Scientia Africana, Vol. 14 (No.1), June 2015. Pp 75-84
 ISSN 1118 – 1931

OPTOELECTRONIC CHARACTERIZATIONS OF VACUUM EVAPORATED Cu_2SnS_3 THIN FILMS FOR DEVICE APPLICATION.

J. A. Amusan[1], S. O. Azi[2], D. A. Abubakar[3] and, M. G. Zebaze Kana[4]

[1] *Department of Physics, University of Port Harcourt, P. M. B. 5323, East-West Road, Choba, Port Harcourt, Rivers State, Nigeria*
[2] *Department of Physics, University of Benin, P. M. B. 1154, Benin City, Edo State, Nigeria.*
[3] *Department of Physics, Modibbo Adama University of Technology, Yola, Nigeria*
[4] *Department of Physics, Physics Advanced Laboratory, SHESTCO, Abuja, Nigeria.*

[1] *Email : amusanabiodun@yahoo.com*
Tel. : +2348035622473
[2] *Email : ogochukwuazi@uniben.edu*
Tel. : +2348032395000
[3] *E-mail : bukar64@yahoo.com*
Tel. : +2348065326308
[4] *E-mail : zebaze@shestco.org*
Tel : +2347062128098

Received: 15-04-15
Accepted:04-05-15

ABSTRACT

The search for new materials suitable for application in photovoltaic cell necessitates the growth of non-toxic, cheap earthly abundant, ternary compound of Cu_2SnS_3 thin film. Thin films of Cu_2SnS_3 semiconductors were prepared by thermal evaporation and sulphurization techniques in vacuum. The bi-layer of Cu-Sn precursors was deposited on cleaned microscopic glass substrate at controlled thickness of 100nm, 500nm and 1000nm and at different substrate temperatures of 27^0, 100^0C and 200^0C.The bi-layer of Cu-Sn was sulphurized in a custom-built reactor for 1hour at 400^0C to form Cu_2SnS_3 ternary films. The structure and morphology characteristics of Cu_2SnS_3 ternary film were investigated by X-Ray Diffraction and Scanning Electron Microscope. Four point probe and semiconductor characterization system were used to determine the electrical properties of the deposited Cu_2SnS_3 ternary films. UV –Vis Spectrophotometer measured the optical characteristics of the Cu_2SnS_3 ternary film. The film samples deposited at 27^0C and at thickness of 100nm and 500nm yielded Cu_2SnS_3 ternary film .The grain size of deposited Cu_2SnS_3 ternary film is about 1µm and the films were rough (Average Roughness, Ra = 3133.50nm and Root Mean Square, Rq = 3942.60nm). The elemental composition of the film as determined by Energy Dispersive X-Ray System (EDS) are Cu (24.89%), Sn (15.82%), S (16.29%) and artefacts such as Na, Si, Mg and O.The surface profiler shows that the deposited Cu_2SnS_3films are rough. Monoclinic, Cu_2SnS_3 [-1 3 1] at peak $2\theta = 28.4^0$ and Anorthic Cu_2SnS_3 [-2 0 10] at peak $2\theta = 47.25^0$ were identified. The electrical resistivity, ρ, of the Cu_2SnS_3 ternary film is 2.55×10^{-3} Ω-cm. The Energy band gap, Eg, of the deposited Cu_2SnS_3 film is 1.65eV, Refractive Index, n is 1.14, Extinction Coefficient, K,is 5.27×10^9 and Optical Conductivity , σ_0 is 6.74708E+16 $\Omega^{-1}cm^{-1}$. These results clearly show good potentials of deposited Cu_2SnS_3 ternary film as an abundant, cheap, non-toxic absorber layer of photovoltaic solar cell.

Key words: Vacuum Evaporation, Sulphurization, Energy band gap, Absorber layer, solar cells.

INTRODUCTION

Interest on the preparation and study of physical properties of ternary chalcogenide compounds for their possible applications in optoelectronic devices, solar cells, infra-red detectors and light emitting diodes, has been increasing in the recent years (Anuar et al., 2009).

Recent interest in thin film photovoltaics is primarily due to improvements in conversion efficiency of cells, and effective lowering of the manufacturing costs compared to expensive crystalline and poly crystalline silicon technology. Attempts have been made for searching non-toxic, cost-effective new materials which are tailor-made for that purpose (Gosh et al., 2008).

The solar cell made of polycrystalline thin film is one of the most promising low cost candidates for terrestrial photovoltaic application (Anuar et al., 2008).

Thin film is a layer of material, typically a few micrometer (µm = 10^6m) or less in thickness, deposited on glass, stainless, steel, ceramic or other compatible substrate materials (Patel, 1999).

There are many techniques for preparing thin films. These include Thermal evaporation (Miles et al, 2009) , Chemical bath deposition (Anuar et al, 2009) , Electro deposition (Anuar et al., 2009), Vacuum evaporation (Gosh et al., 2008), Photochemical (Kobayashi et al., 2003), Plasma-enhanced chemical vapour deposition (Ali et al., 2006), metal-organic chemical vapour deposition (Berrigan et al., 1998), closed-spaced sublimation (Armstrong et al., 2002), molecular beam epitaxy (Gautier et al., 1998), spray pyrolisis (Oja et al., 2005) and sputter deposition (Gupta et al., 2006).

