International Journal of Thin Films Science and Technology

http://dx.doi.org/10/12785/ijtfst/020201

An Analytical Study Of The Optical Properties Of Copper-Antimony Sulphide Thin Films And Possible Applications Of The Film

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Received: 16 Dec. 2012, Revised:18 Dec 2012; Accepted: 7 Apr. 2012
Published online: 1 May 2013

Abstract: Copper-antimony sulphide thin films were successfully deposited on glass substrates at different dip time using solution growth technique. Optical studies of the grown films are presented. Transmittance and reflectance measurements were obtained from an AVASPEC-2048 UV/VIS/NIR spectrophotometer in the wavelength range of 200-900nm. The thickness of the films was obtained by surface profile analysis using a Dektak Veeko-150 stylus surface profiler. The thickness obtained for the films were in the range of 1.0µm to 1.45µm depending on the dip time. Results show that the film exhibited poor transmittance and high reflectance of solar radiation in the Infra-Red (IR) region of the electromagnetic spectrum respectively. A high absorption coefficient in the range of $3.11 \times 10^{6}\ m^{-1}$ to $4.35 \times 10^{6}\ m^{-1}$ was obtained for the film in the Ultra-Violet (UV) region of the electromagnetic spectrum depending on the dip time. Other properties studied include optical conductivity, dielectric function, extinction coefficient and refractive index respectively. Optical studies reveal that this material could be exploited for various purposes which include being used as an absorber material for the construction of solar cells, for the fabrication of optical devices and for the manufacture of highly reflective mirrors commonly found in desktop scanners, photocopy machines, halogen lamps, astronomical telescope and car head lamps. The material was observed to have a direct band gap between 2.05eV and 2.85eV depending on the dip time.

Keywords: Photovoltaic devices, semiconductor thin films, optical properties, dip time, solution growth technique.

1. Introduction

The quest by scientists and researchers over the years for improved technology in the area of solid-state electronics and the construction of photovoltaic devices has led to serious research in the growth and characterization of semiconductor thin films. These semiconductor thin films have proved useful in the fabrication of solar cells, optoelectronic devices, transistors, and so on.

Optical properties of a material can well be defined as those properties exhibited by the material when it interacts with electromagnetic radiation [1]. Optical properties of semiconductor thin films such as transmittance, reflectance, absorbance, refractive index, extinction coefficient, absorption coefficient and dielectric function can be studied for possible determination of the band gap energy of the material in order to determine the transition process of the material thus suggesting possible applications of the film [1]. Several techniques such as chemical bath deposition [2], vacuum evaporation [3-5], spray pyrolysis

[6-7] have previously been used to deposit CuSbS2 thin films. The effect of air annealing on CuSbS2 thin film has also been reported [8].

In this research, efforts were made to deposit thin films of copper-antimony sulphide (CuSbS2) on glass substrate using solution growth technique at different dip time. The optical properties such as transmittance and reflectance were obtained using an AVASPEC-2048 UV/VIS/NIR spectrophotometer in the wavelength range of 200-900nm with an uncoated glass substrate as a reference frame. Other properties such as absorption coefficient, refractive index, extinction coefficient, optical conductivity and dielectric function (real and imaginary parts) were calculated from the transmittance and reflectance values. These properties were then carefully analyzed to suggest possible applications of the film.

2. Experimental Procedure

The bath constituent for the deposition of $CuSbS_2$ consists of 5ml of 0.1M of $CuCl_2$. $2H_2O$, 2ml of triethanolamine (TEA), 5ml of 1.0M of $SbCl_3$, 25ml of 1.0M of $Na_2S_2O_3$ and 13ml of distilled water put in that order in a 50ml beaker. The solution was stirred continuously for 2mins to ensure a homogeneous solution. Four experimental set-ups were made with each containing a clean microscopic glass slide inserted vertically through a synthetic foam cover. The pH of each of the resulting solution was 2.52. The resulting transparent solution became lemon yellow after 15mins and subsequently became brown after 1hr, thus indicating the initiation of a chemical reaction. The deposition process was allowed to proceed at room temperature (~ 300K). Thereafter, the coated glass substrates were removed, rinsed thoroughly with distilled water and allowed to dry in open air under atmospheric pressure. The deposition time was varied at 12hrs interval making the dip time to be 12hrs, 24hrs, 36hrs and 48hrs respectively. The deposited films were labeled according to the dip time: D1 (12hrs), D2 (24hrs), D3 (36hrs) and D4 (48hrs) respectively.

The chemical process involved for the deposition of copper-antimony sulphide thin film is shown below.

