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FABRICATION, STRUCTURAL AND OPTICAL CHARACTERIZATIONS OF THERMALLY EVAPORATED Cu_2SnS_3 THIN FILMS.

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ABSTRACT

The bi-layer of metallic Cu-Sn precursors was thermally evaporated sequentially on microscopic glass substrates at the controlled thickness of 100nm, 500nm and 1000nm and at different substrate temperatures of 27^0C, 100^0C and 200^0C. The bi-layer was subsequently sulphurized in a custom-built reactor for 1hour at 400^0C to form Cu_2SnS_3 ternary films.

The deposited Cu_2SnS_3 thin film samples were placed in the Scanning Electron Microscope (SEM) and the embedded SMARTSEM software produced the micrographs of each film. The micrographs from SEM show that the grain size increases with increasing substrate temperature (about 1μm) from 27^0C to 200^0C. Elemental Cu, Sn, S and glass substrate constituents such as Na, Si, Mg and O were identified through EDS. The surface profile shows that the deposited Cu_2SnS_3 films are rough. The XRD spectra identified the crystal structure, phases and lattices as Monoclinic Cu_2SnS_3 [-1 3 1], Anorthic Cu_2SnS_3 [-2 0 0] and Cubic Cu_2SnS_3 [1 1 1]. The UV-Vis Spectrophotometer measured the transmittance and reflectance of deposited Cu_2SnS_3 thin films in the range of 250nm – 900nm. The transmittance and reflectance data were used to calculate the optical absorption coefficient, α. The extrapolation of graph of $(\alpha h\nu)^2$ against hν intercept hν axis which correspond to energy gap of the film. An Energy band gap, Eg, of the deposited Cu_2SnS_3 film is 1.65eV. Subsequently, refractive index n, extinction coefficient, k and optical conductivity σ_0 were inferred. Refractive Index, n is 1.14, Extinction Coefficient, K, is 5.27×10^9 and Optical Conductivity , σ_0 is 6.74708E+16 $\Omega^{-1}cm^{-1}$.

Key words: Thermal Evaporation, Sulphurization, Energy band gap, grain sizes, Optical Conductivity, crystal structure.

INTRODUCTION

Many single and binary semiconductor thin films have been extensively studied but a few considerations have been given to ternary and quaternary compounds.

Semiconductors are technologically important because modification in their physical and optical properties through doping produce semiconductors useful for diverse device applications such as

Thermistor, IR Sensors, Optoelectronic devices, Hall probes, Diodes, Transistors, Solar cells, Integrated circuits, Charged-couple devices, Electroluminiscent, LASER, Optical fibre, Photodetectors, Photoconductors, Particle counters, Power remote telecommunication system and many other thin film devices.

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 plasma-enhanced chemical vapour deposition (Ali et al, 2006), metal organic chemical vapour deposition (Berrigan et al, 1998), thermal evaporation (Timoumi et al, 2005), chemical bath deposition (Khallaf et al, 2008), closed spaced sublimation (Armstrong et al, 2002), vacuum evaporation (Barkat et al, 2006), electrodeposition (Beyhan et al, 2007), molecular beam epitaxy (Gautier et al, 1998), spray pyrolisis (Oja et al, 2005), and sputter deposition (Gupta et al, 2006).

The present paper reports the growth of Cu_2SnS_3 ternary thin films by thermal evaporation technique. The employed sulphurization technique is as reported by (Agrawal et al, 2008). The structural and optical characterizations of Cu_2SnS_3 thin films shall be discussed.

MATERIALS AND METHODS

The bi-layer of Cu-Sn precursors was thermally evaporated sequentially on cleaned glass substrates at different substrate temperatures of 27^0C, 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 in a custom-built reactor for 1hour at 400^0C as shown in figure 1.

The structural characteristics of the deposited Cu_2SnS_3 thin films were studied using 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 Energy Dispersive X-Ray System (EDS) was applied to determine the morphology and point by point composition of the film whereas the surface profile determined 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 (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 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.