Most recently, powder of Cu_2SnS_3 thin film is synthesized from metal salts using different sulphur sources (Tiwari et al., 2011), Cu_2SnS_3 thin films obtained by direct-coating from single metal-organic precursor solution (Tiwari et al., 2013), Cu_2SnS_3 and Cu_3SnS_4 thin films by successive ionic layer adsorption and reaction (Guan et al., 2013).

The requirements from materials for suitability as optoelectronic device are high optical transparent, low dark electrical resistivity, high photoconductivity and better crystallinity (Gosh et al., 2008).

A thin film of energy gap, $1.0 \leq Eg \leq 1.5$ is usually considered suitable as absorber layer for solar cells. Energy gap that is a little above or below this range can also be considered because further optimisation of deposition conditions can yield the range to suit the purpose.

A deposited film of large grain size encourages high charge mobility and less resistivity (Kallaf et al., 2008).

In this work, preparation of non-toxic, abundant, cheap Cu_2SnS_3 thin film by evaporation in vacuum and sulphurization methods is reported. The structural, optical and electrical properties of the deposited films were investigated. Also, suitable device application of the deposited Cu_2SnS_3 thin films is proposed.

MATERIALS AND METHODS

Elemental Cu and Sn of high purity (99.9%) as precursor were sequentially evaporated on previously cleaned microscopic glass substrate in the vacuum. The evaporations were carried out in oil pumped vacuum system operated in the order of 10^{-5} to10^{-6} Torr range of vacuum pressures. Both the substrate and the source material were heated using resistive elements with a shutter incorporated to control the deposition time. The depositions were done at different substrate temperatures of 27^0C,

Scientia Africana, Vol. 14 (No.1), June 2015. Pp 75-84
© College of Natural and Applied Sciences, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

100^0C and 200^0C and at various thicknesses of 100nm, 500nm and 1000nm.The employed thermal evaporation model is Edwards FL 400 Auto 306 system.

The deposited bi-layer of Cu-Sn thin films was further sulphurized (Agrawal et al., 2008) in a custom-built reactor for 1hour at 400^0C (Figure1).

The structural characteristics of the deposited Cu_2SnS_3 thin films were studied from micrographs produced by Scanning Electron microscope (ZEISS EVO/MA 10), Surface Profilometer (DEKTAK 150) and X-Ray Diffractometer (PAN analytical X-Pert pro).

The Scanning Electron Microscope (SEM) with embedded Energy Dispersive X-Ray System (EDS) was used to determine the morphology and composition of the films. The surface profiler was used to determine the thickness and roughness of the deposited Cu_2SnS_3 thin film. Spectra pattern from X-Ray Diffractometer (XRD) indicates the film structure, phases and lattices. The XRD with CuKα radiation source (λ_1 = 1.54060A^0, λ_2 = 1.5444A^0) and CuKβ (λ_F = 1.39225A^0) was employed. The sample films were mounted at 4^0 and scanned from 10^0 to 80^0 in steps of 0.05^0.

The optical properties of the deposited Cu_2SnS_3 thin films such as transmittance, reflectance and absorbance versus wavelength were used to determine the energy band gap, refractive index, extinction coefficient and optical conductivity of the film using Avantes Ava Spec. 2048 Fibre optic UV-Vis Spectrophotometer.

The electrical properties such as I - V characteristics, resistivity, and conductivity were determined using Four point probe and Semiconductor Characterization System (Keithley 4200).

The obtained results were compared with standard values for its suitability in device applications.

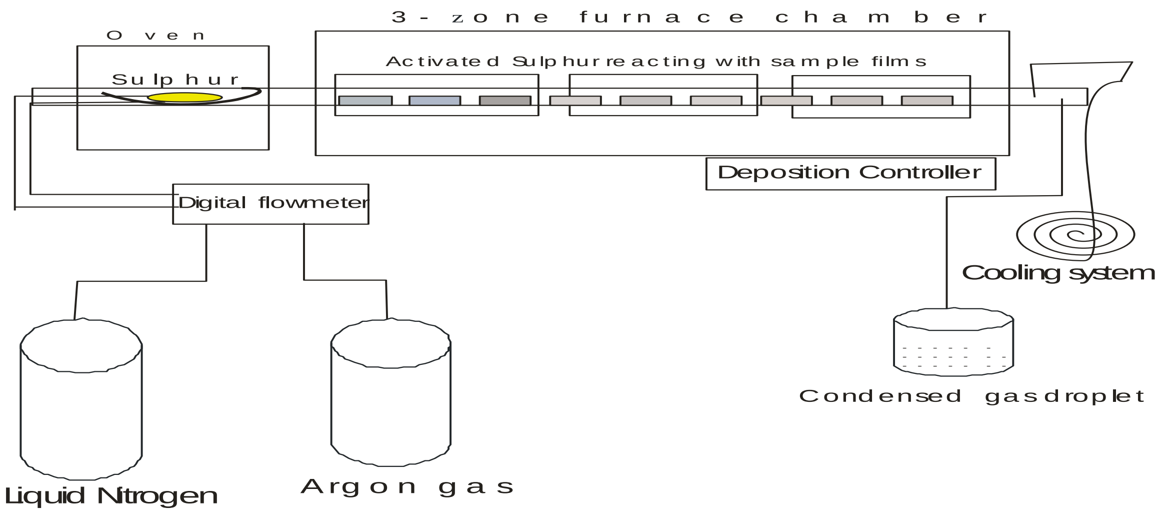

Figure1: Schematic diagram of sulphurization setup.

