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SYNTHESIS, STRUCTURAL AND ELECTRICAL CHARACTERIZATIONS OF THERMALLY EVAPORATED Cu_2SnS_3 THIN FILMS.

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ABSTRACT

Ternary compound of Cu_2SnS_3 thin films were grown on microscopic glass substrates. The bi-layer of metallic Cu-Sn precursors were first deposited 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 using Thermal Evaporation technique. The depositions were uniformly spread on the glass substrates. The films were subsequently sulphurized in a custom-built reactor for 60 minutes at 400^0C. The micrographs from Scanning Electron Microscope show that the grain size increases to about 2µm with increasing substrate temperature from 27^0C to 200^0C. Energy Dispersive X-Ray System (EDS) identified Cu, Sn, S and glass substrate constituents such as Na, Si, Mg and O with their percentage composition in the deposited ternary film. The surface profilometer shows that the deposited films are rough. The XRD spectra identified the crystal structure, phases and lattices as Cubic Cu_2SnS_3 [1 1 1], Anorthic Cu_2SnS_3 [-2 0 0] and Monoclinic Cu_2SnS_3 [-1 3 1]. The electrical characteristics of the deposited Cu_2SnS_3 films were determined by Semiconductor Characterization System and Four Point probe. The cross-planar i-v characteristics curves of Cu_2SnS_3 films were non-Ohmic while in-planar i-v characteristic curves were Ohmic. The electrical resistivity of the deposited Cu_2SnS_3 film is 2.55 x 10^{-3} Ωcm. The conductivity is in the order of 10^3 $\Omega^{-1}cm^{-1}$.

Key words: Ternary compound, microscopic glass substrate, Thermal Evaporation, Sulphurization, Micrographs and Electrical Resistivity.

INTRODUCTION

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

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).

In this work, we report the preparation of Cu_2SnS_3 thin films by thermal evaporation and sulphurization technique (Agrawal et al, 2008). The evaporation technique was adopted because it allows precise control of the deposited films and maintains uniform deposition on the substrate. The structural and electrical characteristics of evaporated Cu_2SnS_3 thin films are discussed.

MATERIALS AND METHODS

Amongst the materials employed in the preparation and characterizations of Cu_2SnS_3 thin films were masks, elemental samples of metallic Cu, Sn and S, Thermal evaporator, Three-chamber furnace, Digital flow meter, Surface profilometer, Scanning Electron Microscope, Semiconductor Characterization Systems, Four point Probe and X-Ray Diffractometer.

The bi-layer of Cu-Sn precursors were sequentially evaporated at different temperatures of 27^0C, 100^0C and 200^0C with thickness of 100nm, 500nm and 1000nm on cleaned glass substrates using thermal evaporator (Edward FL 400 Auto 306) shown in Figure 1. The evaporated bi-layer of Cu-Sn thin films was further sulphurized in a custom-built reactor (Figure 2) for 60 minutes at 400^0C.

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

The Scanning Electron Microscope (SEM) with embedded Energy Dispersive X-Ray System (EDS) determined the morphology and compositions of the deposited films. The surface profiler measured the thickness and roughness of the deposited Cu_2SnS_3 thin film. Spectra from X-Ray Diffractometer (XRD) provided 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 electrical properties of evaporated Cu_2SnS_3 films (Figure 3) were measured using Four point probe and Semiconductor Characterization System (Keithley 4200) shown in Figure 4.

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Figure 1: Thermal evaporator (Edward FL 400 Auto 306 System).