$CuCl_2.2H_2O + TEA \rightarrow [Cu(TEA)]2+ + 2Cl- + 2H_2O$

$[Cu(TEA)]^{2+} \rightarrow Cu_2+ + TEA$

$SbCl_3$ dissociates in the acidic medium to form the complex Sb3+ according to the reaction:

$SbCl_3 \rightarrow Sb^{3+} + 3Cl^-$

Sodium thiosulphate dissociates to form the complex according to the reaction:

$Na_2S_2O_3 \rightarrow 2Na + S_2O_3^{2-}$

$S_2O_3^{2-} + H_2O \rightarrow SO_4^{2-} + S^{2-} + 2H^-$

The copper ion, Cu^{2+} then combines with the antimony ion, Sb^{3+} and the sulphide ion, S^{2-} on the glass substrate to form brownish $CuSbS_2$ thin films according to the reaction:

$Cu^{2+} + Sb^{3+} + 2S^{2-} \rightarrow CuSbS_2 \downarrow$

3. Results and Discussion

3.1 Thickness Variation of the $CuSbS_2$ Films

The thickness of the $CuSbS_2$ thin film grown in this research was obtained from surface profile analysis using a Dektak Veeko 150 Stylus Surface Profiler. It was observed that the thickness of the films grown lies in the range of 1.0μm to 1.45μm depending on the deposition time. The thickness of the film increases gradually from 1.0μm to 1.45μm as dip time increases from 12hrs to 48hrs. The thickness variation of as-deposited $CuSbS_2$ thin film with dip time is shown in figure 1.

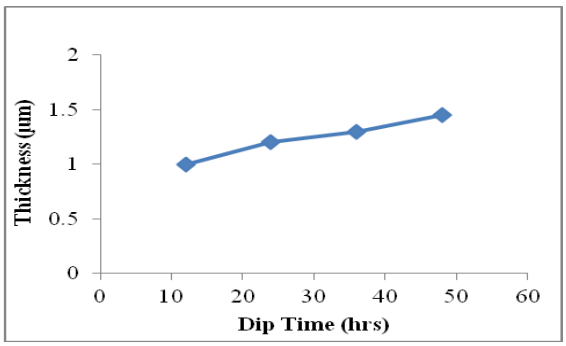

Figure 1: Variation of thickness of as-deposited $CuSbS_2$ thin films with dip time.

Table 1: Thickness variation of CuSbS2 thin films with dip time.

Dip Time (hrs)	Thickness (μm)
12	1.0
24	1.2
36	1.3
48	1.45

The surface profile for all the films grown in this research are displayed in fig. 2 (a-d).

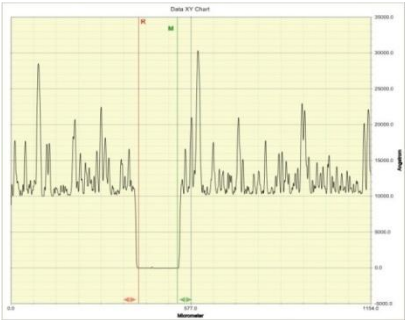

Figure 2a: Surface profile of the as-deposited $CuSbS_2$ thin film obtained at 12hr dip time.

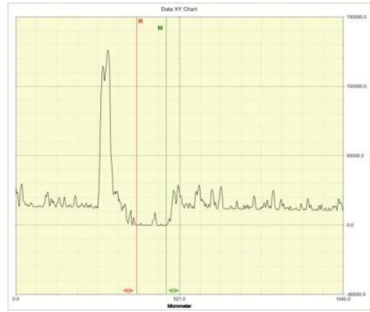

Figure 2b: Surface profile of the as-deposited $CuSbS_2$ thin film obtained at 24hr dip time.

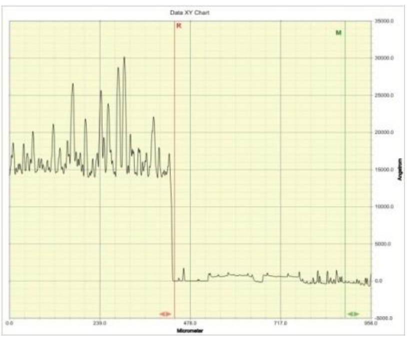

Figure 2c: Surface profile of the as-deposited $CuSbS_2$ thin film obtained at 36hr dip time.

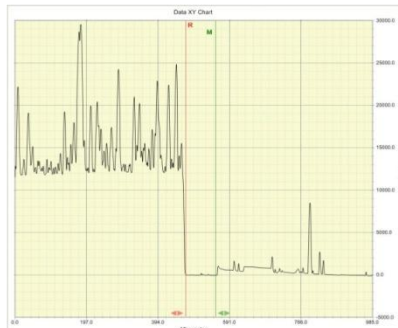

Figure 2d: Surface profile of the as-deposited $CuSbS_2$ thin film obtained at 48hr dip time.

3.2 Optical Studies of The As-Deposited $CuSbS_2$ Thin Films

Figure 3 show the transmittance curves for the as-deposited CuSbS2 thin films grown at room temperature. The transmittance of the films deposited at 12hrs, 24hrs and 36hrs show poor transmission of solar radiation. However, the film deposited at 48hrs dip time exhibited an average transmission of solar radiation of 57.27% in the visible region of the electromagnetic spectrum. The poor transmittance exhibited by these films suggests high absorption of solar radiation which makes the film an important absorber material for the construction of photovoltaic devices such as solar cells.

