Influence of Annealing Temperature on the Physical Properties of Cu_2SnSe_3 Thin Films Prepared by Thermal Vacuum Evaporation Technique

ABSTRACT

Ternary compound of semiconductor polycrystals Copper Tin Selenide, Cu_2SnSe_3, thin films have been prepared by vacuum thermal evaporation technique on well-cleaned glass substrate and annealed in purified nitrogen atmosphere from room temperature to 500°C for different annealing temperature. The annealing effects on surface morphologies, elemental compositions, and electrical behaviour of these films have been investigated using Scanning Electron Microscope (SEM), Energy Dispersive X-Ray (EDX), and Van der Pauw techniques. EDX studies showed that increasing the annealing temperature resulted in drastic loss of Cu content. It is observed that elemental compositions of the Cu_2SnSe_3 thin films were close to the ideal stoichiometric value 2:1:3. The annealed Cu_2SnSe_3 thin films were found to be p-type semiconductor with activation energy, ΔE_a, of 0.018 eV obtained from I-V characteristic analysis.

Keyword: *Cu_2SnSe_3; Thin Film; Annealing Temperature; Vacuum Evaporation; Physical Properties*

1. INTRODUCTION

Current efforts are being made in developing new photovoltaic materials [1]. The band gap energy, absorption coefficient, cost of large-scale production, radiation tolerance and environmental stability are important factors that must be considered during the research and development of photovoltaic materials [2,3]. Cu_2SnSe_3, the ternary chalcogenide materials of type I_2-IV-VI_3 is one of the well-known semiconductors for wide area applications such as photovoltaic applications. It is also regarded as small or middle band gap semiconductors and these ternary chalcogenide functional materials are suitable for solid lubricant due to their outstanding thermal and mechanical properties [4]. Crystal structure refinement of semiconducting compound Cu_2SnSe_3 has been investigated by means of the Rietveld method and revealed that the films were structured in mixed phases between cubic space group F-43m (no. 216) and orthorhombic space group Pnma (no. 62) [5,6].

Bulk samples of Cu_2SnSe_3 are normally prepared by the solid-state method and vertical Bridgman–Stockbarger technique before depositing process [5,7]. Thin films of metal chalcogenides can be deposited onto glass, metal, plastics and other substrates by a variety of techniques such as flash evaporation method [4], D.C. sputtering [8,9], electrochemical deposition [10], vacuum thermal evaporation [11,12], electroless deposition, to the simplest method of chemical bath deposition [13].

It is known that Cu_2SnSe_3 thin film's surface and electrical properties are very sensitive to the preparation conditions and method of depositions. The composition of Cu_2SnSe_3 thin films used as absorbers in thin film solar cell is a topic of prime importance since many cell properties are influenced by deviations from stoichiometric ratio. Thus, in the present work, we report on the results of the physical and electrical properties of Cu_2SnSe_3 thin films annealed at different annealing temperatures prepared by vacuum thermal evaporation. The chemical composition and elemental analysis of Cu_2SnSe_3 thin films annealed at different temperatures were also investigated and reported.

2. EXPERIMENTAL

The commercially available starting materials (Cu, Sn, and Se) (Alfa Aesar) with a nominal purity of 99.99 wt.% in the stoichiometric ratio were mixed together.. The materials were weighed in a stoichiometric ratio accurate to 0.2 mg. The stoichiometric composition of source material was around 26% Cu, 25% Sn, and 49% Se. Bulk Cu_2SnSe_3 polycrystal were synthesized in our laboratories using the solid-state method. The powder was the placed in a molybdenum boat and fixed to a holder in the thermal evaporator. The copper tin selenide powder was evaporated at a vacuum level of approximately 10^{-5} mBar and the thin films were deposited on well-cleaned glass substrates at room temperature. The thin films were later annealed at 100°C, 200°C, 300°C, 400°C and 500°C under flowing nitrogen, N_2, atmosphere.

The surface and structure morphology of the thin films were examined using SEM and EDX techniques. The atomic composition of the vacuum evaporated copper tin selenide thin films were investigated by EDX (Oxford Instruments Model 7353) attached to a scanning electron microscopy (LEO 1455 VP–SEM) with accelerating voltage of 30 kV at room temperature. Investigation of the I-V characteristic of the films has been investigated by using the Van der Pauw method and the thicknesses of the films were determined by a surface profiler. Samples prepared for Van der Pauw measurement were in typical symmetrical circular sample geometry. A Keithley 2400 Source Meter was used as a constant current source while the voltage was measured with a Keithley 2700 Multimeter/Data Acquisition System.