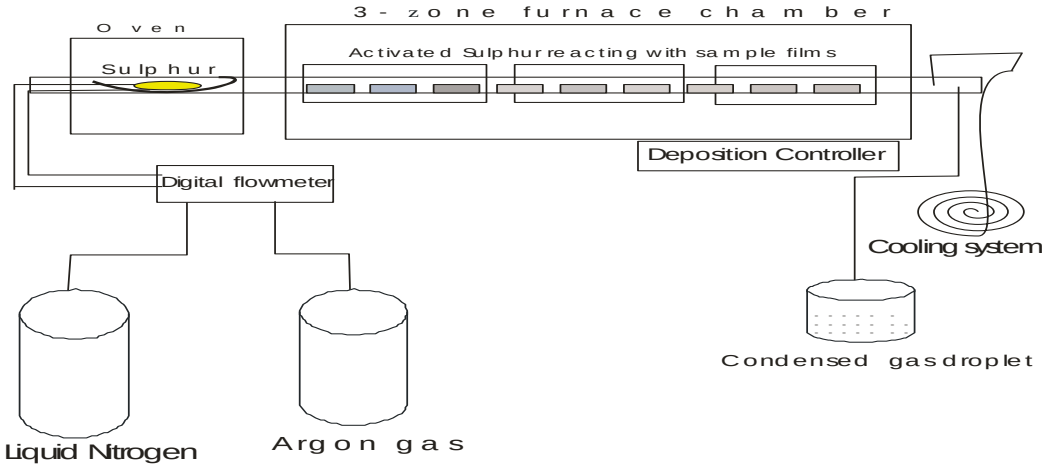

Figure 2: Schematic diagram of sulphurization setup.

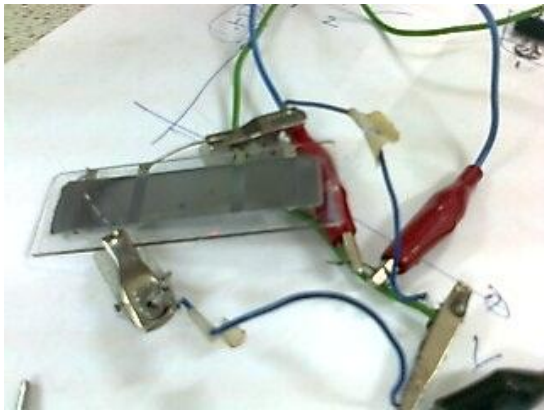

Figure 3: Cross-planar and in-planar i-v measurement of evaporated Cu_2SnS_3 film sample

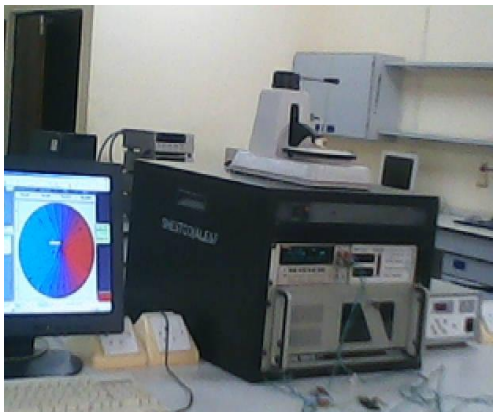

Figure 4: Semiconductor Characterization system (Keithley 4200).

RESULTS AND DISCUSSION

Cu_2SnS_3 thin films were evident on the microscopic glass substrates after deposition. At room temperature of 27^0C, the surface profilometer showed that Cu_2SnS_3 films with thickness 100nm has average roughness values,Ra = 234.53nm and root mean square roughness, Rq = 309.21nm). The average roughness value of Cu_2SnS_3 thin films with thickness of 1000nm is Ra = 3133.50nm and the root mean square roughness, Rq = 3942.60nm. This shows that roughness of the film increases with the thickness of the films.

At elevated substrate temperature of 100^0C, Cu_2SnS_3 thin film deposited with controlled thickness of 100nm produced the lowest roughness values (Ra = 77.85nm and Rq = 99.79nm) among all the deposited film samples.

The SEM study shows that the deposited Cu_2SnS_3 thin films were uniform on the glass substrate and characterized with large grain sizes of about 2µm as the thickness increases from 100nm to 500nm (Figures 5 and 6).

