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Growth and Optical Characterization of Copper Sulphide Thin Films by Sol-Gel Technique

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ABSTRACT

Thin films of Copper sulphide (CuS) with varying annealing temperatures have been deposited on glass substrate using sol-gel deposition technique. The spectral absorbance of the thin films was measured using a spectrophotometer in the VIS-IR regions of the electromagnetic spectrum. The effects of annealing temperatures on other optical properties obtained theoretically were evaluated from the spectrophotometer data. The absorbance of the thin films increased as the annealing temperature increased from 473K-673K with a peak value of 2.2718; the transmittance showed peak value of 46.8% in the VIS region while the reflectance decreases from 20.35% annealed at 523K to 3.69% annealed at 573K.The energy band gap increased as the annealing temperature increased to a maximum of 2.35eV. The result also show increase in the absorption coefficient and values for the refractive index reduced to 1.038 from a maximum of 1.23 annealed at 523K. The results of the absorbance, transmittance and reflectance as here presented converged at 500nm and diverge at 1050nm. The thin films showed high optical conductivity with a maximum value of $5.063 \times 10^7 S^{-1}$ as the annealing temperature increases. The high absorbance and index of refraction n>0 makes them good material for application as an anti-dazzling coating for car windscreen and protective coating respectively. The results also provide basis for specific applications in microelectronics for fabrication of computer memories etc.

Keywords: Copper Sulphide, annealing temperatures, sol-gel, optical properties,

1.0 INTRODUCTION

Thin film technology has drawn considerable attention in many important electronic and optoelectronic applications such as solar cells, photo-detectors etc (Barman, J et al., 2008). Copper Sulphides thin films ranging from sulphur rich (CuS) to copper rich (Cu_2S) especially CuS have proven to exhibit favourable materials characteristics for solar application (Devi, R et al., 2007). Copper sulphides thin films have received special attention for such applications because they are of low cost and non-toxic and also exhibit important photovoltaic, photo-catalytic properties (Ezeokoye, 2003). In order to grow CuS thin films with desirable shape and structure, sol-gel deposition technique was employed.

The optical properties of CuS thin films have been investigated at various annealing temperature in order to broaden the range of its application.

2.0 EXPERIMENTAL DETAILS

All the reagents used were of analytical grade. Cupric Acetate $Cu(OAc)_2$ was the source of Cu^{2+} and thiourea $CS(NH_2)_2$ was the source of S^{2-}, were diluted with propanol and distilled water with Cetrimonium bromide (CTAB) as a complex agent and Ammonium hydroxide (NH_4OH) as a pH adjuster. The solution was stirred and the CuS thin film was prepared by dip coating at axial velocity of 2.5cm/mins, and was left to age. The film was then put in a furnace and annealed at 473K. The process was repeated for three samples annealed at different temperatures of 523K, 573K and 673K.

3.0 RESULTS AND DISCUSSIONS

The absorbances of the deposited thin films were measured using Axiom Medicals UV75 spectrophotometer in the wavelength region of 500 nm-1050 nm.