3. RESULTS AND DISCUSSIONS

3.1 Scanning Electron Microscopy (SEM)

In most cases, morphology of Cu_2SnSe_3 thin films has been investigated by using scanning electron microscope (SEM). The wide range of magnification makes it suitable for investigation of microstructure of Cu_2SnSe_3 thin films. With the help of SEM images, one can correlate the electrical behaviour, crystallinity, mechanical, properties, etc. of Cu_2SnSe_3 thin films with is surface morphology. Morphological investigations were carried out on six samples of Cu_2SnSe_3 thin films annealed at different temperatures using scanning electron microscope (SEM). All micrographs were taken at 2,000 and 10,000 times magnification and shown in Figures 1 and 2 respectively. The shape of Cu_2SnSe_3 thin films in Figures 1 and 2 was smooth and uniform with spherical-like grain and the size was estimated to be below 1 µm. However, after temperatures were employed, the surface shows the flake-like structure and disappearance of the flake-like structure can be seen at Figure 2(e) and (f) due to increasing flake-like structure at higher annealing temperature. They are in good agreement with previous work done by Chuah *et al.* (2003) on effect of bath temperature on the electrodeposition of copper tin selenide films from aqueous solution [10]. It is well known that morphology of semiconductor thin films is influenced by the method of synthesis and the annealing temperature employed.

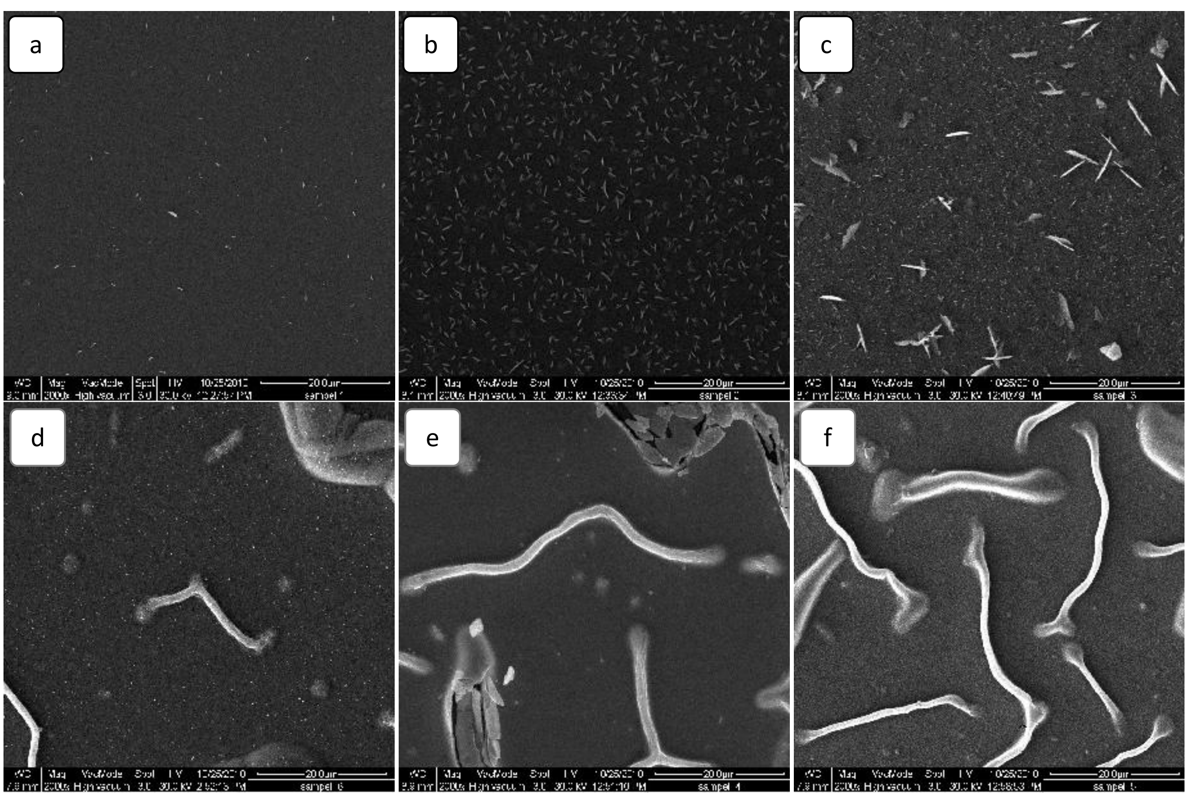

Figure 1: SEM micrograph of 2000x magnification of Cu_2SnSe_3 thin film deposited on glass substrate with annealing temperature for (a) as-deposited (b) 100ºC (c) 200ºC (d) 300ºC (e) 400ºC and (f) 500ºC.