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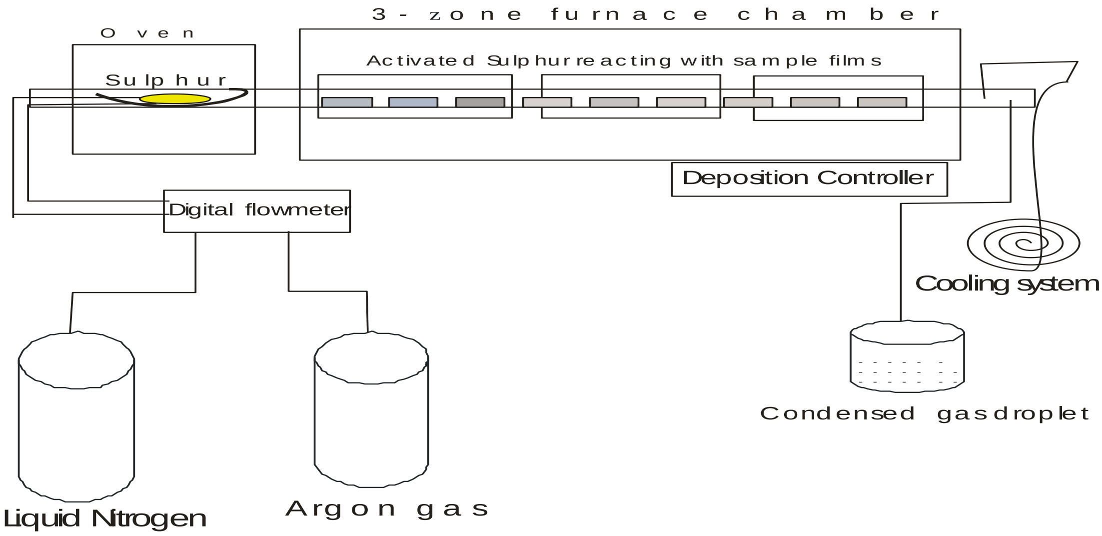

Figure 1: Schematic diagram of sulphurization setup.

RESULTS

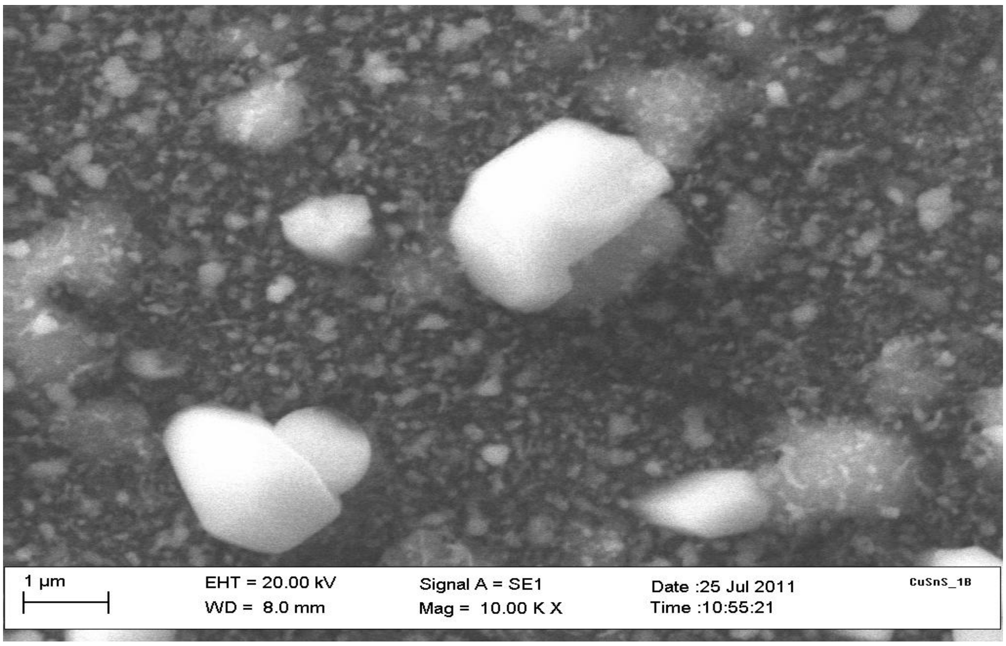

Figure 2: Micrograph of Cu_2SnS_3 thin films deposited at 27^0C at controlled thickness 100nm