RESULTS

Ternary films of Cu_2SnS_3 were evident on the microscopic glass substrates. The SEM study revealed that the deposited Cu_2SnS_3 thin films were uniformly spread on and adhered firmly to the microscopic glass substrates. The films were characterized with large grain sizes of about 1µm (Figures 2and 3).

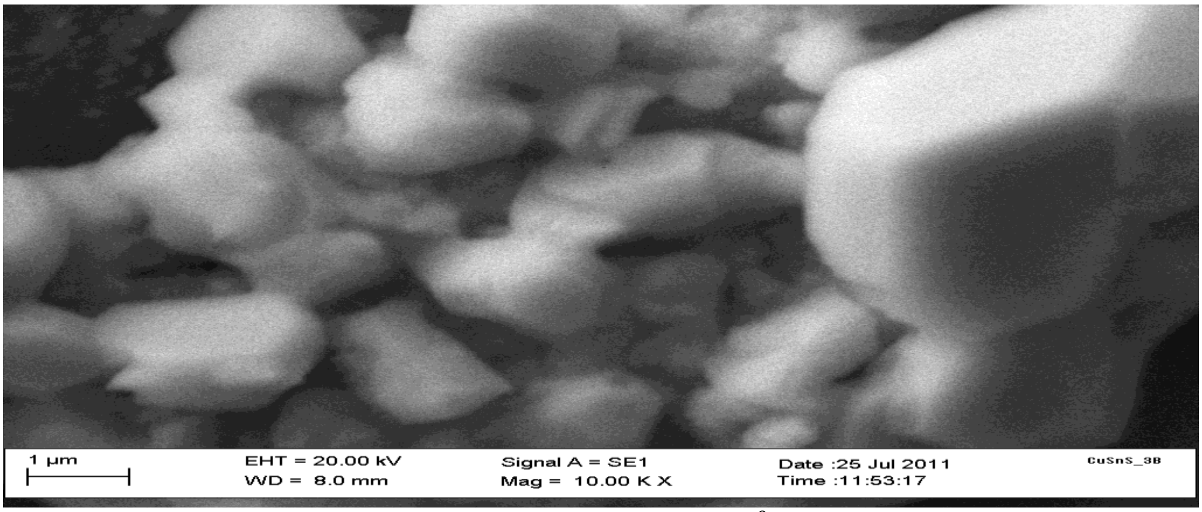

Figure 2: Micrograph of Cu_2SnS_3 thin films deposited at 27^0C at controlled thickness 1000nm

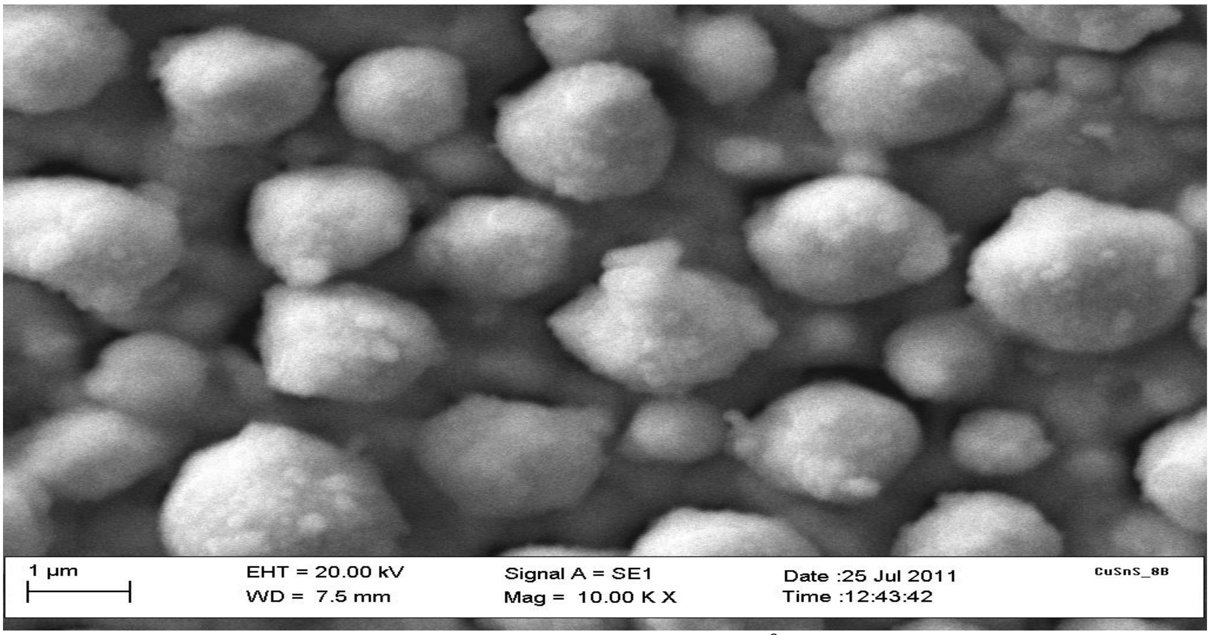

Figure 3: Micrograph of Cu_2SnS_3thin films deposited at 200^0C at controlled thickness 500nm.