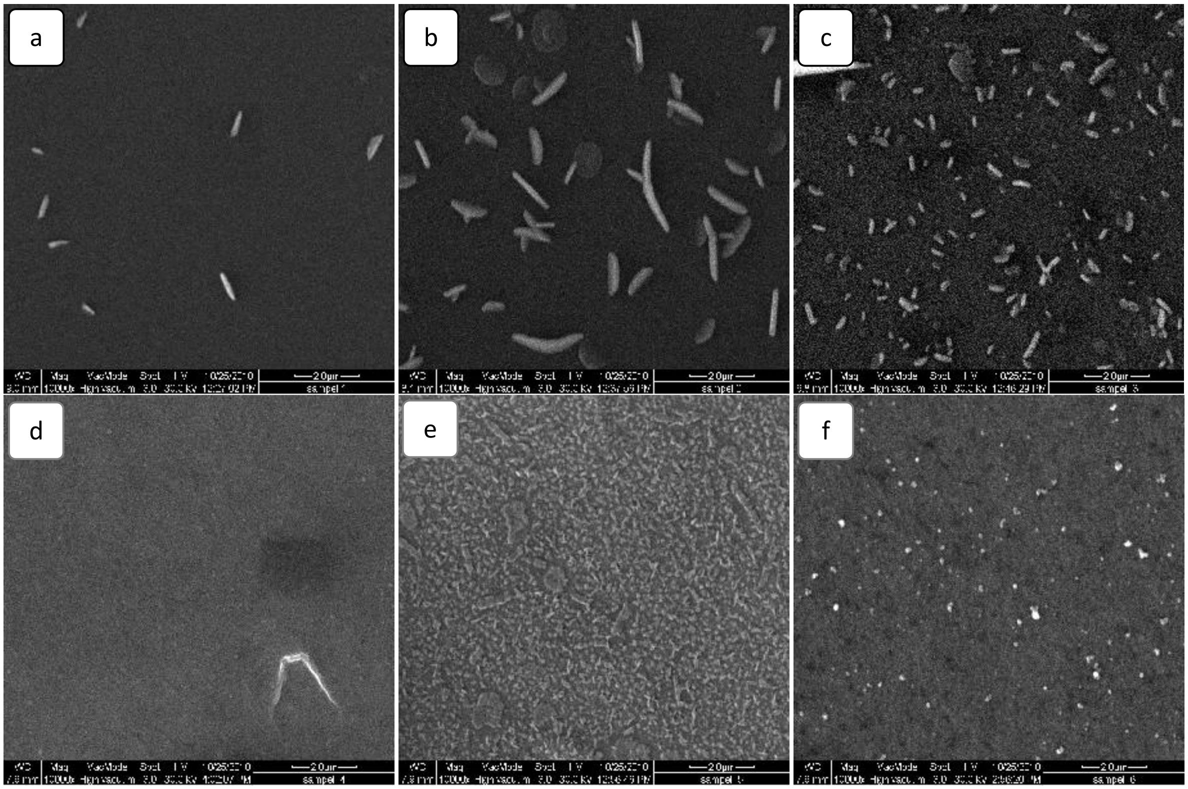

Figure 2: SEM micrograph of 10000x magnification of Cu_2SnSe_3 thin film deposited on glass substrate with annealing temperature for (a) as-deposited (b) 100ºC (c) 200ºC (d) 300ºC (e) 400ºC and (f) 500ºC.

Kuo *et al.* (2010) reported the microstructure shape of sputtered Cu_2SnSe_3 thin films indicated the existence of different phases [8]. This is in good agreement to our work which also shows that the films had loose microstructure with flaky grains with size estimated to be around 2 µm and become bigger when subject to increase annealing temperatures. The SEM results show that the morphology of Cu_2SnSe_3 thin films was strongly influenced by the annealing temperature employed. The change in morphology due to change in the annealing temperature from room temperature to 500ºC may be caused by a change in crystallization of the compound.