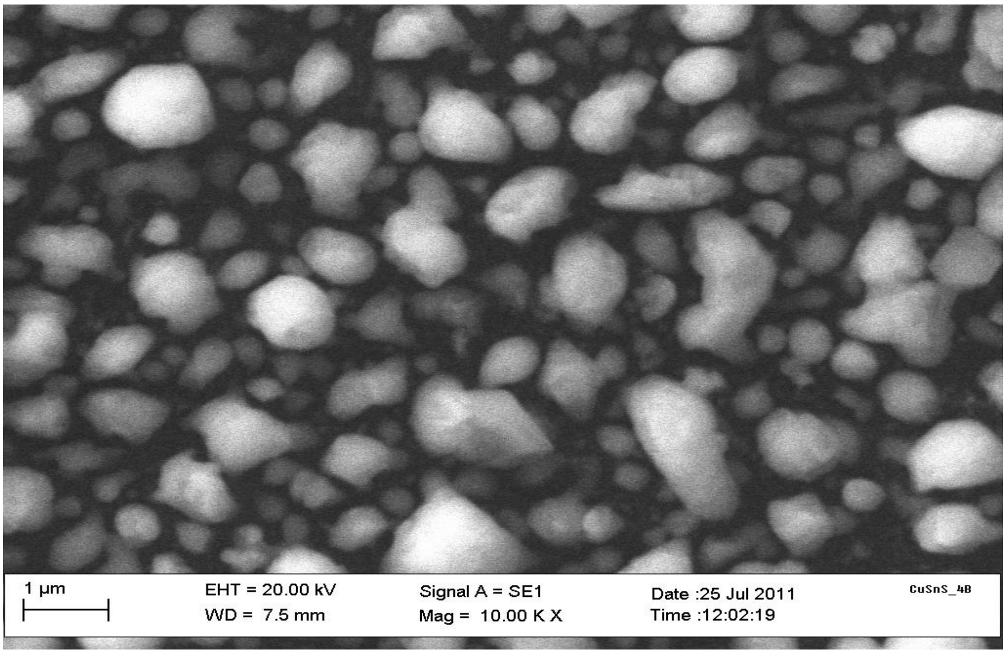

Figure 3: Micrograph of Cu_2SnS_3 thin films deposited at 100^0C at controlled thickness of 100nm