A close observation of figure 3 show that the film exhibited interference pattern in the IR region of the electromagnetic spectrum. This phenomenon exhibited by the film is as a result of the differences in refractive index of the film and the glass substrate which results in multiple reflections. A similar result has been reported for antimony sulphide thin films [9].

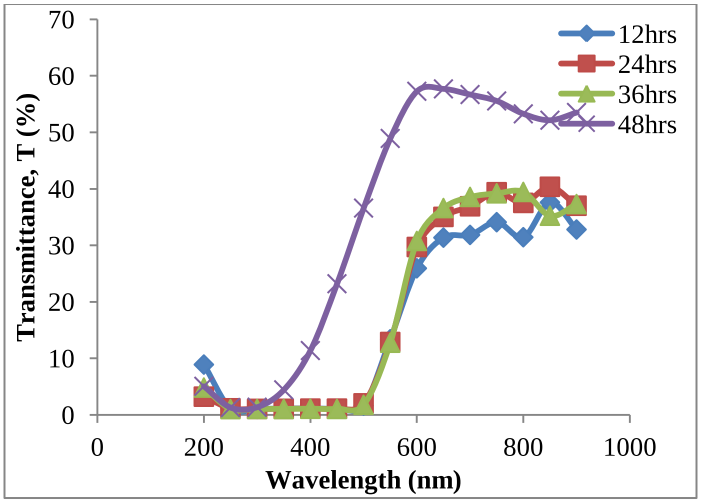

Figure 3: Transmittance spectra for the as-deposited $CuSbS_2$ thin films.

The reflectance spectrum of the film is shown in figure 4.

The reflectance curves of all the films are observed to increase gradually as wavelength increases. It is however pertinent to state that a high reflectance between 60% and 90% is recorded for the thin films in the wavelength range of 700-900nm corresponding to the IR region of the electromagnetic spectrum. This high reflectance exhibited by the material suggests that it could be useful for the manufacture of highly reflective mirrors that are commonly found in desktop scanners, photocopy machines, astronomical telescope, car head lamps and halogen lamps respectively.

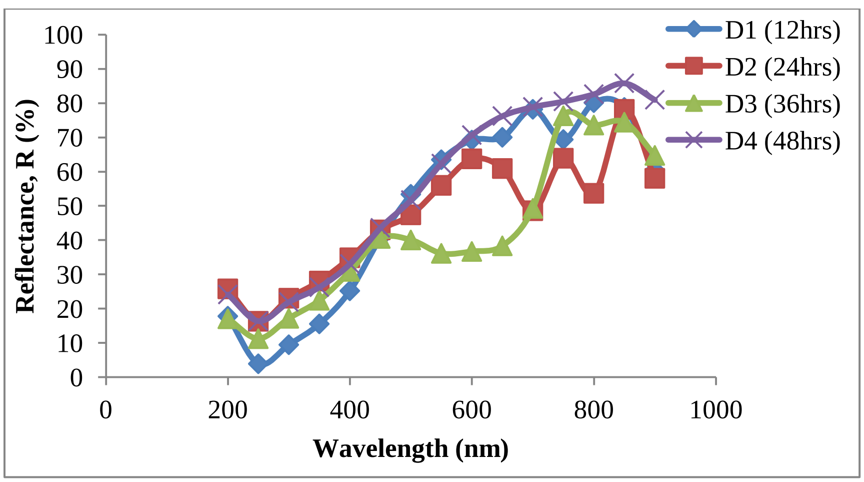

Figure 4: Reflectance spectra for the as-deposited $CuSbS_2$ thin films.

The absorption coefficient of a material is a property of the material which defines the amount of light absorbed by it. Hence, if a material exhibits a high absorption coefficient, it implies that much light (electromagnetic radiation) will be absorbed by the material which in turn, could make the material a potential absorber for the photovoltaic conversion of solar energy.

The absorption coefficient for the film under study was calculated from transmittance and thickness values using the expression:

$$\alpha = - [\ln T] / t$$

where T and t represents transmittance and thickness values of the film respectively.

The plot of absorption coefficient versus wavelength obtained at different dip time is displayed in figure 5.

