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A Study on The Structural, Optical and Electrical Properties of $CuSbS_2$ Thin Films and Possible Applications

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Abstract: Direct deposition of amorphous copper-antimony sulphide, CuSbS2 thin films on glass substrates using solution growth technique is reported. Structural analysis, morphological studies and elemental composition of the films were investigated by means of x-ray diffraction (XRD) technique, scanning electron microscopy (SEM) and energy-dispersive analysis x-ray spectroscopy (EDAX) respectively. The effect of dip time on each of these properties was examined. The thickness of the films was estimated from surface profile analysis and was found to be in the range of 1.0μm to 1.45μm depending on the dip time. The resistance of the films was obtained from V/I values given by the surface profiler. The films were found to have high resistance value in the range of 2.26 x 108Ω to 2.94 x 108Ω depending on the dip time. The resistivity of the material was obtained by four-point probe method and found to increase from 1.33 x 103Ω-m to 1.48 x 103Ω-m as dip time increases from 12hr to 48hr respectively. Optical characterization was performed on the films using an AVASPEC-2048 UV-VIS-NIR spectrophotometer in the wavelength range of 200-900nm. Optical studies reveal a decrease in the direct band gap of the material from 2.85eV to 2.05eV for the CuSbS2 thin films grown in this research depending on the dip time.

Keywords: Thin films, CuSbS2, band gap, surface profile, solution growth technique, film resistance.

1. Introduction

Since the last decade, there has been much interest in the growth and characterization of binary and ternary semiconductor compounds. This is probably due to the fact that these thin films find applications in photovoltaic devices, optoelectronic and microelectronic devices, anti-reflective (AR) and reflective coatings and so on [1].

The ternary chalcogenide compound, CuSbS2 thin film is considered as one of the important semiconductors with a narrow band gap showing potential applications in various optoelectronic devices such as infrared detectors and solar cells [2]. Several techniques such as chemical bath deposition [3], vacuum evaporation [4-6], spray pyrolysis [7-8] have previously been used to deposit CuSbS2 thin films. The effect of air annealing on CuSbS2 thin films has also been reported [9].

In this research, we report the direct deposition of the ternary compound CuSbS2 on glass substrates using solution growth technique. The structural, morphological and elemental compositions were investigated for possible applications of the CuSbS2 thin films. The resistance of the CuSbS2 thin films grown in this research was also calculated. All the properties of the film stated were carefully analyzed to suggest possible applications of the film.

2. Materials and Methods

The bath constituents for the deposition of CuSbS2 thin film consists of 5ml of 0.1M of copper chloride-dihydrate, CuCl2.2H2O, 2ml of triethanolamine (TEA), 5ml of 1.0M of antimony tri-chloride, SbCl3, 25ml of 1.0M of sodium thiosulphate, Na2S2O3 and 13ml of distilled water put in that order into a 50ml beaker. The solution was stirred continuously for 2mins to ensure a homogeneous solution. Four experimental setups 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). After deposition, the coated glass substrates were removed, rinsed thoroughly with distilled water and allowed to dry in open air. Deposition time was varied at 12hrs interval making the dip time to be 12hrs, 24hrs, 36hrs and 48hrs respectively. The chemical process involved in the deposition of the CuSbS2 thin films is suggested by the author as follows:

$$CuCl2.2H2O + TEA \rightarrow [Cu(TEA)]2+ + 2Cl- + 2H2O$$

$$[Cu(TEA)]2+ \rightarrow Cu2+ + TEA$$

SbCl3 dissociates in the acidic medium to form the complex Sb3+ according to the reaction:

$$SbCl3 \rightarrow Sb3+ + 3Cl-$$

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

$$Na2S2O3 \rightarrow 2Na + S2O32-$$

$$S2O32- + H2O \rightarrow SO42- + S2- + 2H-$$

The copper ion, Cu2+ then combines with the antimony ion, Sb3+ and the sulphide ion, S2- on the glass substrate to form brownish CuSbS2 thin films according to the reaction:

$$Cu2+ + Sb3+ + 2S2- \rightarrow CuSbS2 \downarrow$$

3. Results and Discussion

3.1 Thickness Variation of the $CuSbS_2$ Films

The thickness of the CuSbS2 thin films grown in this research was obtained from surface profile analysis using a Dektak Stylus 7.0 surface profiler. The thickness of the films was found to be in the range of 1.0μm to 1.45μm depending on the dip time as displayed in figure 1.