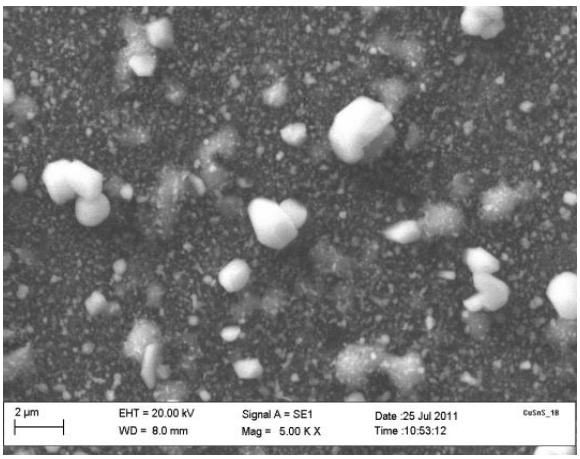

Figure 5: Micrograph of Cu_2SnS_3 thin films deposited at 27^0C at controlled thickness 100nm

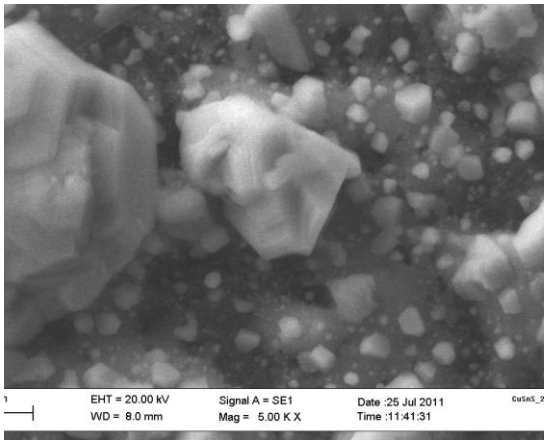

Figure 6: Micrograph of Cu_2SnS_3 thin films deposited at 27^0C at controlled thickness 500nm

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The typical Energy Dispersive X-Ray spectra of Cu_2SnS_3 thin film evaporated at room temperature with precursor thickness of 500nm is shown in Figure 7. The spectra confirmed the presence of Copper (Cu), Tin (Sn) and Sulphur (S) elements in the evaporated film. Cu is 24.89% weight, Sn is 15.82% weight and S is 16.29% weight. The film was Cu- rich. Other elements, such as Sodium (Na), Magnessium (Mg), Silicon (Si) and Oxygen (O) were the artefacts from glass substrate.