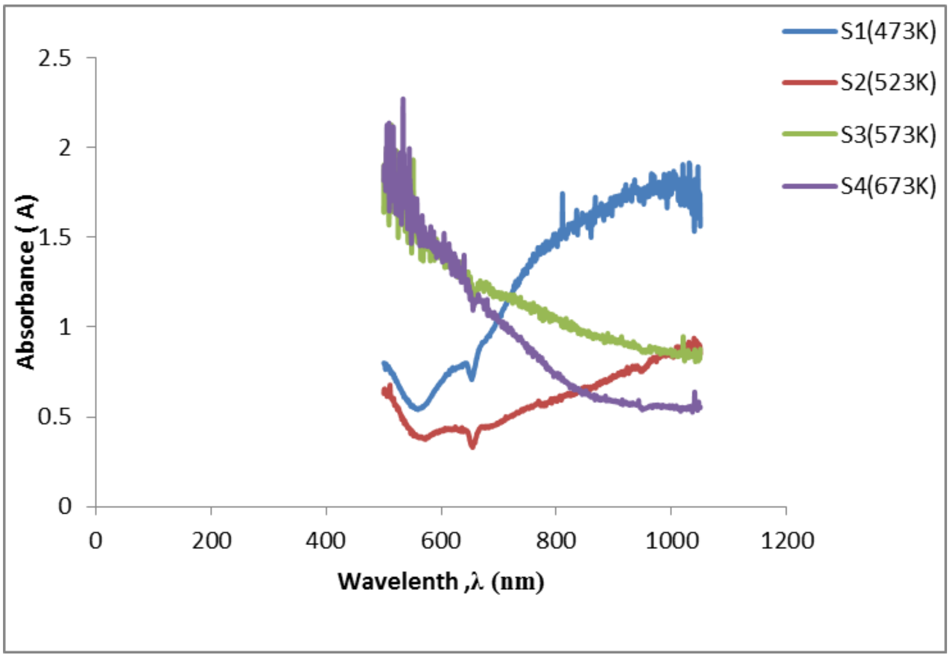

Fig 1: Absorption spectra of CuS thin film annealed at different temperatures

Figure 1 shows the spectral absorbance values of sol-gel deposited CuS thin films, annealed at various temperatures. Sample S1 and sample S2 showed maximum values of about 1.9151 and 0.9389 respectively.. Sample S3 showed maximum absorbance of about 2.1271 while Sample S4 showed peak absorbance of 2.2718, all corresponding to the wavelength range of 514.33nm−1039.30nm in the (VIS – NIR) region of the electromagnetic spectrum. The result shows that the annealing temperatures have a significant effect on the absorbance of sol-gel deposited CuS. High absorbance in the visible region makes CuS films efficient for window glaze materials for visibility and buffer layer in solar cell.

The values for the transmittance and reflectance were obtained using the relation

$T= 10^{-A}$ (1)

Where T is Transmittance and A is the Absorbance

$R= 1-(A+T)$ (2)

Where R is Reflectance, A is Absorbance and T is Transmittance

Figure 2 below shows the variation in spectral transmittance value of sol-gel deposited CuS thin films annealed at different temperatures. Sample S1 showed maximum transmittance of 28.8% at 559.36nm, sample S2 showed peak value of 46.8% at 654.55nm, sample S3 showed maximum transmittance of 15.59% at 1041.58nm, while sample S4 showed maximum transmittance of 29.8% at 1036.5nm. The spectral transmittance is high towards the VIS and low towards the NIR regions of the electromagnetic spectrum. High transmittance in the VIS-NIR regions makes S1, S2 and S4 good materials for the construction of poultry roofs and walls and for coating eyeglasses.

The reflectance spectra of Figure 3 shows that sample S1 showed maximum reflectance of 17.16% at 559.36nm, sample S2 showed peak value of 20.35% at 657.97nm, sample S3 showed maximum value of 3.69% at 1041.38nm, sample S4 showed maximum value of 17.62% at 1037.32nm. The spectral reflectance of sample S3 decreases as the annealing temperature increases. The high reflectance of sample S2, S4 and S1 makes them good materials for reflecting films. The coating of glasses with reflecting films helps in cutting the thermal radiation of sunlight coming into a room. Copper sulphide thin films were prepared for this purpose which will help to absorb sunlight.

