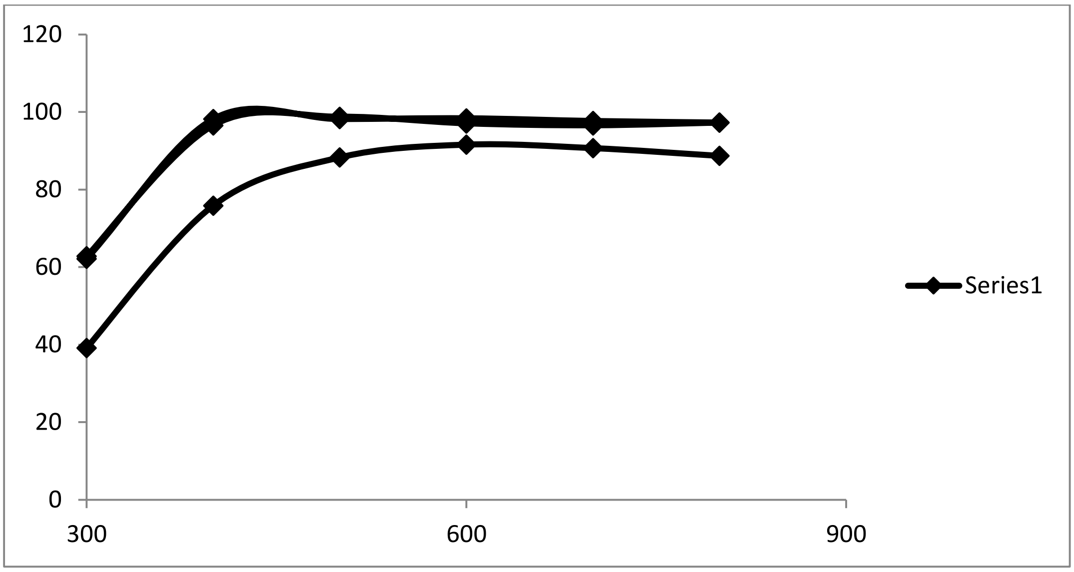


Fig. 15: Transmittance vs Wavelength (of thickness vs time deposition)

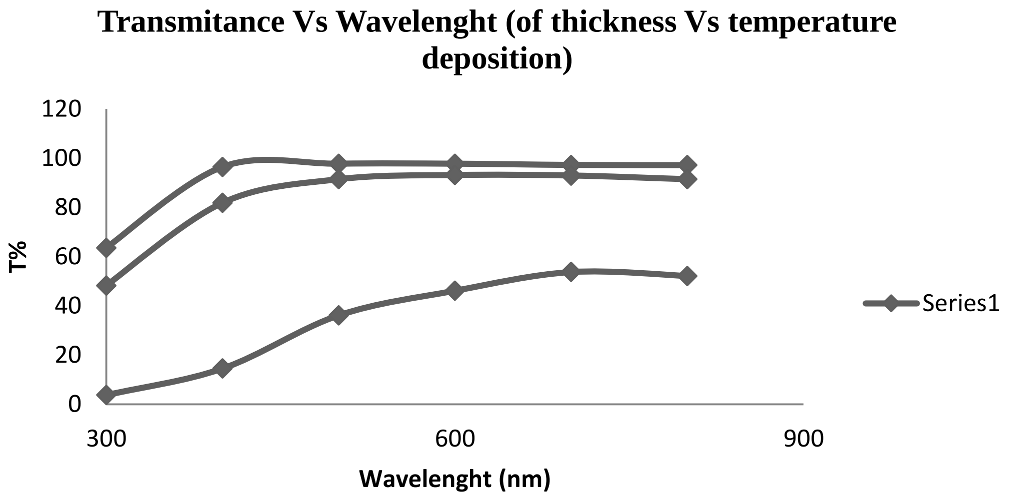


Fig. 16: Transmittance vs Wavelength (of thickness vs time deposition)

From the result it is shown that thickness varies linearly with time and temperature attains its terminal point at 55 – 65 minutes and 53^{0}C – 54^{0}C, the best deposition was obtained at 60^{0}C which is in accordance with previously report that deposition of CuS is obtained at 55^{0}C to 65^{0}C (Anyika, 1988; Turner, 1976). The decrease in absorbance after 400nm show that beyond this wavelength the film absorb little electromagnetic wave in the visible light range even into the infrared region. In other word, the film is transparent to electromagnetic wave of these wavelengths. The corresponding values in the table are within the range of reported band gap, 1.20 – 3.0 eV. However, though the absorbance method is less accurate than that of absorption coefficient of figure 9 – 14 from table 1 and 3, because it does not include reflectance and thickness of the film, it gives a measure of defects in the deposited films (Benno & Joachim, 2003). Thus the very close agreement of the band gaps deduced at both methods for 14950 Å film emphasizes the fine microstructure of the film, which is in agreement with Anyika (1988) and Turner (1976). One measure interesting things about transmittance is that the 14950Å film has just 3.7% transmittance at 300nm wavelength and this have the best microstructure. So it can be inferred that films grown at 60^{0}C and above can be employ in UV – light and microwave shielding.

CONCLUSION

The optical properties of the thin film, copper sulphide (CuS) were investigated in this work. Solution growth method was used for the preparation of CuS thin films on glass substrates at various temperatures and deposition times. Best deposition was obtained at 600C. The corresponding 14950 Å film showed 3.7% transmittance at 300 nm and the band gap of the films was within 1.35 – 2.35 eV.

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