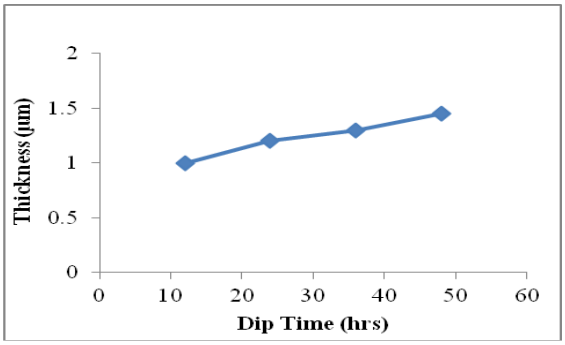

Figure 1: Variation of thickness of as-deposited $CuSbS_2$ thin films with dip time.

The thickness of all the films was estimated from the lower part of the Data XY chart obtained from surface profile analysis. The surface profile for all the films deposited in this research are shown in figure 2 (a,b,c,d).

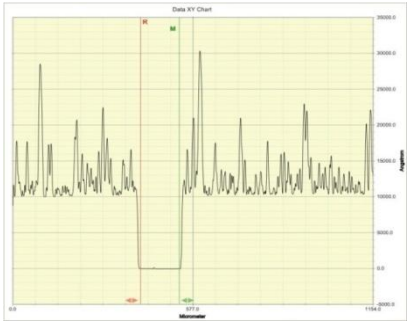

Figure 2a: Surface profile of the as-deposited $CuSbS_2$ thin film obtained at 12hr dip time.

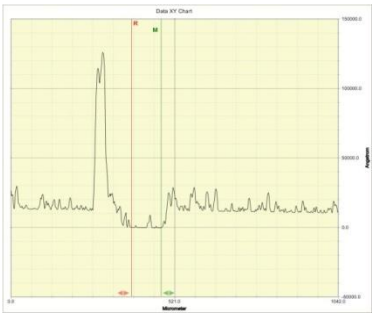

Figure 2b: Surface profile of the as-deposited $CuSbS_2$ thin film obtained at 24hr dip time.

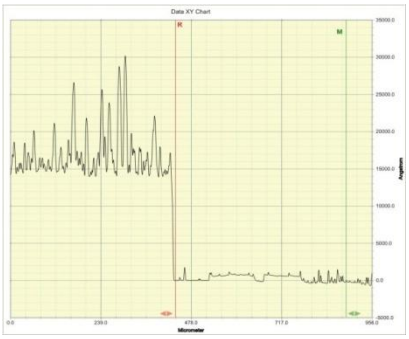

Figure 2c: Surface profile of the as-deposited $CuSbS_2$ thin film obtained at 36hr dip time.

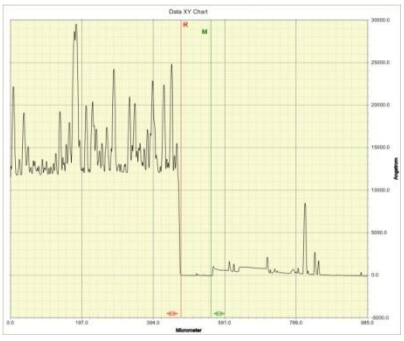

Figure 2d: Surface profile of the as-deposited $CuSbS_2$ thin film obtained at 48hr dip time.

3.2 Structural Characterization

The structural property of the as-deposited CuSbS2 thin films was investigated by means of x-ray diffraction (XRD) technique using an X'PERT PRO diffractometer with CuKα radiation (λ = 1.54060Å). The accelerating voltage and current were respectively 40kV and 30mA with the value of 2θ in the range of 10˚ to 80˚ at a measurement temperature of 25˚C. The CuSbS2 thin films were scanned continuously between 10˚ and 80˚ at a step size of 0.004 and at a time per step of 3.175secs.