The Energy dispersive X-Ray System (EDS) identified the constituent elements of Cu_2SnS_3 thin films and their weight percentage as Cu(24.89%), Sn (15.82%), S (16.29%) with glass substrate's constituents such as Si, Mg, O and Na (Figure 4).

Scientia Africana, Vol. 14 (No.1), June 2015. Pp 75-84
© College of Natural and Applied Sciences, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

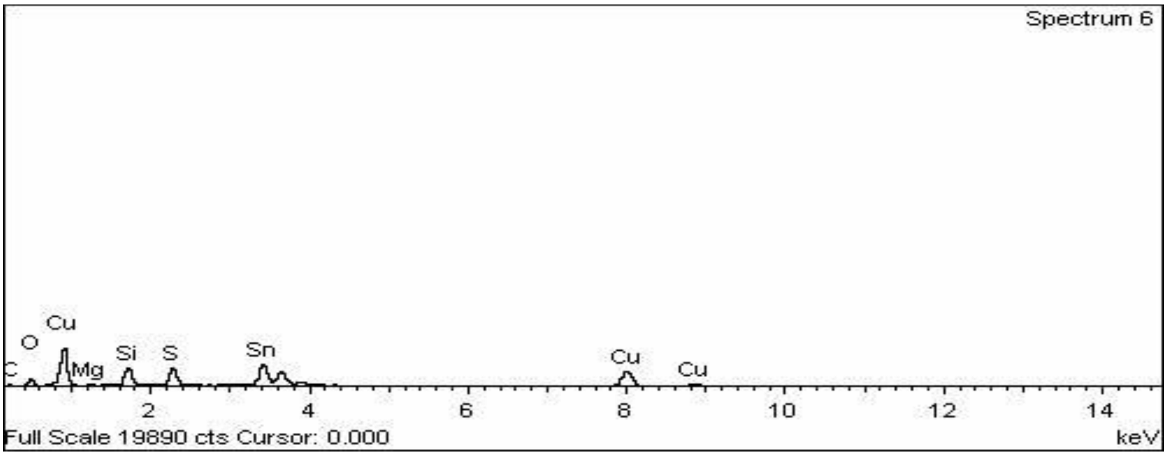

Figure 4 : EDS spectra of Cu_2SnS_3 thin film.

The spectra from the XRD pattern revealed Mohite Syn, Monoclinic Cu_2SnS_3 [-1 3 1], lattice d = 3.139 at peak $2\Theta = 28.4^0$ (Figure 5), and Mohite Syn, Anorthic Cu_2SnS_3[-2 0 10], lattice d = 1.922 at peak $2\Theta = 47.25^0$ (Figure 6).

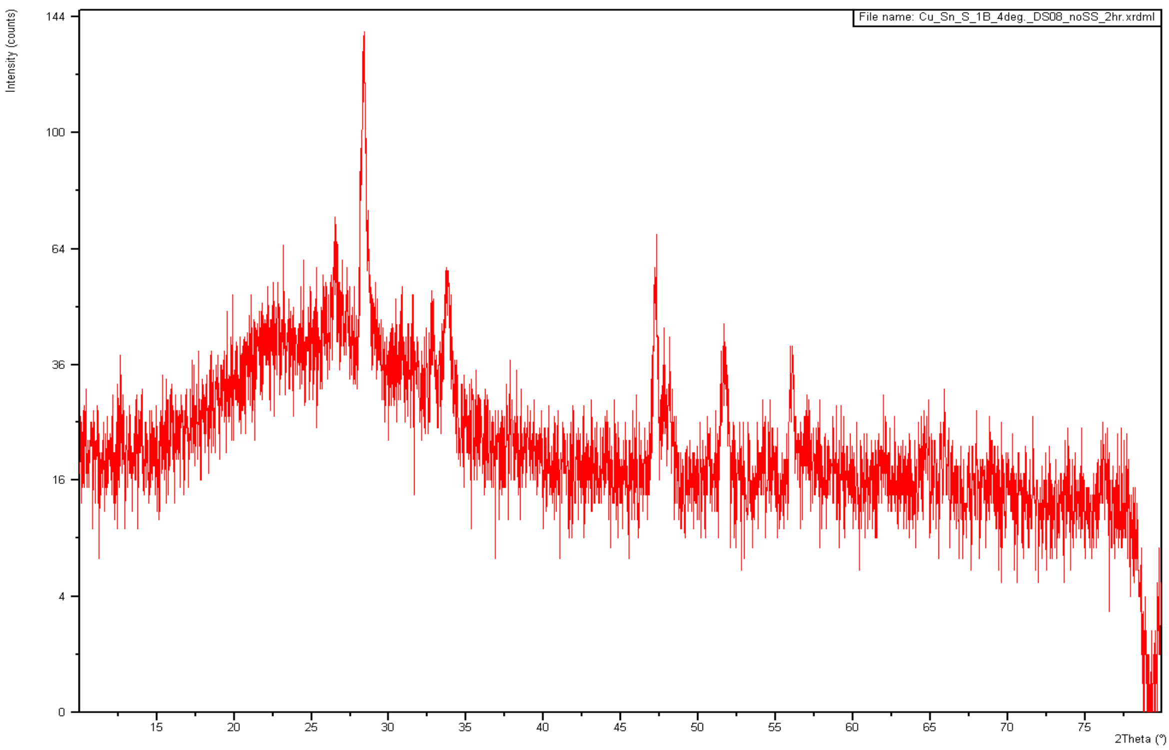

Figure 5: XRD Spectra of deposited Monoclinic C_2SnS_3 thin film.