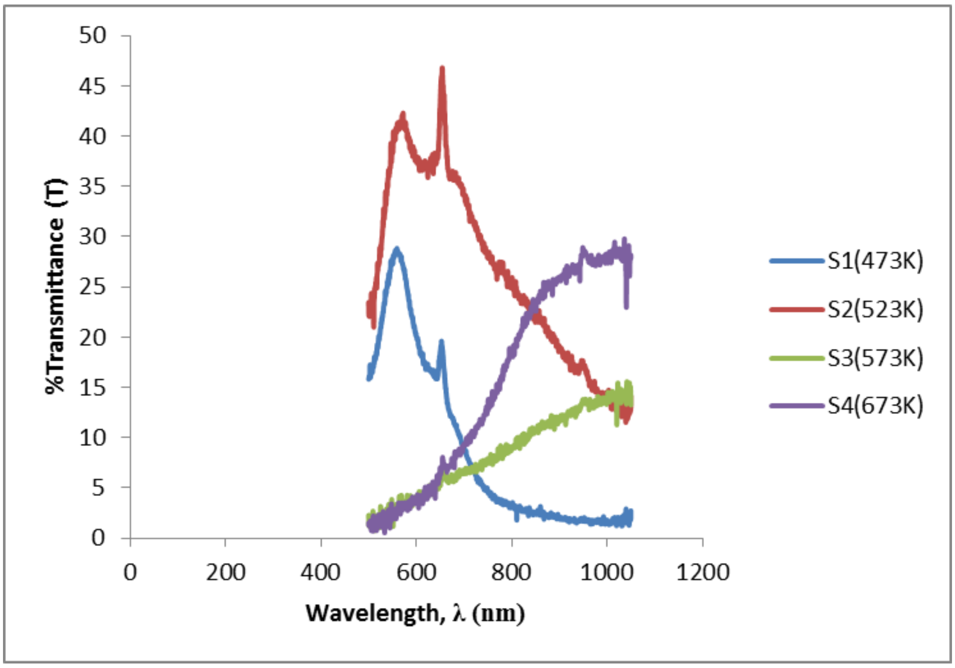

Fig 2: Transmittance spectra of CuS thin films annealed at different temperatures.

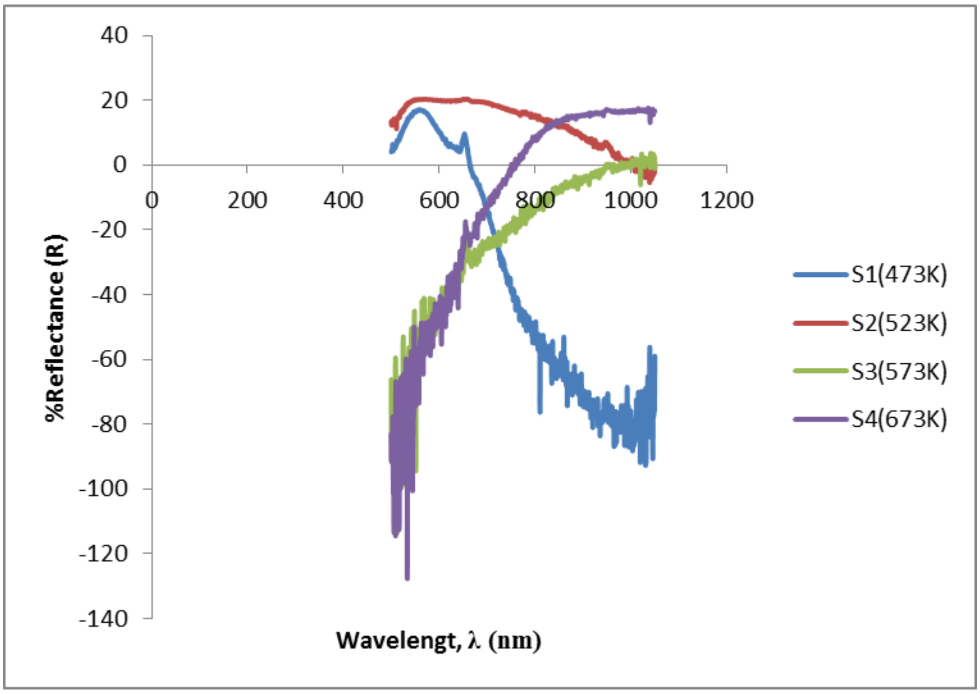

Fig 3: Reflectance spectra of CuS thin films annealed at different temperatures.

The above results indicate that CuS thin films annealed at different temperatures are potential good materials for different applications. Distinctive effects of annealing are shown in the plots of the absorption coefficient of figure 4 in the VIS-NIR region. . Sample S3 showed maximum absorption coefficient (α) at photon energy 2.422348eV and sample S2 showed minimum value at photon energy

1.195463eV. it was also observed that absorption coefficient of sample S1 increased at temperature 423K, sample S2 decreased at temperature (523K), while the absorption coefficient of sample S3(573K) and sample S4 (673K) increased as the annealing temperature was increased. Sample S4 (673K) having the highest absorption coefficient of 5.231013 at 2.329eV. These results are of importance for the films because the spectral dependence of absorption, affects the solar conversion efficiency (Jiang, et al., 2005) (Lai et al., 2010). Their high absorption coefficient makes them good materials for solar energy applications. This is achieved when these thin films materials are coated on the surface of solar cell collector (Mgbaja, 2010).