Typical diffraction patterns of the CuSbS2 thin films deposited at different dip time (12hrs and 24hrs respectively) are displayed in figure 3 (a & b). The non-existence of sharp diffraction peaks and the presence of broad hump in the XRD patterns of the as-deposited CuSbS2 thin films under study suggest amorphous nature of the films.

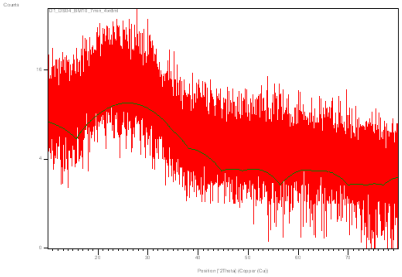

Figure 3a: Typical XRD pattern of as-deposited $CuSbS_2$ thin film deposited at 12hr dip time.

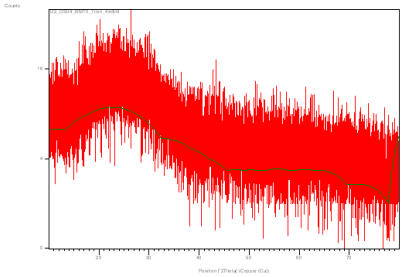

Figure3b: Typical XRD pattern of as-deposited $CuSbS_2$ thin film deposited at 24hr dip time.

3.3 Surface Structure Analysis

The surface micrographs of the films deposited at different dip time were obtained at room temperature by a Carl-Zeiss MA-10 scanning electron microscope at a magnification of 1.00KX.

The surface micrographs of the chemically deposited CuSbS2 thin films for different dip time are displayed in figure 4 (a, b, c).

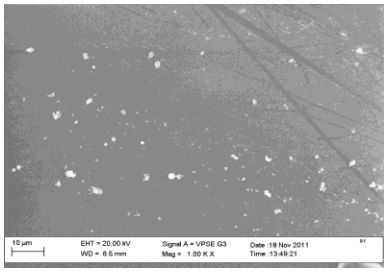

Figure 4a: SEM micrograph of as-deposited CuSbS2 thin film deposited at 12hr dip time.

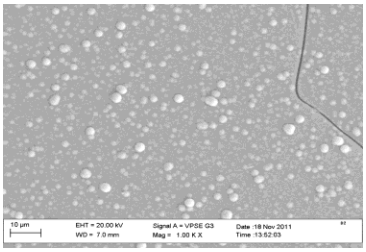

Figure 4b: SEM micrograph of as-deposited CuSbS2 thin film deposited at 24hr dip time.

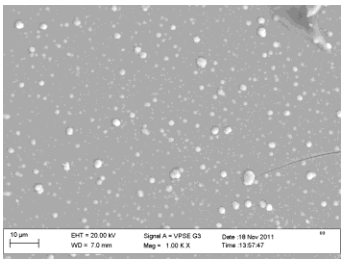

Figure 4c: SEM micrograph of as-deposited CuSbS2 thin film deposited at 36hr dip time.

The SEM image of the $CuSbS_2$ thin films deposited at 12hrs appeared as smooth, dense and homogeneous in nature. The micrograph of the $CuSbS_2$ thin films indicates that the as-deposited film grown at 12hrs dip time is purely amorphous. However, a careful observation of figure 4b and 4c shows that the $CuSbS_2$ particles in the form of well-defined very tiny spheres are distributed irregularly over the surface of the film. The thin films deposited at 24hrs and 36hrs show very poor crystalline nature of the films. Hence the films are amorphous in nature.

3.4 Energy-dispersive analysis x-ray (EDAX) spectrum

The EDAX spectrum of the CuSbS2 thin films deposited in this research is shown in figure 5 (a & b). The presence of Cu, Sb, S and Cl can be observed from the figure. The oxygen peak detected from the EDAX spectrum is unavoidable in any chemically deposited films as previously reported [10]. The presence of Cl in the EDAX spectrum is due to the precursor $SbCl_3$ while the presence of Na is due to the precursor $Na_2S_2O_3$. Other elements present may have come from the glass slide and starting materials used.