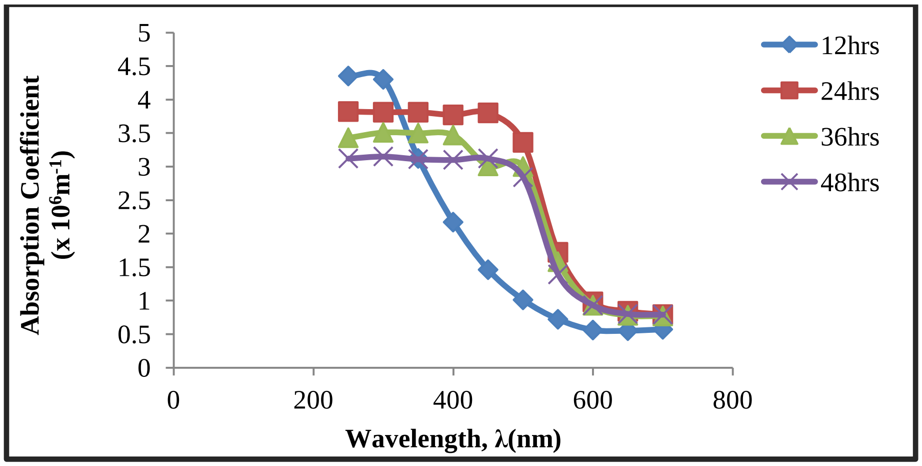

Figure 5: Plot of Absorption Coefficient versus Wavelength for the CuSbS2 thin films deposited at different dip time.

The $CuSbS_2$ thin films deposited at different dip time are observed to have high absorption coefficient in the UV region of the electromagnetic spectrum, the highest being 4.35 x $10^6 m^{-1}$ obtained at 12hr dip time. It is to be noted that the sun is the most important source of UV light. This UV light is the main source of energy needed in photovoltaic devices for the conversion of solar energy to electricity. Since this material is characterized by high absorption coefficient (between 3.11 x $10^6 m^{-1}$ to 4.35 x $10^6 m^{-1}$) in the UV region of the electromagnetic spectrum, it is very certain that the material could be useful as an absorber material for the fabrication of photovoltaic devices.

The extinction coefficient of the copper antimony sulphide thin film was calculated using the equation:

$k = \alpha\lambda/4\pi$, where k is the extinction coefficient, α is absorption coefficient.

The plot of extinction coefficient versus photon energy for the $CuSbS_2$ thin films deposited at different dip time is shown in figure 6. A close observation of fig. 6 reveals that the extinction coefficient of the film deposited at 12hrs dip time decreases gradually to the point where the photon energy is 2.26 and thereafter increases steadily. However, the films deposited at 24hrs, 36hrs and 48hrs dip time show a slightly different trend. The extinction coefficient for the films deposited at 24hrs, 36hrs and 48hrs dip time are seen to increase gradually as the photon energy increases, attains a maximum and thereafter, decreases with photon energy. The highest extinction coefficient of the films is 0.136 obtained at photon energy of 2.76eV at dip time of 24hrs.

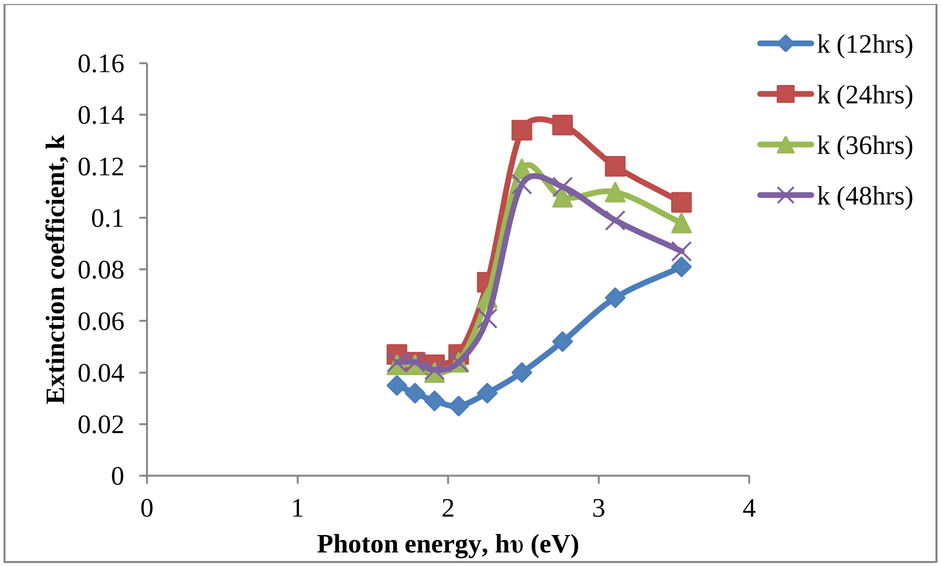

Figure 6: Plot of extinction coefficient versus photon energy for the $CuSbS_2$ thin films deposited at different dip time.

The refractive index of the material under study was calculated from reflectance values using the expression:

$$n = 1 + R^{1/2} / 1 - R^{1/2}$$

where n and R represents refractive index and reflectance respectively.

Figure 7 shows how the refractive index of the material varies with photon energy.