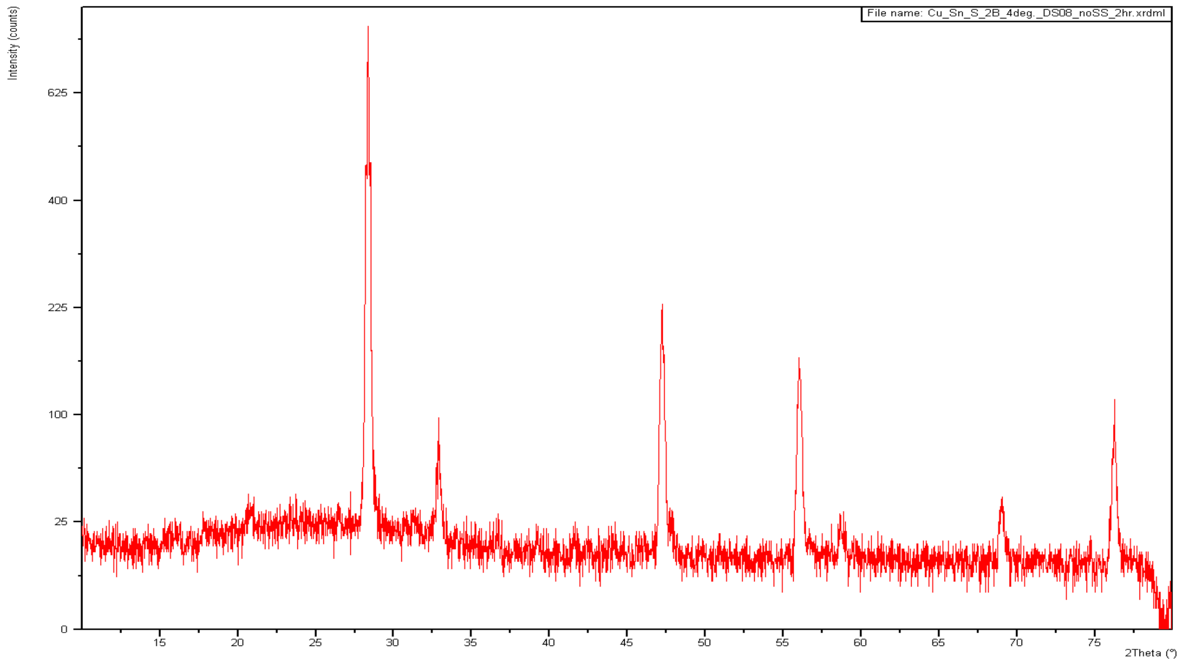

Figure 6: XRD Spectra of deposited Anorthic C_2SnS_3 thin film.

The UV-Visible spectrophotometer in the wavelength range of 200nm – 950nm produced the transmittance and reflectance data and characteristic curves. The transmittance versus wavelength characteristics was consequently used to determine the Energy band gap, Refractive Index, Extinction coefficient and Optical conductivity of the films.

The optical absorption coefficient, α , of the Cu_2SnS_3 thin film was determined from the relation:

$$\alpha = -\frac{1}{t}\ln\sqrt{\frac{(1-R)^4 + 4T^2R^2 - (1-R)^2}{2T^2R^2}} \qquad (1)$$

where:

t = thickness of the film.

R = Reflectance value.

T = Transmittance value

The optical absorption coefficient, α , of the Cu_2SnS_3 ternary film was in the order of 10^4 cm^{-1}.

For direct energy band gap semiconductor, the optical energy band gap is derived from the relation:

$$\alpha = \frac{A}{hv}(hv - E_g)^{\frac{1}{2}} \qquad (2)$$

This means that a plot $(\alpha hv)^2$ versus *hv* should be a straight line with an intercept on the *hv* axis equal to Eg(Figure 7). The energy band gap, Eg , of deposited Cu_2SnS_3 thin film is ***1.65eV.***

The refractive index was determined from the relation:

$$n = \frac{(1+R)^{\frac{1}{2}}}{(1-R)^{\frac{1}{2}}} \qquad (3)$$

The obtained refractive index,*n*, of Cu_2SnS_3 thin film is ***1.14.***

Scientia Africana, Vol. 14 (No.1), June 2015. Pp 75-84
© College of Natural and Applied Sciences, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

The Extinction coefficient, K was determined from the relation:

$$K = \frac{\alpha\lambda}{4\Pi} \quad (4)$$

where:

α is the absorbance coefficient.

λ is the wavelength.

The obtained Extinction coefficient, K, is $\boldsymbol{5.27x10^9}$.

The Optical conductivity, σ_0 , of the film was determined from the relation:

$$\sigma_0 = \frac{\alpha nc}{4\Pi} \quad (5)$$

where c is the speed of light.