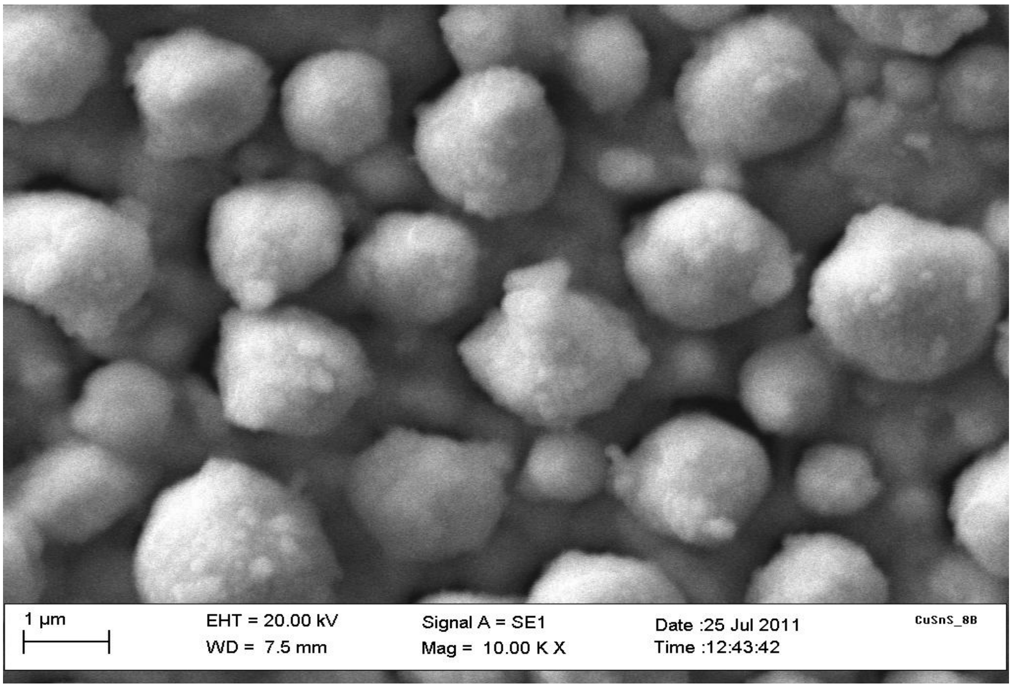

Figure. 4: Micrograph of Cu_2SnS_3 thin films deposited at 200^0C at controlled thickness 500nm.

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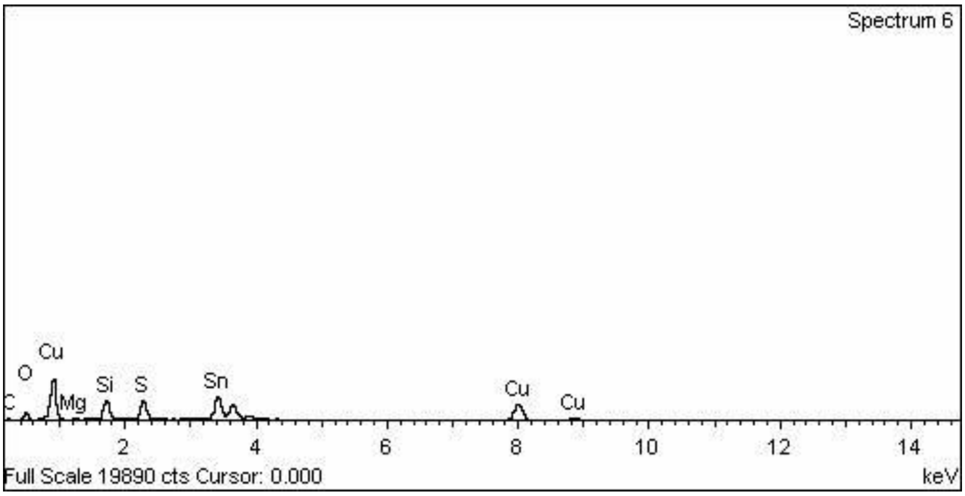

Figure 5: EDS compositional analysis of Cu_2SnS_3 thin film.