Figure 1(e) presents Cu_2SnSe_3 thin films annealed at 400ºC revealed that the microcracks has been taking part. It is observed that the surface of as-deposited Cu_2SnSe_3 thin films was nearly uniform until annealed at 300ºC. However, Cu_2SnSe_3 thin films annealed at 400ºC and 500 ºC show some microcracks occurred on the films. It is believed that the sample of Cu_2SnSe_3 thin films is not stable when dealing with high annealing temperature employed (400ºC and 500ºC). The Cu_2SnSe_3 thin films deposited on glass substrate will begin to disappear when annealed over 500ºC and the thin film remains transparent without any coated samples on the surface. This is due to the loss of Cu_2SnSe_3 thin films since it was very thin, they easily to evaporate back and removed with the flowed nitrogen gas.

3.2 Energy Dispersive X-Ray Analysis (EDX)

Figure 3 illustrates the EDX spectrum pattern of the as-deposited and annealed Cu_2SnSe_3 thin films at 100°C, 200°C, 300°C, 400°C, and 500°C. The EDX analysis revealed that the as-deposited and annealed thin films of Cu_2SnSe_3 are found to contain the nearly stoichiometric composition calculated earlier where atomic percentage for each element Cu, Sn, and Se corresponding to 26%, 25%, and 49%, respectively. From observations, the as-deposited film of Cu_2SnSe_3 which does not undergo annealing shows the best stoichiometric (2:1:3) ratio as can be seen in Figure 3. However, the EDX spectrum shows an excess of selenium element in all the thin film samples. These phenomenons were also reported by Khatalingam *et al.* (2007) on effect of deposition potential in zinc selenide films [14].

Five main peak regions at 0.923 keV, 1.379 keV, 3.444 keV, 8.048 keV, and 11.222 keV corresponding to elemental CuL, SeL, SnL, CuK, and CuK, respectively, were observed. Before annealing, energy peak with

0.923 keV and 1.379 keV corresponding to Cu and Se shows more intense compared to the samples annealed at various annealing temperature.