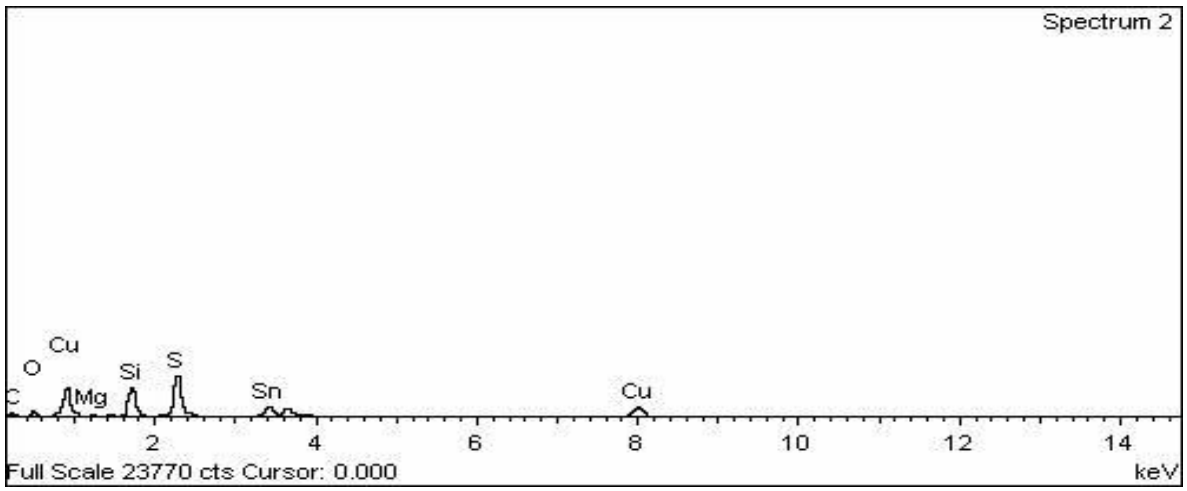

Figure 7: EDX spectra of Cu_2SnS_3 thin film evaporated at room temperature (27^oC) with precursor thickness of 500nm.

The spectra from the XRD pattern showed predominant Mohite Syn, Monoclinic Cu_2SnS_3 [-1 3 1], lattice d = 3.139 at $2\Theta = 28.4^0$ (Figure 8) , Mohyte Syn, Anorthic Cu_2SnS_3 [-2 0 10], lattice d = 1.922 at $2\Theta = 47.25^0$ (Figure 9) and Cubic Cu_2SnS_3 [1 1 1], lattice d = 3.135 at $2\Theta = 28.45^0$ (Figure 10). Other minor reflections and peaks were also evident.

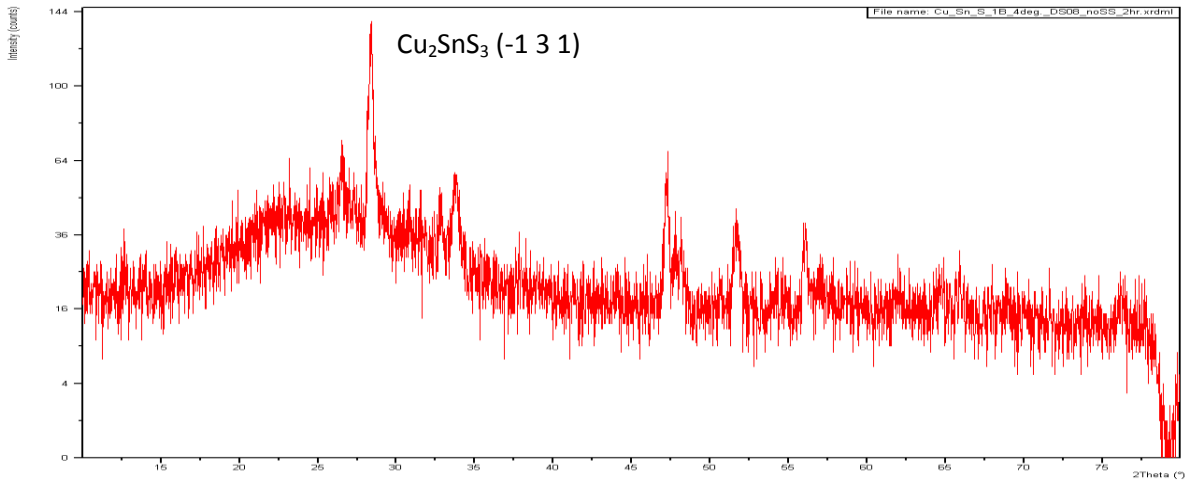

Figure 8: XRD Spectra of Monoclinic C_2SnS_3 thin film evaporated at room temperature with precursor thickness of 100nm.