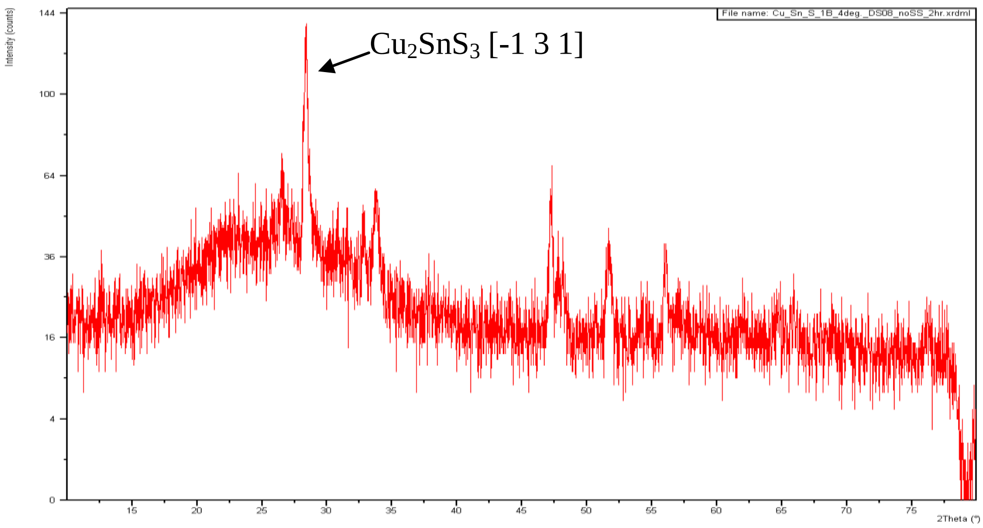

Figure 6: XRD Spectra of Monoclinic C_2SnS_3 thin film.

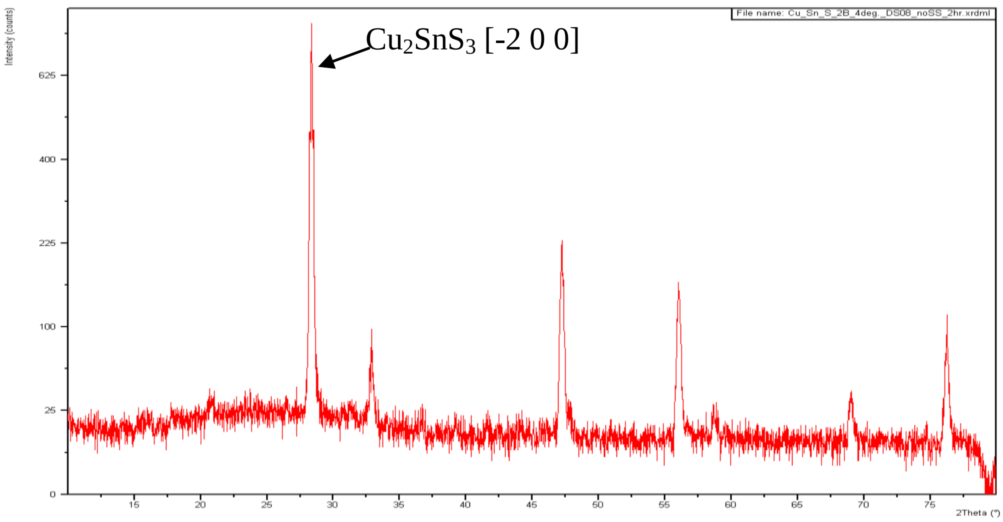

Figure 7: XRD Spectra of Anorthic C_2SnS_3 thin film.