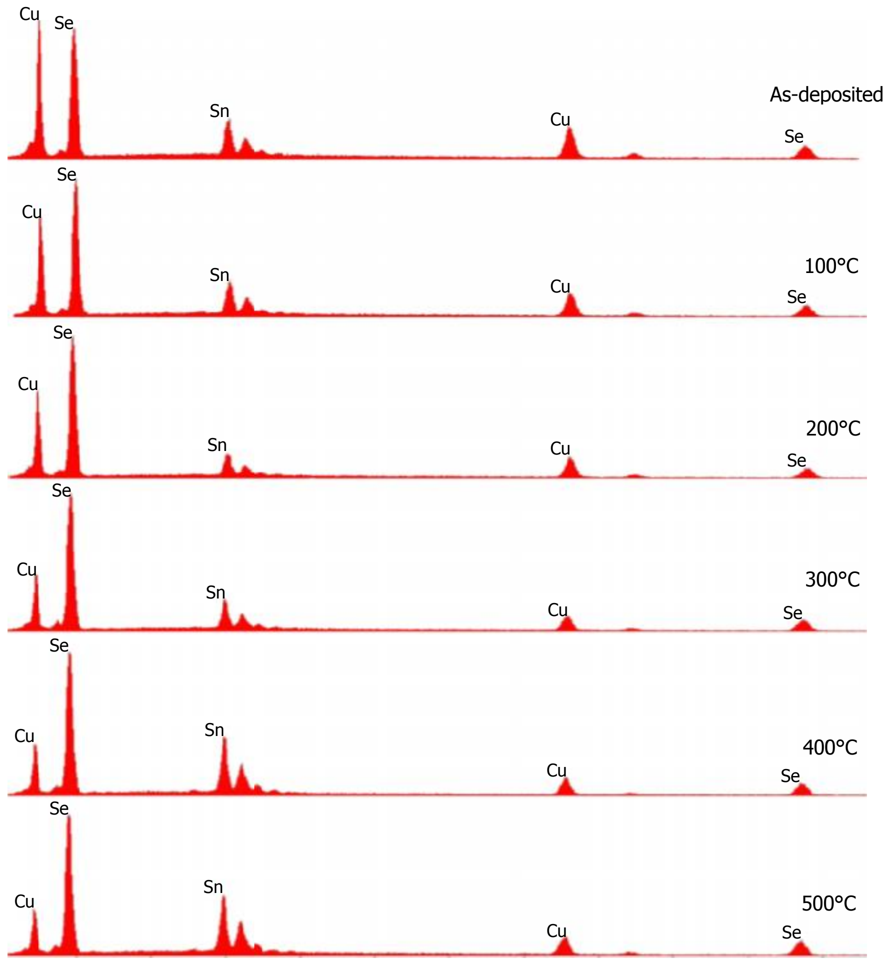

Figure 3: EDX spectrum of the as-deposited and annealed Cu_2SnSe_3 thin films at 100°C, 200°C, 300°C, 400°C and 500°C.

As can be seen in Figure 3, the energy peaks for each element decrease with increasing annealing temperature. However, the percentage of Se increases due to the minor loss in atomic percentage of Cu and Sn when annealing temperature was employed. This result is in good agreement with previous discussion on SEM micrograph and AFM topography reported by Yunos et al. 2011 on effect of annealing temperature and illumination of light on copper tin selenide thin films [12]. It is acknowledged that annealing temperature more than 300°C will cause some elemental loss in Cu_2SnSe_3 thin films.The atomic percentages of each element in Cu_2SnSe_3 thin film composition is tabulated in Table 1 as a function of annealing temperature. The differences between as-deposited films with annealed films of Cu_2SnSe_3 at various annealing temperature can be easily indicates the best stoichiometric of elements which verifies composition of Cu_2SnSe_3 phase is as-deposited films

Table 1: The atomic percentage of Cu, Sn, and Se for the film annealed at different annealing temperature.

Annealing Temperature	Atomic percentage of various elements (%)			Ratio of Cu:Sn:Se
	Cu	Sn	Se	
As-deposited	36.80	12.71	50.49	2.2:0.8:3.0
100 ºC	32.19	13.82	53.99	1.9:0.9:3.2
200 ºC	32.39	10.86	56.75	1.9:0.7:3.4
300 ºC	25.39	14.93	59.67	1.5:0.9:3.6
400 ºC	22.87	22.96	54.17	1.4:1.4:3.2
500 ºC	22.65	22.13	55.22	1.4:1.3:3.3

Figure 4 shows the atomic percentage of Cu, Sn, and Se for the Cu_2SnSe_3 thin films composition as a function of different annealing temperatures. The results show the good atomic percentages of the compositions were observed at lower annealing temperature. However, when annealing temperature is higher, it can be seen that atomic percentage of Cu and Sn become equal each other and show the increasing in Se percentage due to the loss of neither Cu nor Sn in the composition. On the other hand, Figure 5 revealed that the value for weight fraction of Cu will decrease when annealing temperature were employed to the Cu_2SnSe_3 thin films. This will influence to increasing in Sn and Se weight fraction due to the loss of Cu that can be referred in Figure 5 below.

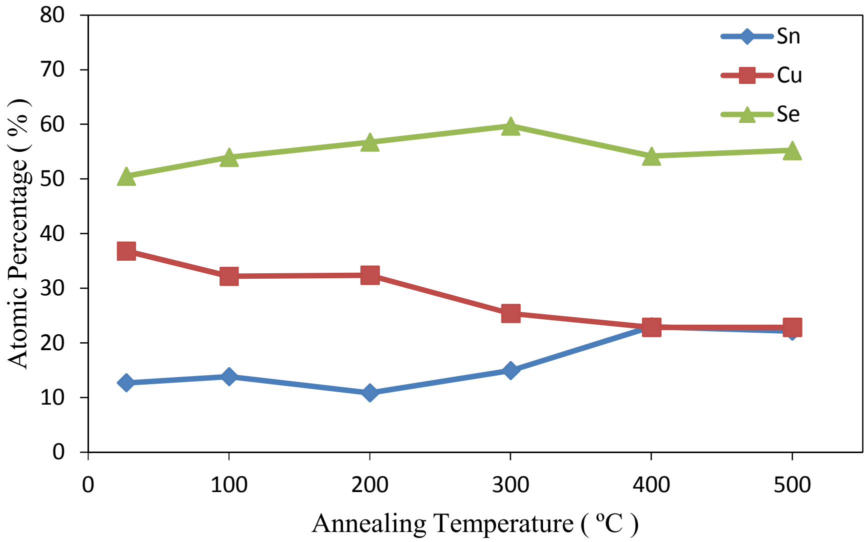

Figure 4: Atomic percentage of Cu, Sn, and Se for the film as a function of different annealing temperature.