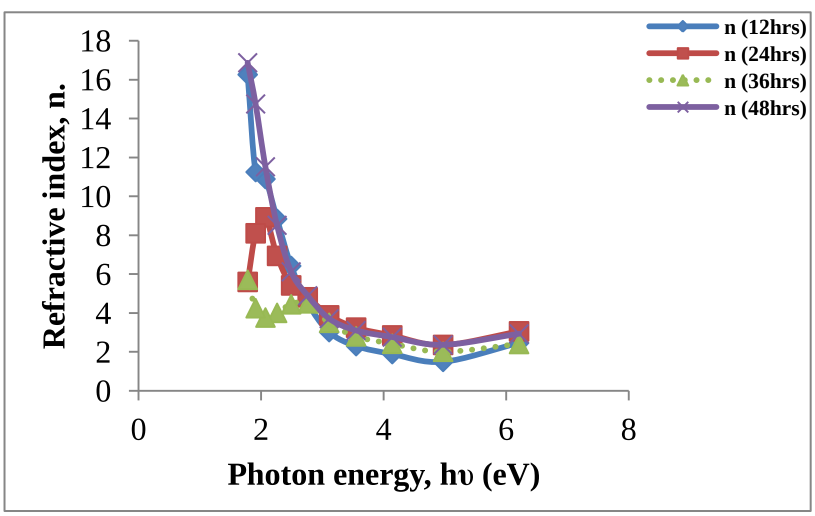

Figure 7: Plot of refractive index versus photon energy for the CuSbS2 thin films deposited at different dip time.

The refractive index of the film is observed to decrease as photon energy increases. The high refractive index exhibited by the film is attributed to the high reflectance observed for the film, since from our equation the refractive index depends squarely on the value of the reflectance.

High refractive index of a material implies a greater critical angle and thus more light (from a broader distribution of incident angles) will be internally reflected by the film. Internal reflection is very important for the transmission of light down an optical fibre. Hence, the $CuSbS_2$ thin film could be useful as a coating material in the internal layers of optical fibres to aid in reflecting much of the incident light internally.

The optical conductivity of a material is the frequency response of the material when it is irradiated by light. The optical conductivity of the film was calculated using the expression:

$$\sigma = \alpha nc/4\pi$$

where α is the absorption coefficient of the material under study, n is the refractive index, c represents the speed of light.

The plot of optical conductivity versus photon energy for the $CuSbS_2$ thin films deposited at different dip time is displayed in fig. 8.

A high optical conductivity within the range of 0.74 x $10^{14}s^{-1}$ to 4.36 x $10^{14}s^{-1}$ is evident from figure 8.

Materials having very high optical conductivity can be useful in the manufacture/fabrication of optical devices. Hence, this material could be useful in this regard.

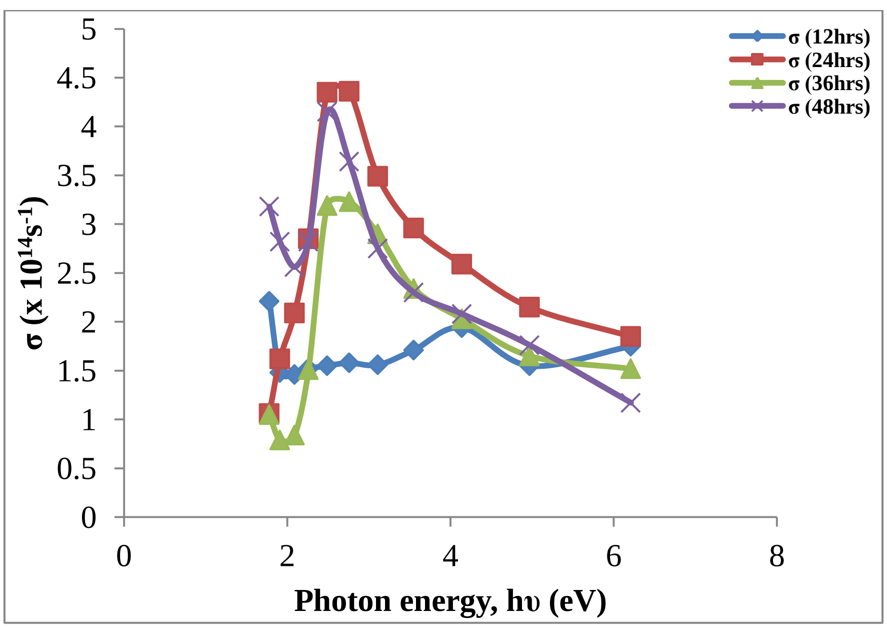

Figure 8: Plot of optical conductivity versus photon energy for the $CuSbS_2$ thin films deposited at different dip time.

From figure 8, it is observed that the optical conductivity of the $CuSbS_2$ thin film has a peak value of 4.36 x $10^{14}s^{-1}$ at photon energy of 2.76 obtained at 24hr dip time.

The dielectric function of a thin film is a complex quantity which consists of both the real and imaginary parts. It is a fundamental intrinsic property of the material. The real part indicates how the speed of light in the material can be slowed down while the imaginary part deals with the absorption of energy by a dielectric from electric field due to dipole motion [1].

The total dielectric function of the $CuSbS_2$ thin film was calculated using the expression:

$$\varepsilon_T = \varepsilon_r + \varepsilon_i$$

where, Ɛr represents the real part and Ɛi represents the imaginary part and they can be calculated using the expressions below:

$$\varepsilon_r = n^2 - k^2$$

$$\varepsilon_i = 2nk,$$

where n and k are the refractive index and extinction coefficient respectively.