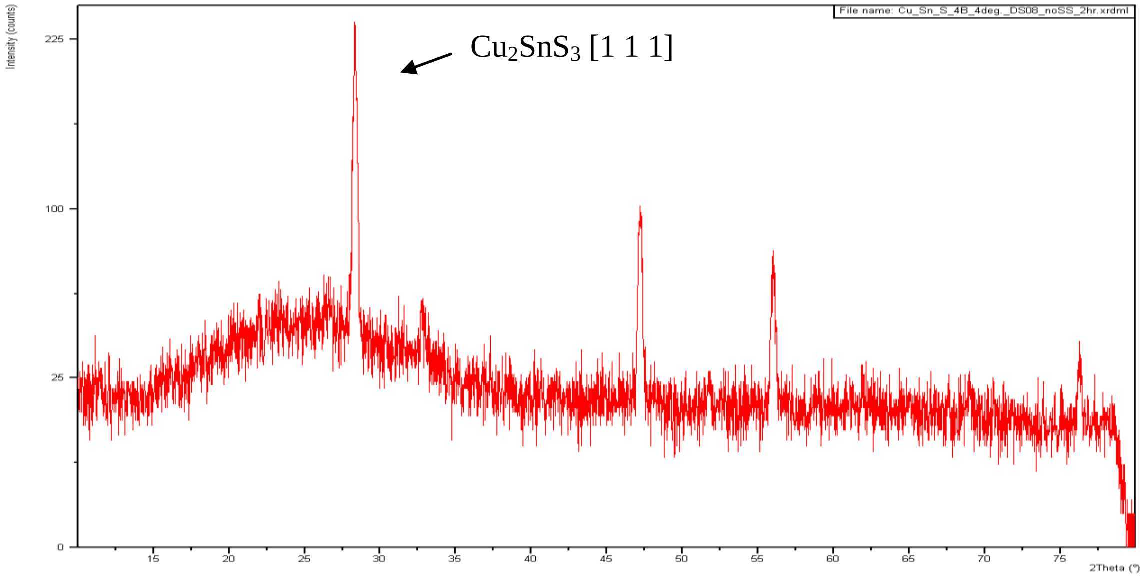

Figure 8 : XRD Spectra of Cubic C_2SnS_3 thin film.

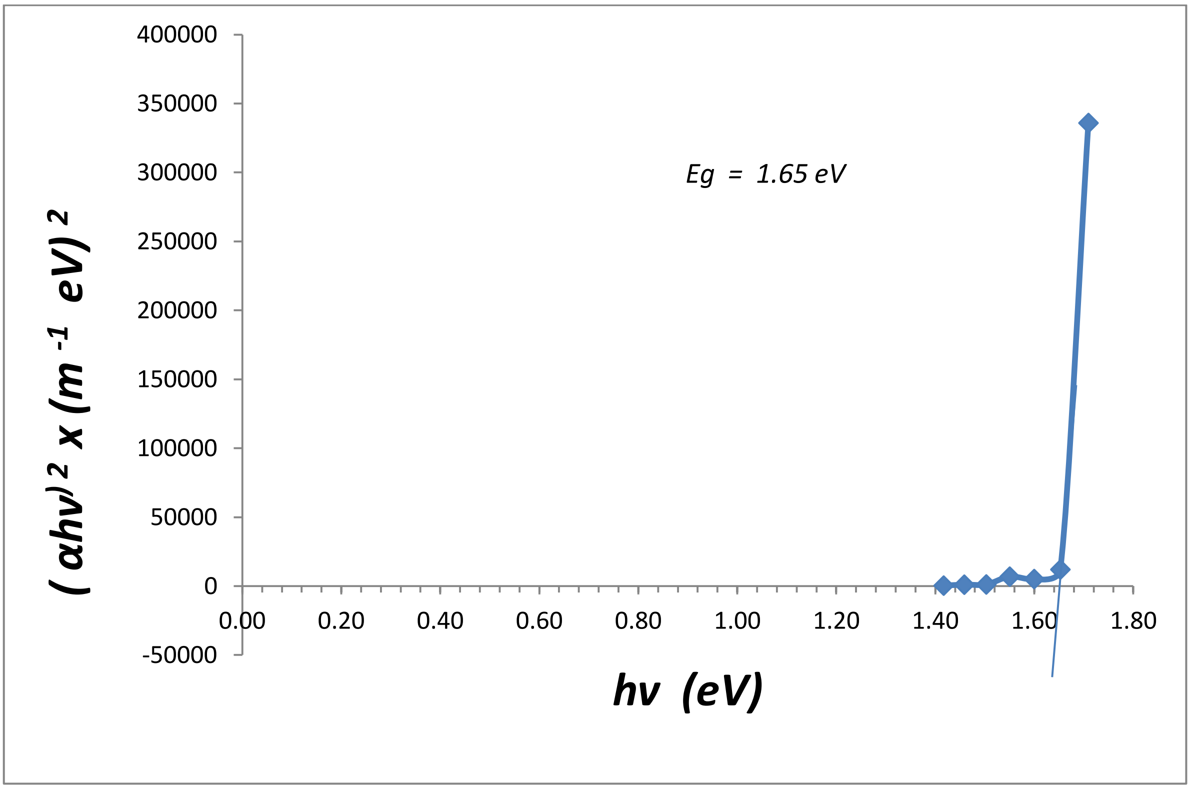

Figure 9: Plot of $(\alpha h\nu)^2$ versus $h\nu$ for Cu_2SnS_3 thin film deposited at 27^0C with thickness 100nm.