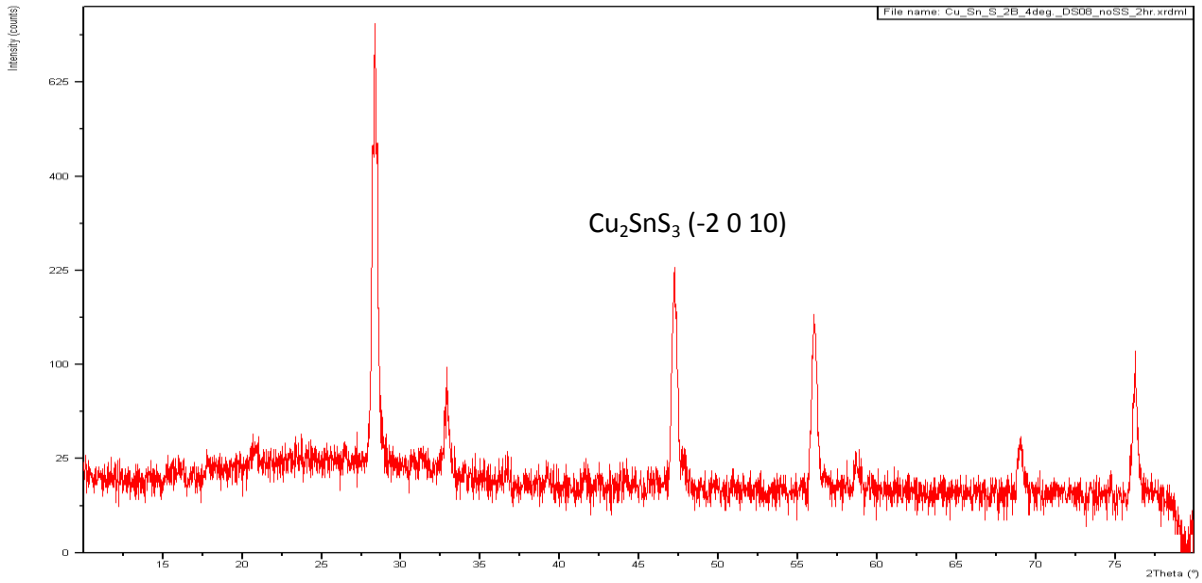

Figure 9: XRD Spectra of Anorthic C_2SnS_3 thin film evaporated at room temperature with precursor thickness of 500nm.

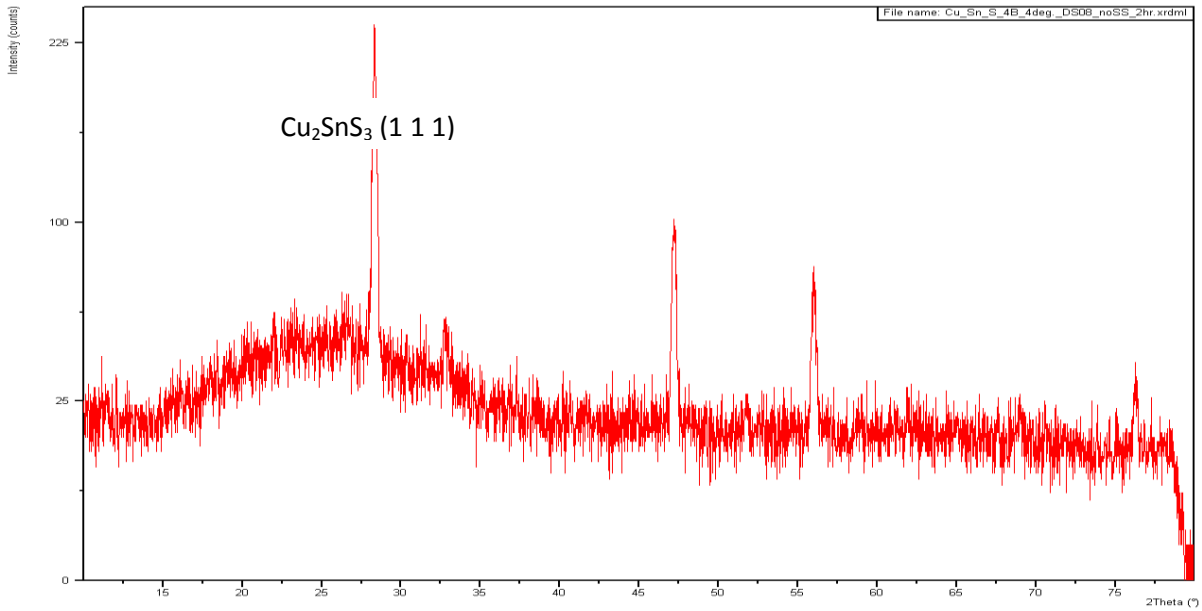

Figure 10: XRD Spectra of Cubic C_2SnS_3 thin film evaporated at room temperature with precursor thickness of 500nm.