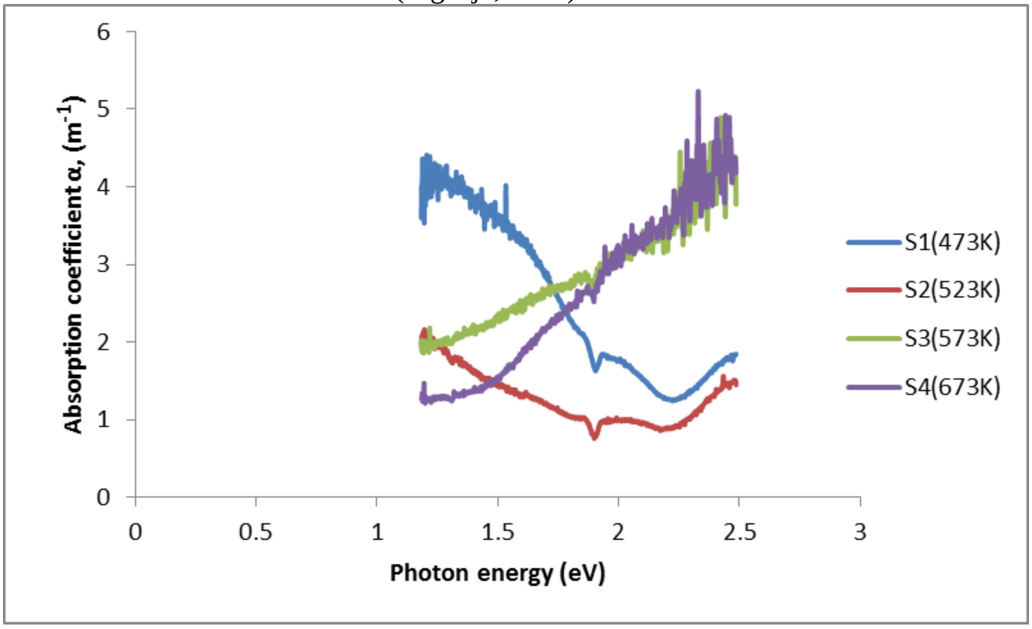

Fig 4: Absorption coefficient as a function of photon energy for CuS thin films with varying annealing temperatures.