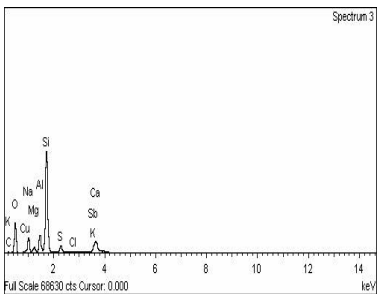

Figure 5a: EDAX spectrum of the as-deposited $CuSbS_2$ thin film deposited at 12hr dip time.

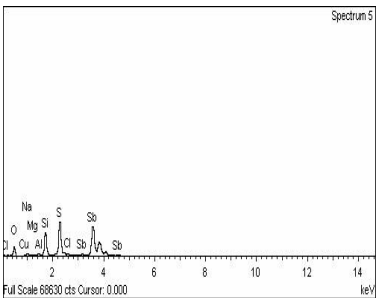

Figure 5b: EDAX spectrum for the as-deposited $CuSbS_2$ thin films deposited at 24hr dip time.

3.5 Electrical Studies

The electrical properties discussed are the resistance, sheet resistance and resistivity of the material. The film resistance R was obtained from V/I values given by the surface profiler, the sheet resistance, Rs was calculated using the expression: Rs = KV/I, where K is a constant and is equal to 4.523 [1]. The resistivity of the material was calculated using the expression: $\rho = Rst$, where t is the thickness of the film.
The values of the film resistance, sheet resistance, resistivity values and thickness of the as deposited copper-antimony sulphide thin films are displayed in table 1.

Photovoltaic devices can be used for space applications. Defects in these devices can arise as a result of high energy particle radiation. This will in turn reduce its quality and functional capacity. Hence the choice of material used for the fabrication of such devices has to have high resistance to radiation.

From our results, we observe that the films grown in this research has very high resistance in the range of 2.26 x 108Ω to 2.94 x 108Ω depending on the dip time. The results obtained in this research indicate that this material can be useful in the fabrication of photovoltaic devices for space applications.

The sheet resistance of this material was also calculated and was found to decrease from 1.33 x 109Ω to 1.02 x 109Ω as dip time increases from 12hr to 48hr respectively.

The resistivity of the material increases gradually from 1.33 x 103Ω-m to 1.48 x 103Ω-m as dip time increases from 12hrs to 48hrs respectively.

Table 1: Some electrical properties of CuSbS2 thin films.

R_s ($\times 10^9\Omega$)	R = V/I ($\times 10^8\Omega$)	Dip Time (Hrs)	Thickness (μm)	ρ ($\times 10^3\Omega$-m)
1.33	2.94	12	1.0	1.33
1.20	2.66	24	1.2	1.44
1.12	2.48	36	1.3	1.46
1.02	2.26	48	1.45	1.48

3.6 Optical Studies

The transmittance (T%) and reflectance (R%) spectra of the films were recorded on an AVASPEC-2048 UV-VIS-NIR spectrophotometer in the wavelength range of 200-900nm with an uncoated glass substrate as a reference frame.

Figure 6 show the transmittance curves for the as-deposited CuSbS2 thin films grown at room temperature. The transmittance curves show an upward trend as dip time increases. It is evident from figure 6 that the samples deposited at 12hr, 24hr and 36hr dip time exhibited poor transmission of solar radiation. However, it is observed that at 48hr dip time, the film show a considerable increase in transmittance of about 57.27% at a wavelength of 650nm.

The differences observed in the transmission of the films could be attributed to difference in thickness and film absorption.