The variation of both the real and imaginary parts of the dielectric function with photon energy is displayed in figure 9 (a & b) respectively.

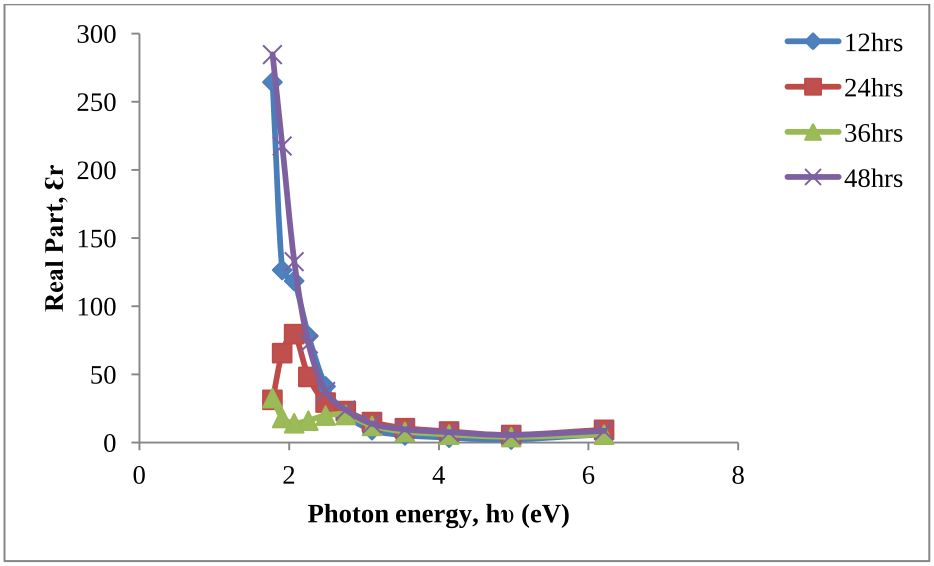

Figure 9a: Real part of dielectric function of CuSbS2 thin film at different dip time versus photon energy.

The real part of the dielectric function of the $CuSbS_2$ thin film is observed to decrease with increase in photon energy for the different dip time. From figure 9a, we observe that the real part of the dielectric function has a peak value of 284.60 obtained at 48hrs dip time.

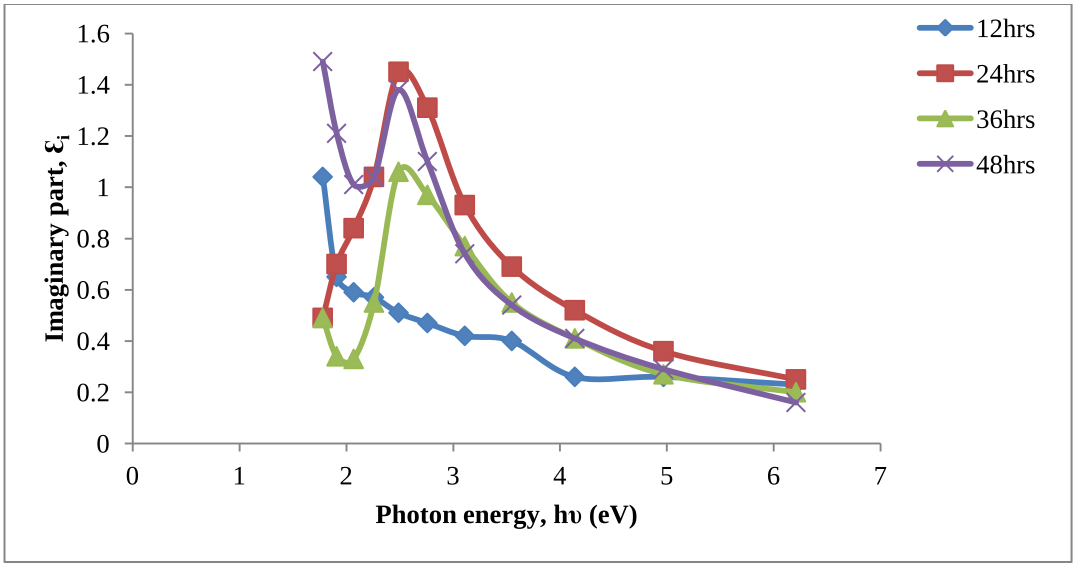

Figure 9b: Imaginary part of dielectric function of $CuSbS_2$ thin film at different dip time versus photon energy.

The imaginary part of the dielectric function of the material under study has values between 0.16 and 1.49, the highest; i.e., 1.49 obtained at 48hr dip time. For the films deposited at 24hr, 36hr and 48hr dip time, the imaginary part of the dielectric function is observed to decrease steadily with increase in photon energy from the point where the photon energy is 2.26eV. However, the film deposited at 12hr dip time show a downward trend as photon energy increases from the point where the photon energy is 1.78eV.