The Optical conductivity, σ_0 of the deposited Cu_2SnS_3 thin film is $\boldsymbol{6.74708E+16\Omega^{-1}cm^{-1}}$.

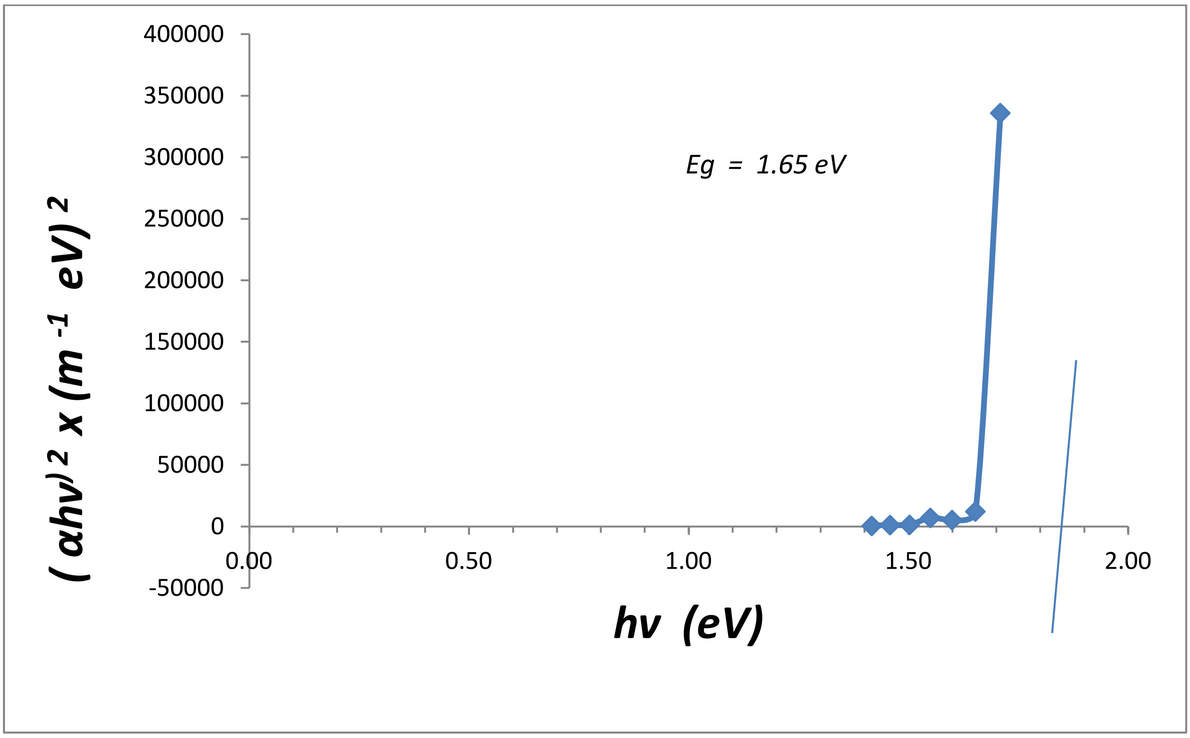

Figure 7: Plot of $(\alpha hv)^2$ versus hv for Cu_2SnS_3 thin film deposited at 27^0C with thickness 100nm.

The Semiconductor Characterization System (SCS) revealed that the cross-planar I – V characteristic curves of C_2SnS_3thin film were non – Ohmic (Figure 8) while the inter – planar I – V characteristic curves were Ohmic (Figure 9). The electrical resistivity, ρ, of deposited C_2SnS_3thin film from Four point probe is $\boldsymbol{2.55 \times 10^{-3}\ \Omega\text{-cm}}$.

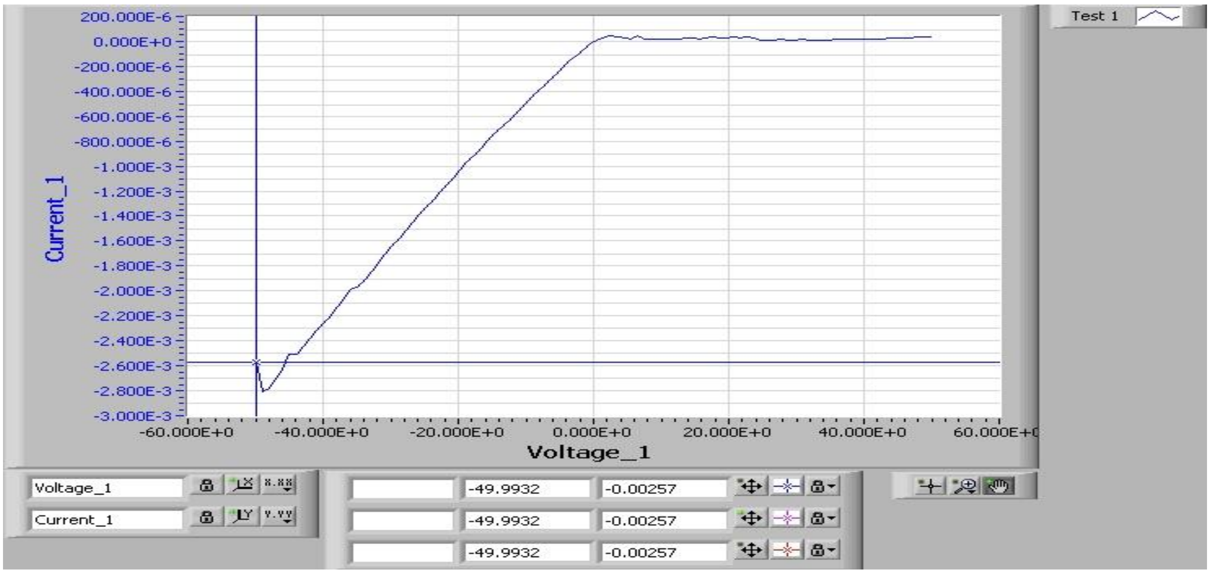

Figure 8 : Cross – planar I-V characteristic curve of deposited Cu_2SnS_3 thin film.