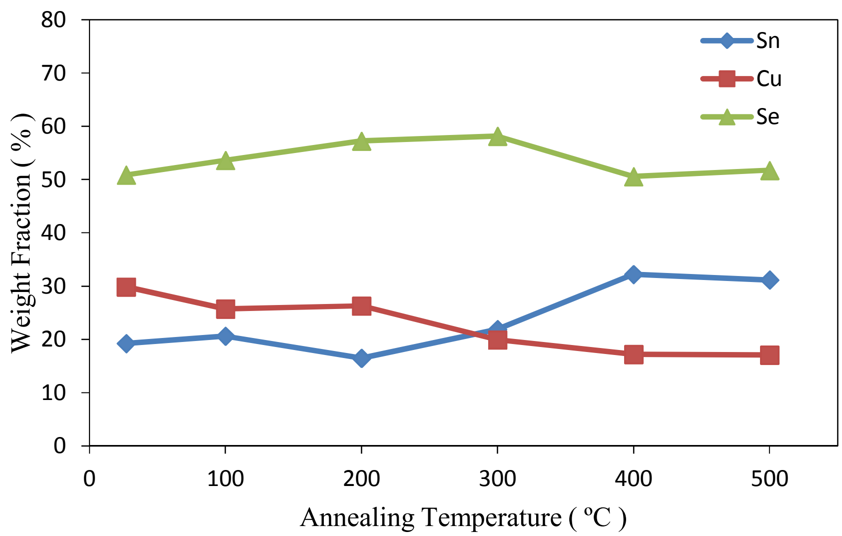

Figure 5: Weight fraction of Cu, Sn, and Se for the film as a function of different annealing temperature.

3.3 I-V Characteristics

Comparison between I-V characteristics of Cu_2SnSe_3 thin films deposited on glass substrate at different annealing temperature is illustrated in Figure 6. Each curve shows a linear response between current and voltage indicating good Ohmic contact with the Cu_2SnSe_3 thin films. Inspection of the graph also shows that gradient of the I-V graph increases with increasing annealing temperature. This phenomenon occurs since the resistance in the thin films was also decreases with increasing annealing temperature and the graph plotted on Figure 6 proven the Ohm's law that the current increase correspondingly to voltage increases because according to Ohm's law, voltage and current values are proportional with resistance values. On the other hand, each graph shows the linear increases indicating that I-V relationship is in good Ohmic contact with the Cu_2SnSe_3 thin films.

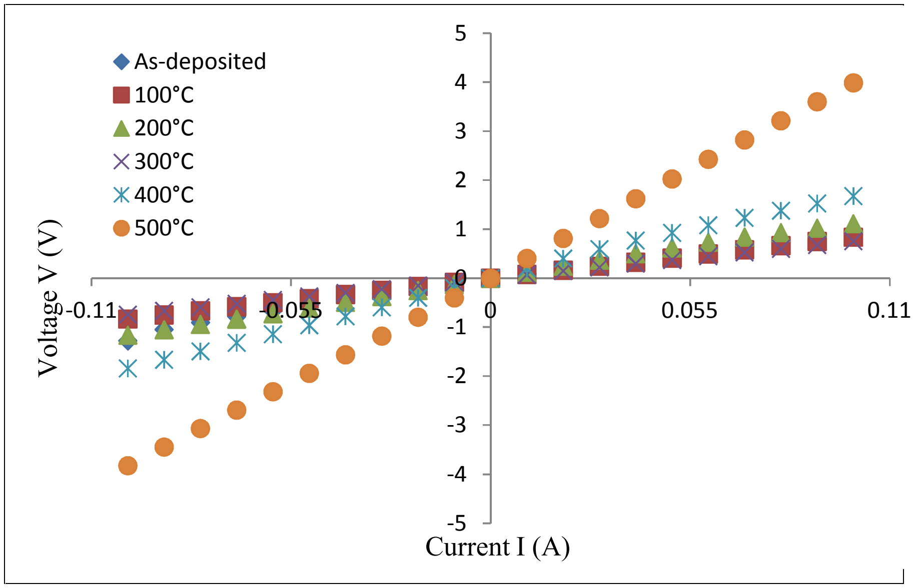

Figure 6: Comparison of I-V characteristics of Cu_2SnSe_3 thin films annealed at different temperature.

