Influence of Annealing Temperature on the Physical Properties of Cu₂SnSe₃ Thin Films Prepared by Thermal Vacuum Evaporation Technique

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Authors’ contributions

This work was carried out in collaboration between all authors. Author MASMY designed the study, performed the statistical analysis, wrote the protocol, wrote the first draft of the manuscript and managed literature searches. Authors ZAT and WMMY managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

ABSTRACT

Ternary compound of semiconductor polycrystals Copper Tin Selenide, Cu₂SnSe₃, 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 Cu₂SnSe₃ thin films were close to the ideal stoichiometric value 2:1:3. The annealed Cu₂SnSe₃ thin films were found to be p-type semiconductor with activation energy, ΔEa, of 0.018 eV obtained from I-V characteristic analysis.

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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]. Bulk samples of Cu$_2$SnSe$_3$, 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$_2$SnSe$_3$ has been investigated by means of the Rietveld method and revealed that the films were structured in mixed phase between cubic space group F-43 m (no. 216) and orthorhombic space group P n m a (no. 62) [5,6].

Bulk samples of Cu$_2$SnSe$_3$ 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], electrodeless deposition, to the simplest method of chemical bath deposition [13].

It is known that Cu$_2$SnSe$_3$ thin film’s surface and electrical properties are very sensitive to the preparation conditions and method of depositions. The composition of Cu$_2$SnSe$_3$ 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$_2$SnSe$_3$ thin films annealed at different annealing temperatures prepared by vacuum thermal evaporation. The chemical composition and elemental analysis of Cu$_2$SnSe$_3$ thin films annealed at different temperatures were also investigated and reported.

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$_2$SnSe$_3$ 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$^{-6}$ 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.

RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy (SEM)

In most cases, morphology of Cu$_2$SnSe$_3$ thin films has been investigated by using scanning electron microscope (SEM). With the help of SEM images, one can correlate the electrical behaviour, crystallinity, mechanical properties, etc. of Cu$_2$SnSe$_3$ thin films with is surface morphology. Morphological investigations were carried out on six samples of Cu$_2$SnSe$_3$ thin films.
annealed at different temperatures using scanning electron microscope (SEM). All micrographs were taken at 2,000x and 10,000x magnification and shown in Figs. 1 and 2 respectively. The shape of Cu$_2$SnSe$_3$ thin films in Figs. 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 Figs. 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. [10] on effect of bath temperature on the electrodeposition of copper tin selenide films from aqueous solution. It is well known that morphology of semiconductor thin films is influenced by the method of synthesis and the annealing temperature employed.

Dong et al. [8] reported the microstructure shape of sputtered Cu$_2$SnSe$_3$ thin films indicated the existence of different phases. 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$_2$SnSe$_3$ 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.

Fig. 1(e) presents Cu$_2$SnSe$_3$ thin films annealed at 400ºC revealed that the microcracks has been taking part. It is observed that the surface of as-deposited Cu$_2$SnSe$_3$ thin films was nearly uniform until annealed at 300ºC. However, Cu$_2$SnSe$_3$ thin films annealed at 400ºC and 500ºC show some microcracks occurred on the films. It is believed that the sample of Cu$_2$SnSe$_3$ thin films is not stable when dealing with high annealing temperature employed (400ºC and 500ºC). The Cu$_2$SnSe$_3$ 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$_2$SnSe$_3$ thin films since it was very thin, they easily to evaporate back and removed with the flowed nitrogen gas.

Fig. 1. SEM micrograph of 2000x magnification of Cu$_2$SnSe$_3$ thin film deposited on glass substrate with annealing temperature for (a) as-deposited (b) 100ºC (c) 200ºC (d) 300ºC (e) 400ºC and (f) 500ºC
3.2 Energy Dispersive X-Ray Analysis (EDX)

Fig. 3 illustrates the EDX spectrum pattern of the as-deposited and annealed Cu$_2$SnSe$_3$ 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$_2$SnSe$_3$ 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$_2$SnSe$_3$ which does not undergo annealing shows the best stoichiometric (2:1:3) ratio as can be seen in Fig. 3. However, the EDX spectrum shows an excess of selenium element in all the thin film samples. These phenomena were also reported by Khatalingam et al. [14] on effect of deposition potential in zinc selenide films.

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.