3.3 Band Gap Analysis of The $CuSbS_2$ Thin Film

In calculating the band gap energy, (αhυ)2 versus photon energy, hυ, was plotted for all the film. The linear part of the plot was extrapolated to the point where (αhυ)2 = 0. The direct band gap obtained for $CuSbS_2$ in this research was observed to decrease from 2.85eV to 2.05eV as dip time increases from 12hrs to 48hrs respectively. Ezugwu, et al, (2010) [2] previously reported that the band gap energy for CuSbS2 thin film lie within the range of 1.30-2.30eV. Thus our result is in close range to that earlier reported [2]. Figure 10(a-d) is shown below.

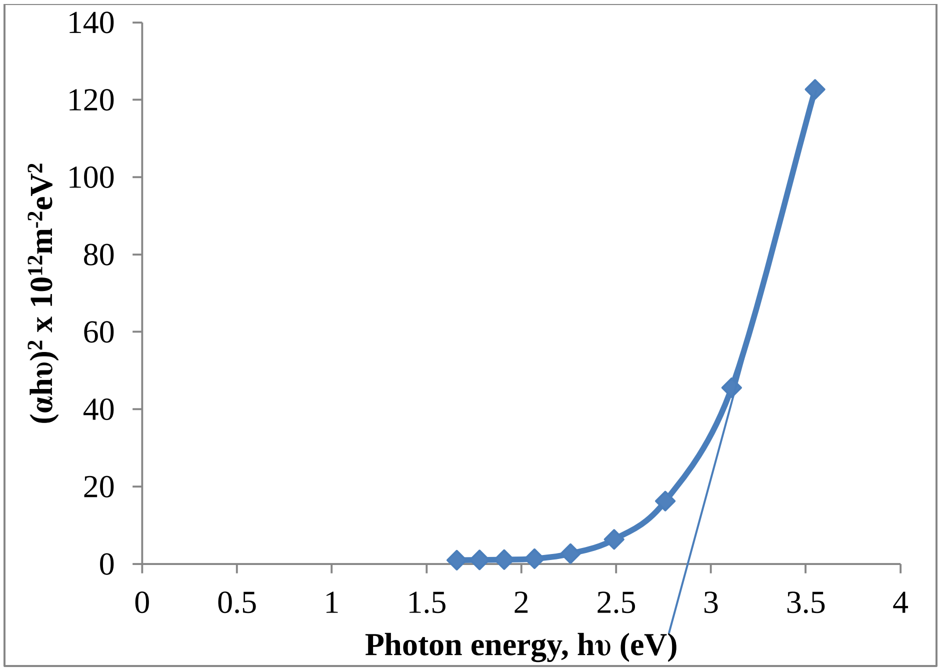

Figure 10a: Plot of (αhυ)2 versus hυ for CuSbS2 thin films at 12hr dip time.

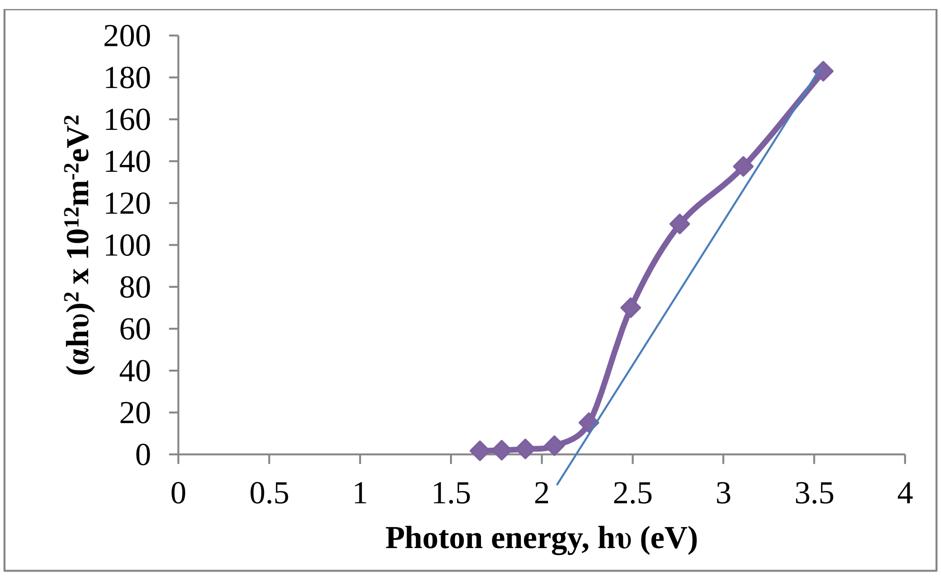

Figure 10b: Plot of (αhυ)2 versus hυ for CuSbS2 thin films at 24hr dip time.