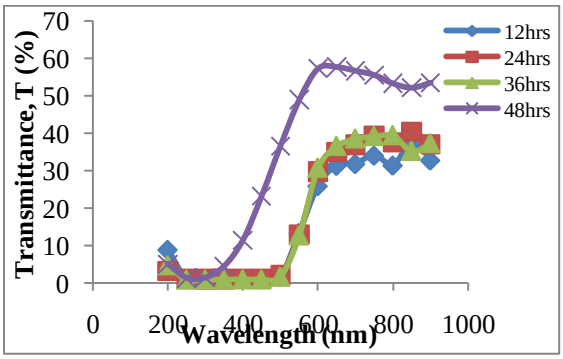

Figure 6: Transmittance curve for the as-deposited $CuSbS_2$ thin film.

A close observation of figure 6 show that the films exhibited interference pattern in the IR region of the electromagnetic spectrum. A similar result has been reported [9]. The interference pattern observed could be attributed to the difference in refractive index of the thin film and the glass substrate used as previously reported [11]. The low transmittance exhibited by this material indicates high absorption of solar radiation. Hence, the material can serve as a potential absorber in devices for photovoltaic conversion of solar energy. The reflectance curve of the film is displayed in figure 7.

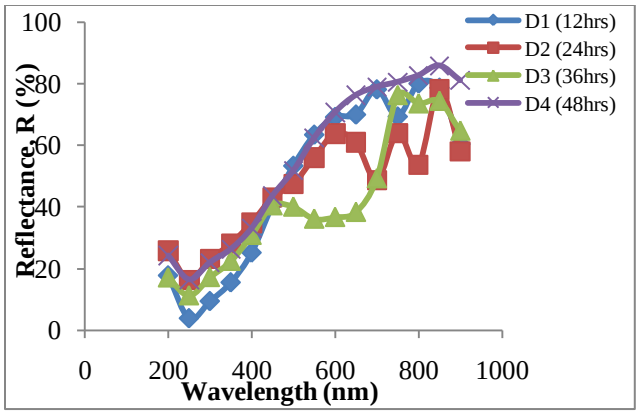

Figure 7: Reflectance curve for the as-deposited CuSbS2 thin film.

The reflectance curves increases with wavelength and also increases as dip time increases.

From figure 7, it is observed that the as-deposited CuSbS2 thin films exhibited high reflectance in the wavelength range of 700-900nm which corresponds to the NIR region of the electromagnetic spectrum with the peak value of 80.11% at a wavelength of 800nm at a dip time of 48hrs. The high reflectance exhibited by this material makes it a potential material for the manufacture of highly reflective mirrors found in desktop scanners, photocopy machines, astronomical telescope, car head lamps and halogen lamps. This material can also be found useful in the coating of the surface of compact disc.

3.7 Band Gap Analysis

The absorption coefficient was calculated from transmittance values using the expression: $\alpha = -[\ln T] / t$,

where, α = Absorption coefficient, T = Transmittance values and t = Thickness of the film. The relationship between absorption coefficient, α, and the incident photon energy, $h\upsilon$, can be expressed as:

$$(\alpha h\upsilon) = M(h\upsilon - Eg)n/2,$$

where M is a constant and n is a number which characterizes the transition process and is theoretically equal to 1 and 4 for direct and indirect transition respectively, Eg is the optical band gap energy of the material.

In calculating the band gap energy, $(\alpha h\upsilon)2$ versus photon energy, $h\upsilon$, was plotted for all the films. The linear part of the plot was extrapolated to the point where $(\alpha h\upsilon)2 = 0$. The direct band gap obtained for $CuSbS_2$ thin films in this research was observed to decrease from 2.85eV to 2.05eV as dip time increases from 12hrs to 48hrs respectively. The decrease in band gap energy of the material is attributed to increase in thickness of the thin films. It has been previously reported that the band gap energy for CuSbS2 thin

film lie within the range of 1.30-2.30eV [3]. Thus our result is in close range to that earlier reported by [3]. Figure 8 (a-d) is shown below.