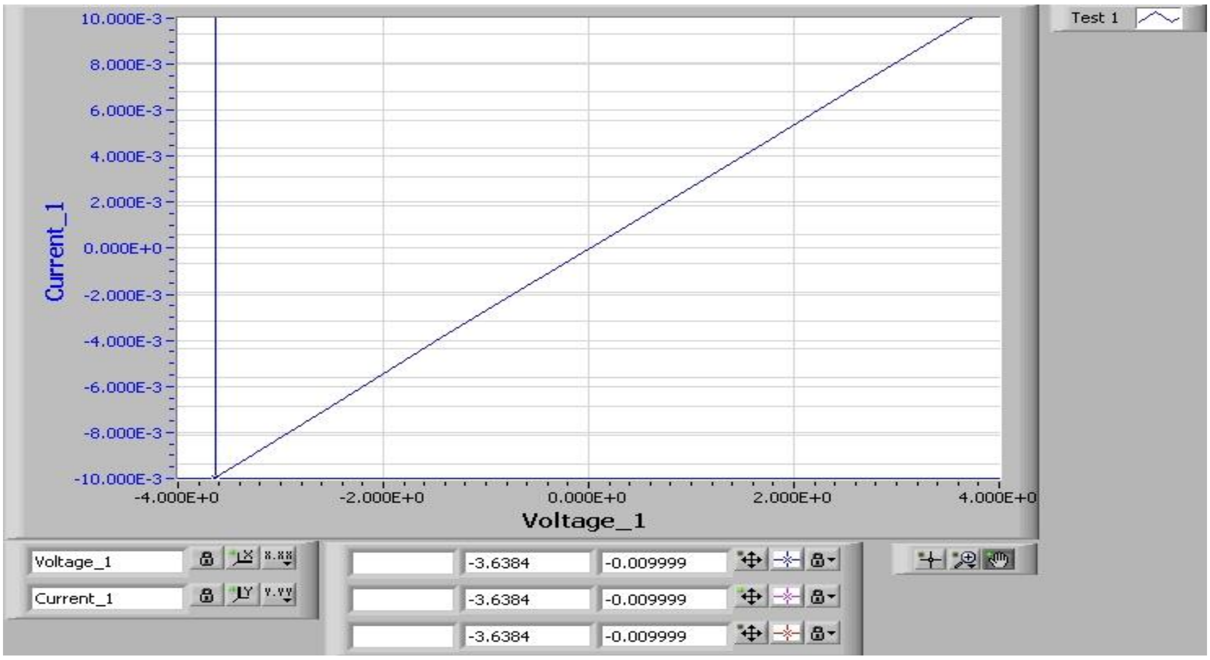

Figure 9 : Inter – planar I - V characteristic curve of deposited Cu_2SnS_3 thin film.

DISCUSSION

Low cost, non-toxic Cu_2SnS_3 thin films at controlled thickness and substrate temperatures have been successively evaporated in vacuum on cleaned microscopic glass substrate. The depositions were uniformly spread and adhered well on the glass substrates.

The SEM results showed grain size of 1µm. The Surface Profilometer showed rough ternary Cu_2SnS_3 thin film. The EDS produced elemental composition of Cu (24.89%), Sn (15.82%), S (16.29%) with glass substrate constituents such as Si, Mg, O and Na. The X-Ray Diffraction pattern yielded Monoclinic, Cu_2SnS_3 [-1 3 1] at

Scientia Africana, Vol. 14 (No.1), June 2015. Pp 75-84
© College of Natural and Applied Sciences, University of Port Harcourt, Printed in Nigeria *ISSN 1118 – 1931*

peak 2ϴ = 28.4^0 and Anorthic Cu_2SnS_3 [-2 0 10] at peak 2ϴ = 47.25^0.

The coefficient of absorbance is in the order of ***10^4** cm^{-1}*, the optical energy band gap is ***1.65eV***, Refractive Index is ***1.14***, Extinction Coefficient is ***$5.27x10^9$*** and optical conductivity is ***6.74708 E+16 $\Omega^{-1}cm^{-1}$.***

The I –V characteristic curve of Cu_2SnS_3 ternary thin film is non-ohmic and the electrical resistivity, ρ, of deposited C_2SnS_3thin film is ***2.55×10^{-3} Ω-cm.***

The study revealed that Cu_2SnS_3 ternary thin film has good potentials as promising absorber layer of solar cell that is cheap, abundant, non- toxic and environmental friendly.