The semiconductor Characterization System (SCS) showed that the cross-planar i – v characteristic curves of C_2SnS_3 thin film were non – Ohmic (Figure 11). This clearly indicates that the evaporated C_2SnS_3 film is a semiconductor material. The in – planar i – v characteristic curves were Ohmic (Figure 12). This shows constant proportionality between current – voltage values. The electrical resistivity, ρ, of evaporated C_2SnS_3 thin film was measured from Four point probe and it was found to be 2.55 x 10^{-3} Ω-cm. So, the conductivity of the evaporated Cu_2SnS_3 film is in the order of 10^3 Ω^{-1}-cm^{-1}.

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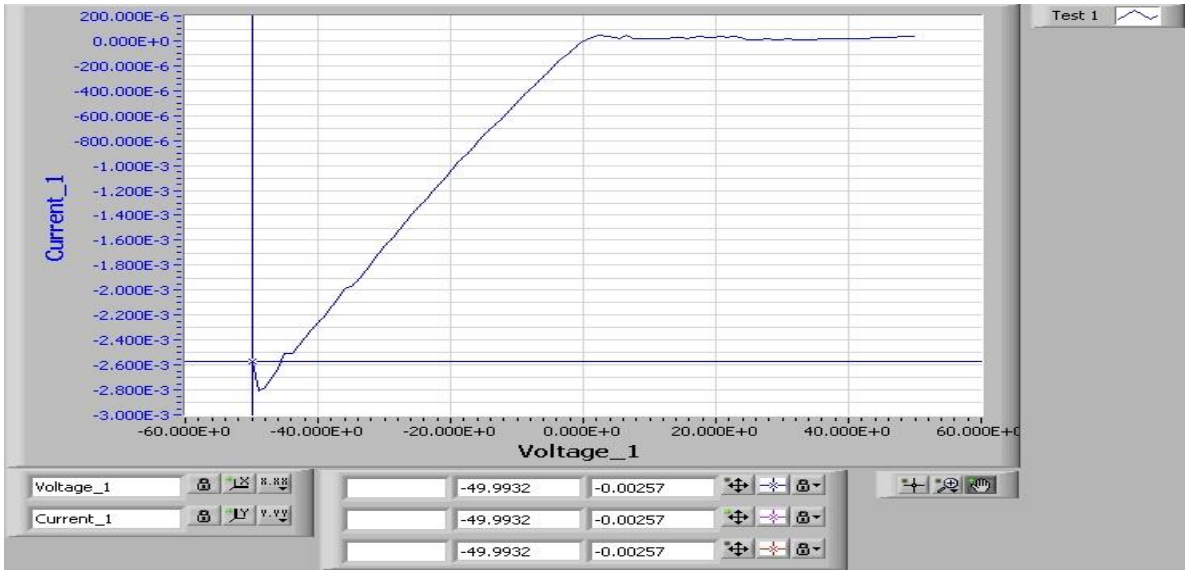

Figure 11: Cross – planar i-v characteristic curve of C_2SnS_3 thin film evaporated at room temperature with thickness 100nm.