3.4 Electrical Resistivity and Conductivity

In this study, electrical resistivity and conductivity were estimated from sheet resistance, R_s, and thickness of the sample. The parameters used to measured electrical resistivity and conductivity using Van der Pauw techniques. The electrical resistivity can be calculated easily by inserted the parameters to equation for sheet resistivity expressed as:

$$\rho = R_S d \tag{1}$$

where, R_S is the sheet resistance and d is the thickness of the sample. Sheet resistance R_S, were obtained from the two characteristics resistance which is ones applies the DC current, I_{12} into contact 1 and out of contact 2 and ones measures the voltage V_{43} from contact 4 to contact 3 for characteristic resistance R_A. For characteristics resistance R_B, the DC current I_{23} applies into contact 2 and out of contact 3 while measuring the voltage V_{14} from contact 1 to contact 4. These two characteristic resistances calculated by means of the following expressions:

$$R_A = V_{43}/I_{12} \text{ and } R_B = V_{14}/I_{23}. \tag{2}$$

R_A and R_B are related to the sheet resistance R_S through the Van der Pauw equation:

$$\exp(-\pi R_A/R_S) + \exp(-\pi R_B/R_S) = 1 \tag{3}$$

which is can be solved numerically for R_S and inserted into equation 1 to calculate electrical resistivity values. Since, electrical conductivity is the reciprocal of electrical resistivity, the values of electrical conductivity can be determined using the equation expressed as:

$$\sigma = \frac{1}{\rho} \tag{4}$$

where, σ is the electrical conductivity and ρ is the electrical resistivity. The electrical resistivity, electrical conductivity conductivity, reciprocal of temperature, and logarithm of conductivity of Cu_2SnSe_3 thin films corresponding to annealing temperature were summarized in Table 2. Figure 7 shows the electrical resistivity and electrical conductivity as a function of annealing temperature on deposited Cu_2SnSe_3 thin films.

Table 2: Electrical Resistivity and Electrical Conductivity of Cu_2SnSe_3 thin films annealed at different annealing temperature.

Annealing Temperature (°C)	1/T (°C^{-1})	Electrical Resistivity ρ (Ω m)	Electrical Conductivity σ (S m^{-1})	ln Electrical Conductivity σ (S m^{-1})
27	0.037	8.50×10^{-5}	1.18×10^{4}	9.373
100	0.010	6.40×10^{-5}	1.15×10^{4}	9.657
200	0.005	8.89×10^{-5}	1.12×10^{4}	9.328
300	0.003	9.22×10^{-5}	1.08×10^{4}	9.292
400	0.025	1.19×10^{-4}	8.40×10^{3}	9.036
500	0.002	2.48×10^{-4}	4.03×10^{3}	8.302

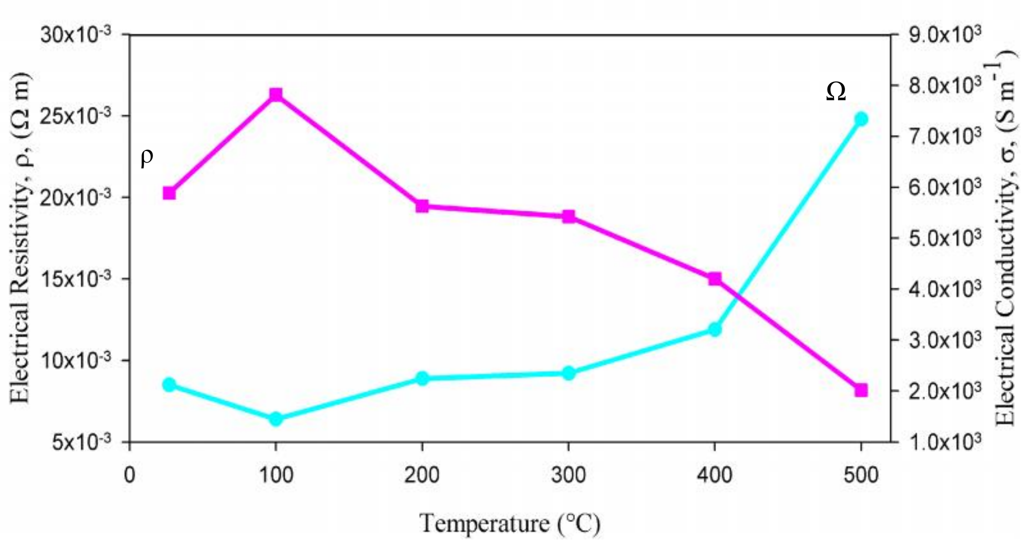

Figure 7: Plot of electrical resistivity and electrical conductivity for Cu_2SnSe_3 thin films annealed at different temperature.