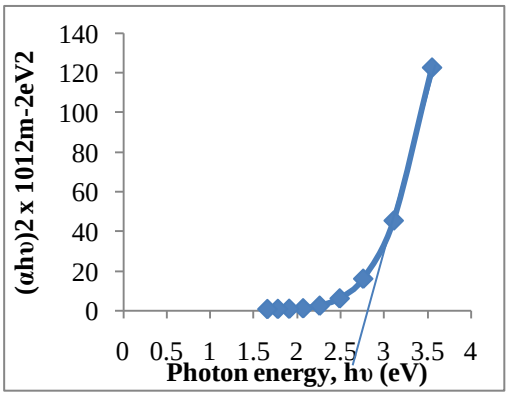

Figure 8a: Band gap energy for the $CuSbS_2$ thin film deposited at 12hr dip time.

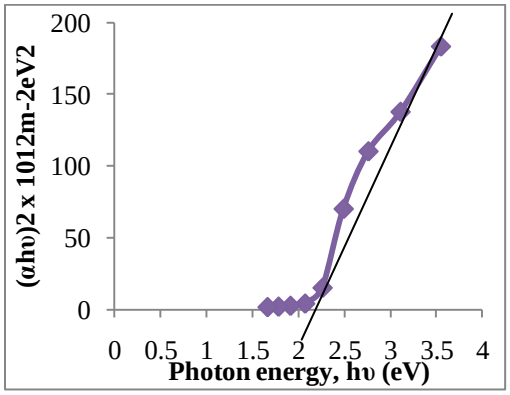

Figure 8b: Band gap energy for the CuSbS2 thin film deposited at 24hr dip time.

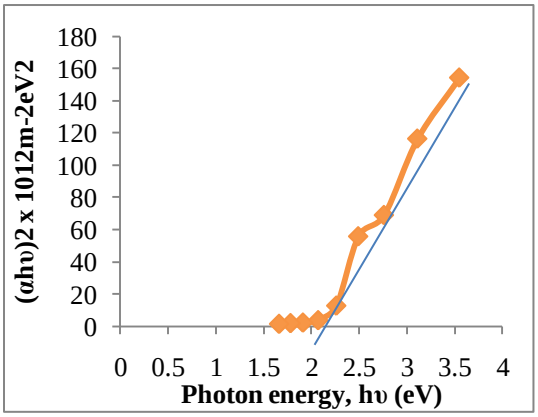

Figure 8d: Band gap energy for the $CuSbS_2$ thin film deposited at 48hr dip time.

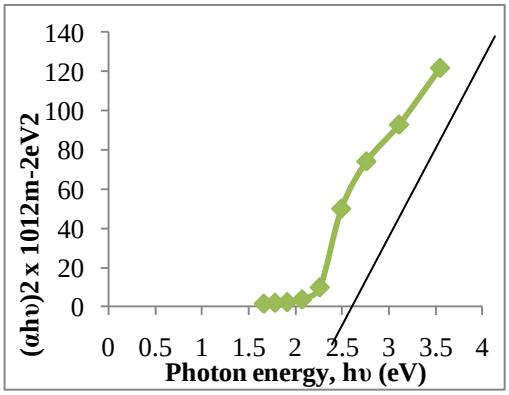

Figure 8c: Band gap energy for the CuSbS2 thin film deposited at 36hr dip time.

4. Conclusion

Copper-antimony sulphide thin films has been successfully deposited on glass substrate using solution growth technique. The reaction bath used for the deposition process contained the following solutions: CuCl2.2H2O, TEA, SbCl3, Na2S2O3 and distilled water. The films obtained in this research have every high resistance values in the range of 2.26 x 108Ω to 2.94 x 108Ω depending on the dip time. XRD and SEM studies confirm that the films deposited at room temperature are amorphous. Optical studies reveal the films exhibited poor transmission and very high reflectance of solar radiation. A direct band gap in the range of 2.05eV to 2.85eV was obtained for the films. The high reflectance exhibited by this material is encouraging for use of this film in the manufacture of highly reflective mirrors commonly found in desktop scanners, photocopy machines, astronomical telescope, car head lamps and halogen lamps and also for coating the surface of compact discs and DVDs. The low transmittance exhibited by this material suggests high absorption of solar radiation, which makes the material a potential absorber for the construction of solar cells. In order to improve the quality of the film and to suggest possible applications of this material, further research by scientists need to be conducted through a better understanding and adequate control of the deposition parameters.

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