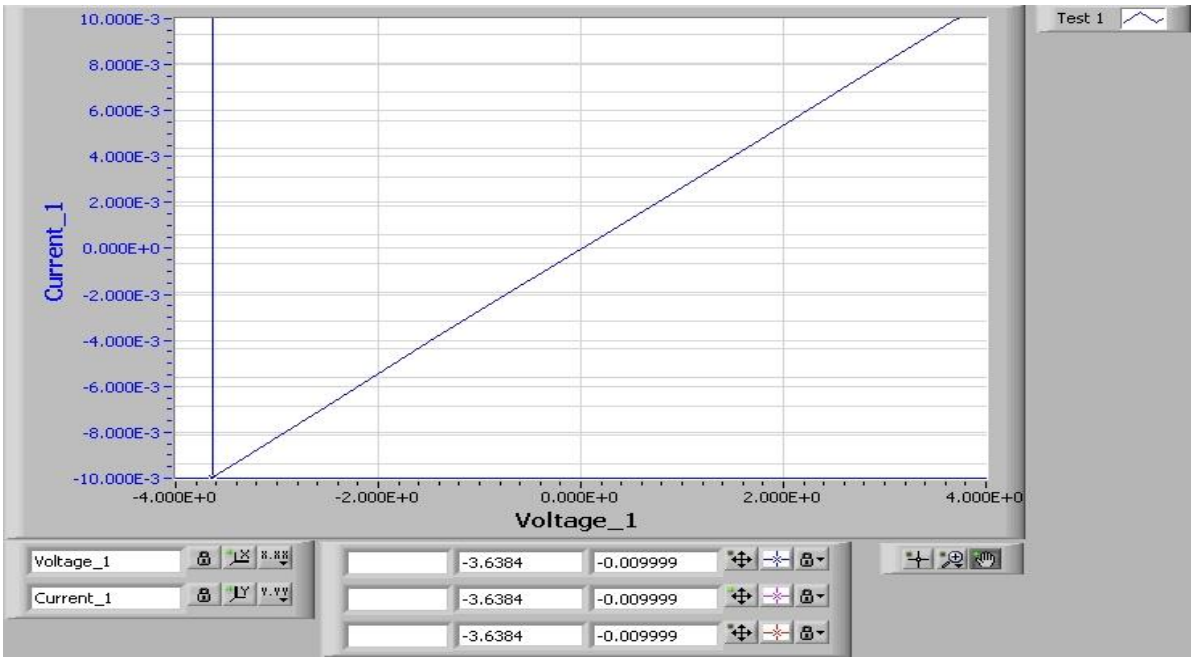

Figure 12: In – planar i-v characteristic curve of C_2SnS_3 thin film evaporated at room temperature with thickness 100nm.

C_2SnS_3 thin films have been successfully grown on the microscopic glass substrates at substrate temperature of 27^0C, 100^0C and 200^0C with controlled deposition thickness of 100nm, 500nm and 1000nm using thermal deposition and sulphurization techniques. The depositions were uniform on the glass substrate. The thickness and topologies of the deposited films were measured. The deposited C_2SnS_3 thin films were rough. The roughness of the film increases with thickness. SEM produced the

micrographs and embedded EDS produced the elemental composition of the films. The C_2SnS_3 thin films were characterized with large grain sizes of about 2µm when substrate temperature increases from 27^0C to 200^0C. The evaporated elements Cu, Sn, S and artefacts from substrate such as Na, Si, Mg and O were also identified. XRD automated the crystal phases, structures and lattices of the deposited films. Monoclinic C_2SnS_3 [-1 3 1], Anorthic C_2SnS_3 [-2 0 10] and Cubic C_2SnS_3 [1 1 1] were identified.

The electrical characteristic of the evaporated C_2SnS_3 thin film were measured from SCS and Four point probe. The cross-planar i-v characteristic curves were non-Ohmic while in-planar i-v characteristic curves were Ohmic. The electrical resistivity of evaporated Cu_2SnS_3 thin film is 2.55 x 10^{-3} Ω-cm. This shows that the conductivity of the evaporated Cu_2SnS_3 is in the order of $10^3\ \Omega^{-1}cm^{-1}$.

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