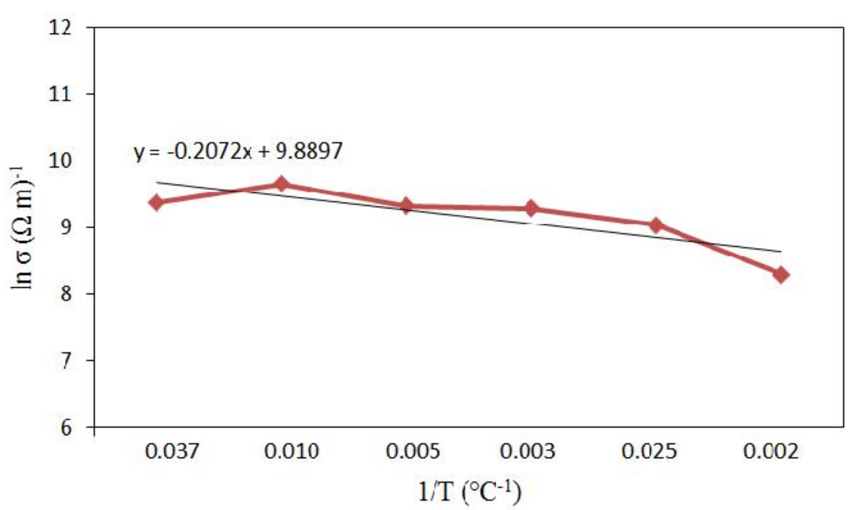

Figure 8: Plot of ln σ versus 1/T for Cu_2SnSe_3 thin films annealed at different temperature.

The result shows the electrical resistivity decreases with increasing annealing temperature. From result shown in Figure 7 below, it is revealed that the optimum annealing temperature for the highest value of electrical conductivity and lowest electrical resistivity is at 500 °C because after annealing temperature increase to higher value, the electrical conductivity values is drastically increased and this is shows the characteristics of extrinsic semiconductor which suggests the presence of impurities on Cu_2SnSe_3 thin film compounds. This is in agreement with composition elemental analysis by EDX suggest that losing in Cu content will decreasing the electrical conductivity values as a function of annealing temperature employed.

From the variation of ln σ versus 1/T graph, we can calculate the activation energy, ΔE_a since the graph shows the straight line plots, which is indicating the deposited Cu_2SnSe_3 thin films is through an activated process. The activation energy of Cu_2SnSe_3 thin films with different annealing temperature were obtained by using equation expressed as:

$$\ln_{\sigma} = \ln_{\sigma o} - \left(\frac{\Delta E_a}{-kT}\right) \quad (5)$$

where, σ is the electrical conductivity, ΔE_a is the activation energy, T is the temperature and k is Boltzmann's constant. This equation was compared with $y = mx + c$, from plots of ln σ versus 1/T graph to obtain activation energy, ΔE_a, of the thin films. Finally, the activation energy, ΔE_a, is found to be 0.018 eV.

4. CONCLUSIONS

In conclusions, Cu_2SnSe_3 films show a strong dependence on the film deposition technique, annealing condition and annealing temperature. The EDX analysis revealed that the annealed thin films of Cu_2SnSe_3 posses the nearly stoichiometric composition earlier where atomic percentage for each element Cu, Sn, and Se corresponding to 26%, 25%, and 49%, respectively. Films annealed at 100°C show the best atomic percentage in stoichiometric ratio among the others. But, it revealed that an excess of selenium element in all the thin film samples and small volume of tin since the loss of copper element with increasing annealing temperature. I-V characteristics result shows good Ohmic contact by using Van der Pauw method and shows an increases with increasing annealing temperature. Conductivity of the samples ranged from 4.03×10^{-3} to 1.18×10^{-4} S m^{-1}. Calculated activation energy ΔE_a, is found to be 0.018 eV. However, it is still hoped that this report serves as a guideline for further research on other physical properties of the material and provides contributions in electrical information on the future studies.

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