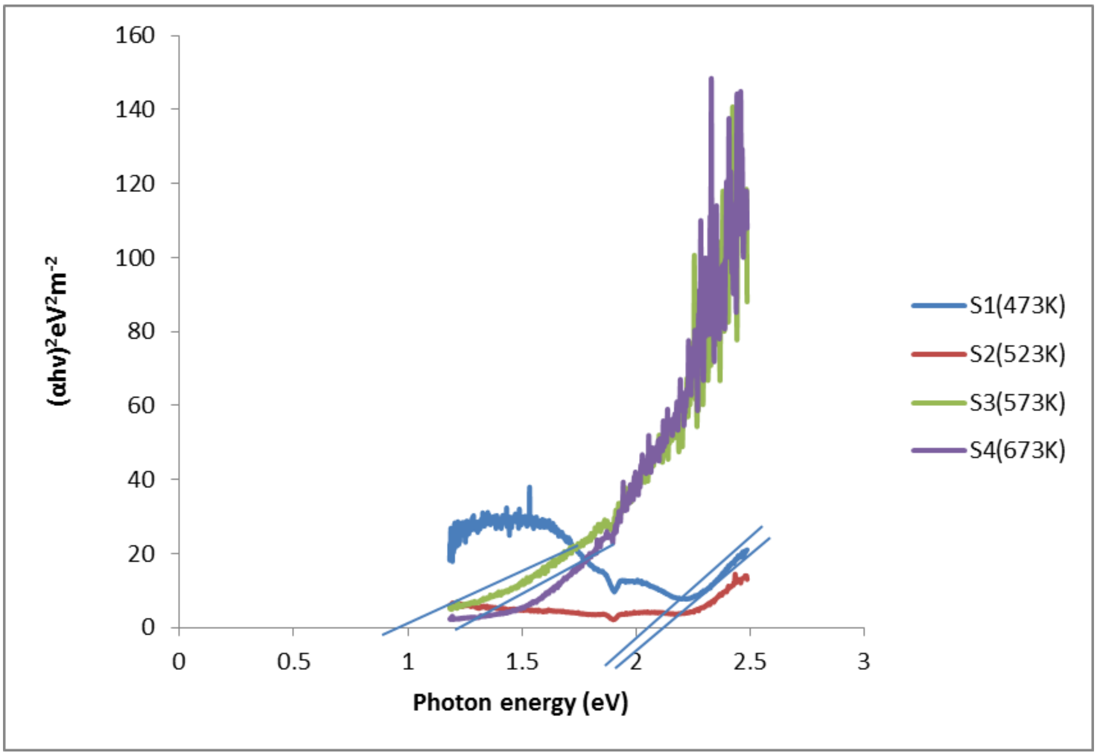

Fig 5: $(\alpha h\nu)^2$ versus photon energy (hν) of CuS thin films with varying annealing temperature

$$(\alpha h\nu)^2 = A(h\nu - Eg) \quad (3)$$

Where A is a characteristic parameter independent of photon energy hν, n is a constant which depends on the nature of the transition between the top of the valence band and bottom of the conduction band. The lowest optical band gap energy in a semiconducting material is referred to as the fundamental absorption edge and the nature of inter-band transition is characterized by n (Osuwa and Anusionwu, 2011) (Smith, 1995). For allowed indirect transition n = ½ and for allowed direct transition n = 2 as contained in figure 5. The values of optical band gap energies Eg were obtained by extrapolating the straight portion to the hν axis at (αhν) = 0. Values of the band gap for the entire samples ranged from 2.38 eV- 1.28eV for the corresponding annealing temperatures of 423K-673K. Thin films with band gaps of 2.38eV such as CuS can be used as a window layer absorber for photocells since its band gap energy lies within the range for visible transmission (Oriaku and Osuwa, 2008) As a wide band gap material, it permits devices to operate at high voltage, frequency and temperature. It has the potential of emitting light in visible colour range.

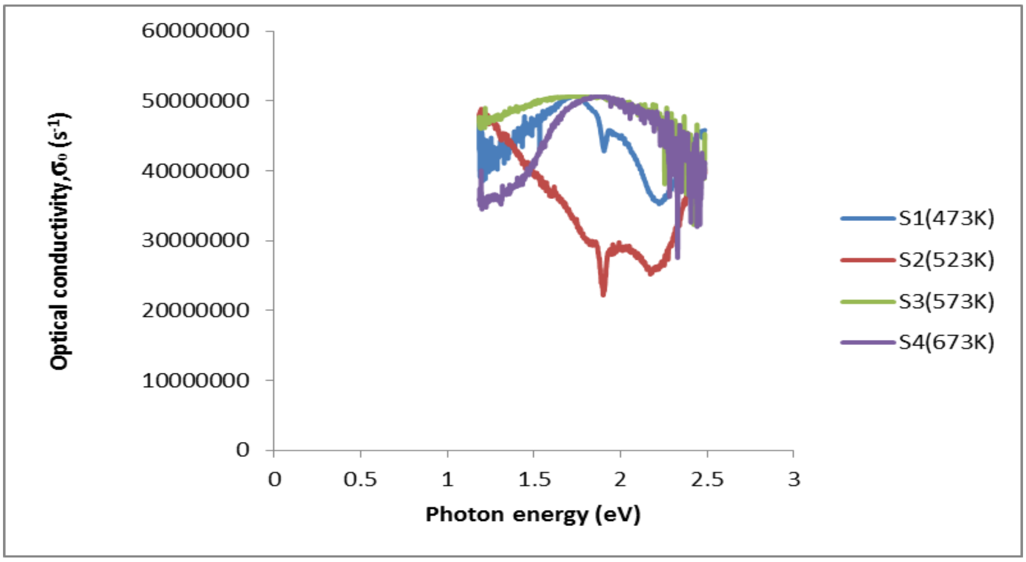

Figure 6: Optical conductivity against photon energy of CuS thin films with varying annealing temperature.