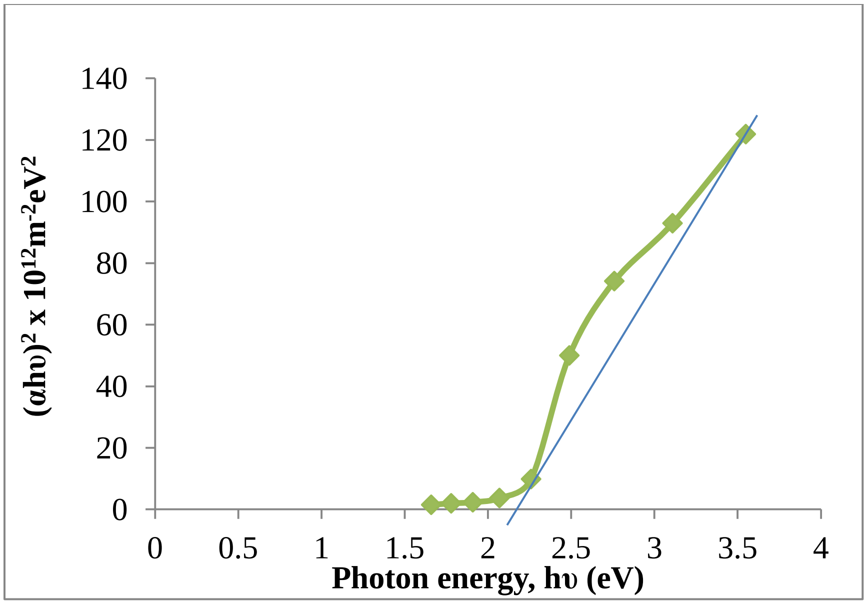

Figure 10c: Plot of $(\alpha h\upsilon)^2$ versus hυ for CuSbS2 thin films at 36hr dip time.

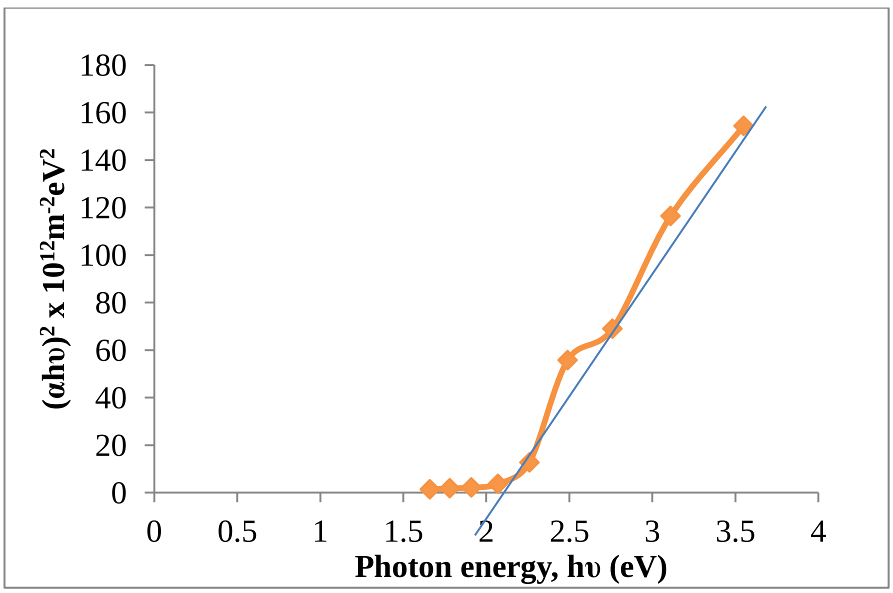

Figure 10d: Plot of $(\alpha h\upsilon)^2$ versus hυ for CuSbS2 thin films at 48hr dip time.

Table 2: Thickness variation of CuSbS2 thin films with dip time.

Dip Time (Hrs)	**Band Gap Energy (eV)**
12	2.85
24	2.30
36	2.10
48	2.05

4. Conclusion

Optical studies conducted on the CuSbS2 thin films show that the films deposited at 12hr, 24hr and 36hr dip time exhibited poor transmittance of solar radiation. However, the films deposited at 48hr dip time exhibited an average transmission of solar radiation of 57.27% in the visible region of the electromagnetic spectrum. High reflectance was also observed for the CuSbS2 thin films in the IR region of the electromagnetic spectrum with the highest reflectance value of 85.79% at the highest dip time (48hrs). The direct band gap for the CuSbS2 thin films obtained in this research lies within the range of 2.05eV to 2.85eV depending on the dip time. Results obtained in this research indicates that the material could be useful for the fabrication of solar cells, optoelectronic devices and for the manufacture of highly reflective mirrors found in desktop scanners, photocopy machines and car head lamps respectively.

Acknowledgment

The author is grateful to all the technical staff of Advanced Physics Laboratory, Sheda Science and Technology Complex (SHESTCO), Federal Capital Territory (FCT), Abuja, Nigeria especially the deputy director, Prof. M.G. Zebaze-Kana for granting me access to the equipment used for characterizing the films.

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