The authors express their profound gratitudes to the Department of Physics, Physics Advanced Laboratory, SHESTCO, Abuja, Nigeria for making available the advanced laboratory facilities used for this study.

REFERENCES

Agrawal Karan, Jin Micheal H. C., Sundaramoorthy, R. (2008): *Thermally Activated Sulfurization of In-Cu bi-layers for $CuInS_2$ Solar cells,* Published thesis in Photovoltaic Specialists Conference (PVSC'08), 33rd IEEE, E-ISBN 978 – 1- 4244 – 1641 – 7, Print ISBN :978-1-4244-1540-0 ; pages 1-5. DOI: 10.1109/PVSC.2008.4922547.

Ali, A. M, Inokuma T., Hasegawa, S. (2006): *Structural and Photo-luminescence properties of nano-crystalline silicon films deposited at low temperature by plasma-enhanced chemical vapour deposition,* Applied Surface Science, Vol. 253, No.3, pages 1198 - 1204.

Anuar Kassim, Tan Wee Tee, Atan Mohd. Sharif, Dzulkelfly Kuang Abdullah, M.D. Jelas Haron, Ho Soon Min and Nagalingam Saravanan (2009): *Influence of Bath Temperature and PH value on properties of chemically deposited C_4SnS_4 thin films,* Journal of Chilean Society, Vol. 54, Number 3, Pages 256 – 259.

Anuar, K., Ho, S.M., Tan, W.T., Atan, S., Kuang, Z., Haron, M. J. and Saravanan, N. (2008): *Effects of Bath temperature on the Electrodeposition of Cu_4SnS_4 Thin Films*, Journal of Applied Sciences Research, Vol. 4, No. 12, pages 1701 – 1707.

Armstrong, S., Datta, P. K., Miles, R.W. (2002): *Properties of Zinc Sulphur Selenide Deposited Using a Close-Spaced Sublimation Method,* Thin Solid Films, Vol. 403 – 404, pages 126 – 129.

Berrigan, R. A., Maung, N., Iruine, S.J.C, Cole-Hamilton, D.J., Ellis, D.J. (1998): *Thin films of CdTe/CdS grown by MOCVD for photovoltaics* **,** Journal of Crystal Growth , Vol. 195, Number 1, pages 718 – 724.

Devendra Tiwari, Tapas K. Chaudhuri, T. Shripathi, U. Deshpande, R. Rawat (2013): *Non-toxic, earth abundant 2% Efficient Cu_2SnS_3 Solar cell based on tetragonal films direct-coated from single metal – organic precursor solution,* Solar Energy Materials and Solar Cells, Vol. 113, pages 165 – 170.

Gautier, C., Breton, G., Novaoura, M., Cambon, M., Chara S., Averous M. (1998) : *Sulfide Films on PbSe thin film layer grown by MBE*, Thin Solid Films; Vol. 315, Issue 1-2, pages 118 – 122.

Ghosh, B., Das, M., Banerjee, P., Das, S. (2008): *Fabrication of vacuum-evaporated SnS/CdS heterojunction for PV applications,* Solar Energy Materials and Solar Cells, Vol. 92, pages 1099 – 1104. DOI: 10.1016/j.solmat.2008.03.016.

Gupta, A., Parikh V., and Compaan, a. D. (2006): *High Efficiency Ultra- Thin Sputtered CdTe Solar Cells; Solar Energy Materials and Solar Cells,* Vol. 90, Issue 15, pages 2263 – 2271.

Hani Khallaf , Isaiah, O.Oladeji, Guangyu Chai, and Lee Chow(2008): *Characterization of CdS thin films grown by Chemical Bath Deposition using four different Cadmium sources*, Thin Solid Films, Vol. 516, Issue 18, pages 7306 – 7312.

Hao Guan, Honglie Shen, Chao Gao, Xiancong He (2013): *Structural and Optical properties of Cu_2SnS_3 and Cu_3SnS_4 thin films by successive ionic layer adsorption and reaction,* Journal of Materials Science, Materials in Electronics, Vol. 24, Issue 5, pages 1490 -1494. DOI: 10.1007/s10854 -012-0960-x.

Kobayashi, R., Sato, N., Ichimura, M. and Arai, E. (2003): *Photochemical Deposition of ZnS Thin Films from $C_4H_4KNaO_6$-Added Solutions,* Journal of Optoelectronics and Advanced Materials, Vol. 5, No. 4, pages 893 – 898.

Oja, I., Nanu, M., Katerski, A., Krunks, M., Mere, A., Raudoja, J., Goossens, A. (2005): *Crystal quality Studies of $CuInS_2$ films prepared by spray Pyrolisis,* Thin Solid Films, Vol. 480 – 481, pages 82 – 86.

Patel, M. R. (1999): *Wind and Solar Power System,* CRC Press, Boca Raton, London, page 27.

Robert W. Miles, Ogah, E. Ogah, Guillaume Zoppi, Ian Forbes (2009): *Thermally evaporated thin films of SnS for application in solar cell devices,* Thin Solid Films, Vol. 517, pages 4702 – 4705. DOI: 10.1016/j.tsf.2009.03.003.

Tiwari, D., Chaudhuri, T. K. (2011): *Synthesis of Earth-abundant Cu_2SnS_3 for solar cells,* AIP conference proceedings; 16/7/2011, Vol. 1349, Issue 1, page 1295.