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DISCUSSION

The films of Cu_2SnS_3 were evident on the microscopic glass substrates. The SEM study indicates that the deposited Cu_2SnS_3 thin films were uniformly spread on the microscopic glass substrates. The films were characterized with large grain sizes of about 1µm when substrate temperature increases from 27^0C to 200^0C as shown in figures 2, 3 and 4.

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 as shown in Fig. 5.

The spectra from the XRD pattern revealed Mohite Syn, Monoclinic Cu_2SnS_3[-1 3 1], lattice d = 3.139 at peak 2Θ = 28.4^0 (fig. 6), and Mohite Syn, Anorthic Cu_2SnS_3 [-2 0 10], lattice d = 1.922 at peak 2Θ = 47.25^0 (fig. 7), and Cubic Cu_2SnS_3 [1 1 1], lattice d = 3.135 at peak 2Θ = 28.45^0 (fig. 8).

The UV-Visible spectrophotometer in the wavelength range of 200nm – 950nm produced the transmittance and reflectance data and characterisic curves. The characteristics curves were 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:

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

Where :
t = thickness of the film.
R = Reflectance value.
T = Transmittance value

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

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

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. One of such plots for Cu_2SnS_3 thin film sample is shown in Fig. 9. The energy band gap, Eg , of deposited Cu_2SnS_3 thin film is **1.65eV.**

The refractive index was determined from the relation:

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

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

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 $\mathbf{5.27x10^9}$.

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 $\mathbf{6.74708E+16\Omega^{-1}cm^{-1}}$.

Using thermal evaporation and sulphurization techniques, it is possible to produce low cost, non-toxic Cu_2SnS_3 thin films at controlled thickness and substrate temperatures. The depositions were uniformly spread and adherent well on the glass substrates.

The SEM results shows increase in grain size up to 1µm as substrate temperature increases from 27^0C to 200^0C. The elemental composition of Cu (24.89%), Sn (15.82%), S (16.29%) with glass substrate constituents such as Si, Mg, O and Na were evident through EDS. Monoclinic, Cu_2SnS_3 [-1 3 1], Anorthic Cu_2SnS_3 [-2 0 10] and Cubic Cu_2SnS_3 [1 1 1] were identified through XRD.

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 $\Omega^{-1}cm^{-1}$.

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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, Number 3, pages 1198 - 1204.

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.

Barkat, l., Hamdadou, N., Mordi, M., Khehil, A., Bernede, J. C. (2006): Growth and Characterization of $CuFeS_2$ Thin Films; Journal of Crystal Growth; Vol. 297; pages 426 – 431.

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.

Beyhan, S., Suzer, S., Kadirgan, F. (2007): Complexing agent effect on the stoichiometric ratio of the electrochemically prepared $CuInSe_2$ thin film; Solar Energy Materials and Solar Cells; Vol. 91, pages 1922 – 1926.

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.

Gupta, A., Parikh V., and Compaan, a. D. (2006): High Efficiency Ultra- Thin

Scientia Africana, Vol. 12 (No.2), December 2013. Pp53-61
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Sputtered CdTe Solar Cells; Solar Energy Materials and Solar Cells; Vol. 90, Issue 15, pages 2263 – 2271.

Khallaf H., Oladeji, I. O., Chai, G. and Chow, L. (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.

Oja, I., Nanu, M., Katerski, A., Krunks, M., Mere, A., Raudoja, J., Goossens, A. (2005) : Crystal quality Studies of CuInS2 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.

Timoumi, A., Bouzouta, H., Kanzari M., Rezig, B. (2005): Fabrication and Characterization of In_2S_3 Thin Films Deposited by Thermal Evaporation Technique, Thin Solid Films, Vol. 480 – 481, page 124 – 128.