As can be seen in Fig. 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. [12] on effect of annealing temperature and illumination of light on copper tin selenide thin films. It is acknowledged that annealing temperature more than 300°C will cause some elemental loss in Cu$_2$SnSe$_3$ thin films. The atomic percentages of each element in Cu$_2$SnSe$_3$ 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$_2$SnSe$_3$ at various annealing temperature can be easily indicates the best stoichiometric of elements which verifies composition of Cu$_2$SnSe$_3$ phase is as-deposited films.
Fig. 3. EDX spectrum of Cu$_2$SnSe$_3$ thin films as-deposited and annealed at (100, 200, 300, 400 and 500°C)

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 |
|-----------------------|------------------------------------------|------------------|
| As-deposited           | 36.80, 12.71, 50.49                      | 2.2:0.8:3.0      |
| 100°C                 | 32.19, 13.82, 53.99                      | 1.9:0.9:3.2      |
| 200°C                 | 32.39, 10.86, 56.75                      | 1.9:0.7:3.4      |
| 300°C                 | 25.39, 14.93, 59.67                      | 1.5:0.9:3.6      |
| 400°C                 | 22.87, 22.96, 54.17                      | 1.4:1:4:3.2      |
| 500°C                 | 22.65, 22.13, 55.22                      | 1.4:1:3:3.3      |

Fig. 4 shows the atomic percentage of Cu, Sn, and Se for the Cu$_2$SnSe$_3$ 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, Fig. 5 revealed that the value for weight fraction of Cu will decrease when annealing temperature were employed to the Cu$_2$SnSe$_3$ thin films. This will influence to increasing in Sn and Se weight fraction due to the loss of Cu that can be referred in Fig. 5.
3.3 I-V Characteristics

Comparison between I-V characteristics of Cu$_2$SnSe$_3$ thin films deposited on glass substrate at different annealing temperature is illustrated in Fig. 6. Each curve shows a linear response between current and voltage indicating good Ohmic contact with the Cu$_2$SnSe$_3$ 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 Fig. 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$_2$SnSe$_3$ thin films.
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:

\[
R_A = \frac{V_{43}}{I_{12}} \quad \text{and} \quad R_B = \frac{V_{14}}{I_{23}} \tag{2}
\]

\( R_A \) 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:

\[
\sigma = \frac{1}{\rho} \tag{4}
\]

Fig. 6. Comparison of I-V characteristics of \( \text{Cu}_2\text{SnSe}_3 \) thin films annealed at different temperature.

The result shows the electrical resistivity decreases with increasing annealing temperature. From result shown in Fig. 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 \( \text{Cu}_2\text{SnSe}_3 \) thin film compounds.
Table 2. Electrical resistivity and electrical conductivity of Cu$_2$SnSe$_3$ thin films annealed at different annealing temperature

| Annealing temperature (°C) | 1/T (°C$^{-1}$) | Electrical resistivity $\rho$ (Ω m) | Electrical conductivity $\sigma$ (S m$^{-1}$) | ln electrical conductivity $\sigma$ (S m$^{-1}$) |
|---------------------------|-----------------|--------------------------------------|-----------------------------------------------|---------------------------------------------|
| 27                        | 0.037           | 8.50 x 10$^{-5}$                     | 1.18 x 10$^4$                                  | 9.373                                       |
| 100                       | 0.010           | 6.40 x 10$^{-5}$                     | 1.15 x 10$^4$                                  | 9.657                                       |
| 200                       | 0.005           | 8.89 x 10$^{-5}$                     | 1.12 x 10$^4$                                  | 9.328                                       |
| 300                       | 0.003           | 9.22 x 10$^{-5}$                     | 1.08 x 10$^4$                                  | 9.292                                       |
| 400                       | 0.025           | 1.19 x 10$^{-4}$                     | 8.40 x 10$^3$                                  | 9.036                                       |
| 500                       | 0.002           | 2.48 x 10$^{-4}$                     | 4.03 x 10$^3$                                  | 8.302                                       |

Fig. 7. Plot of electrical resistivity and electrical conductivity for Cu$_2$SnSe$_3$ thin films annealed at different temperature

Fig. 8. Plot of ln $\sigma$ versus 1/T for Cu$_2$SnSe$_3$ thin films annealed at different temperature
This is in agreement with composition elemental analysis by EDX 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, since the graph shows the straight line plots, which is indicating the deposited Cu₂SnSe₃ thin films is through an activated process. The activation energy of Cu₂SnSe₃ thin films with different annealing temperature were obtained by using equation expressed as:

\[ \ln \sigma = \ln \sigma_0 - \left( \frac{-\Delta E_a}{kT} \right) \]  \hspace{1cm} (5)

where, \( \sigma \) is the electrical conductivity, \( \Delta E_a \) 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 \( \sigma \) versus 1/T graph to obtain activation energy, \( \Delta E_a \), of the thin films. Finally, the activation energy, \( \Delta E_a \), is found to be 0.018 eV.

4. CONCLUSIONS

In conclusions, Cu₂SnSe₃ 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 Cu₂SnSe₃ 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 \( 4.03 \times 10^{-3} \) to \( 1.18 \times 10^{-4} \) S m⁻¹. Calculated activation energy \( \Delta E_a \), 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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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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