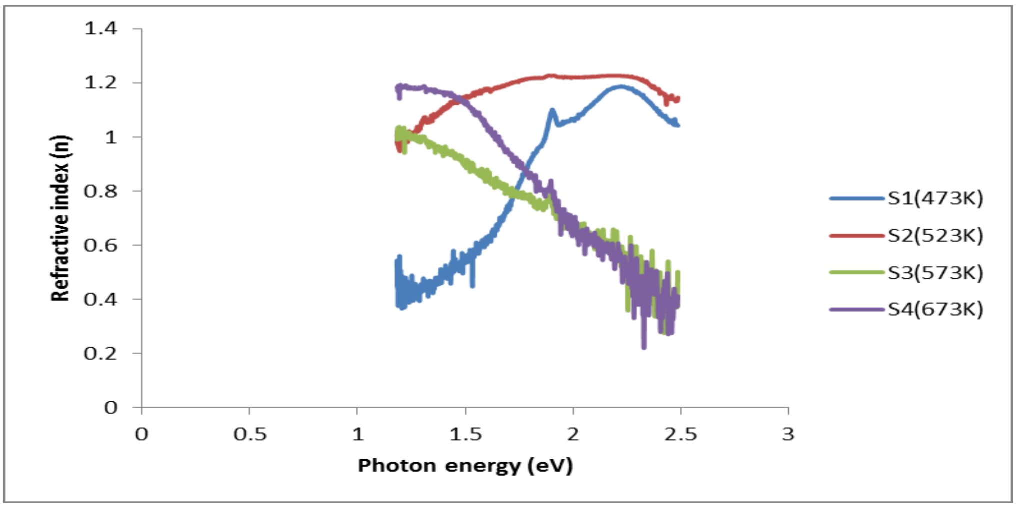

Fig 7: Refractive index against photon energy of CuS thin films annealed at different temperatures.

Figures (6, 7) show plots of optical conductivity and refractive index respectively. The sample has a high optical conductivity of 5.06 x 10^7 S^{-1} for the sample annealed at 423K-673K. The CuS thin films show no regular trend but exhibits distinctive dependence on the annealing temperature. The refractive index of figure 7 exhibits distinctive dependence on the annealing temperatures but shows no regular trends. But the refractive index n>0 makes the thin films good for protective coating (Mgbaja, 2010).

4.0 CONCLUSION

The sol-gel process is one of simplest method for preparing the ceramic materials. It can be used for preparing thin films, fibers, spheres, powders, aerogels, xerogels and glasses. There are many parameters influencing the sol-gel process, such as compositions and concentrations of alkoxides and solvents, catalyst, sequence in which the components are added and temperatures. There are many techniques to fabricate thin films by the sol-gel process, such as dip coating process, spin coating process, spray coating techniques, and capillary techniques. A great variety of the sol-gel deposited thin films have been prepared for different applications. For the optical application, the sol-gel deposited Copper Sulphide thin films have a wide range of application such as, window coating, solar cell collectors, and anti-reflecting films, reflecting films, electro-optics and nonlinear optic.
Table 1 below contains peak values of the measured optical and solid state properties. Figure 5 shows the plot of $(\alpha h\nu)^2$ versus photon energy, hν. Values of the energy band gap were obtained using the e following relation (Oriaku and Osuwa, 2008).

Table 1: Values of peak optical and solid state properties of the deposited and annealed CuS thin films

Film Sample	Extinction coefficient, (K)	Absorption coefficient(m^{-2})	Optical conductivity $\sigma_o(\times 10^7)$	Refractive index(n)	Optical energy band gap E_g(ev)
S1	3.63E-07	4.419681	5.06333	1.187701	37.962
S2	1.79E-07	2.161897	4.88755	1.226539	14.423
S3	2.00E-07	4.897829	5.06334	1.037611	140.760
S4	2.22E-07	5.231013	5.06329	1.193199	148.454

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