Effect of Copper Concentration on Characterization of 
\(\text{Cu}_2\text{Zn}_{0.8}\text{Cd}_{0.2}\text{SnS}_4\) Pentrary Alloy Nanostructures

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Abstract. \(\text{Cu}_2\text{Zn}_{0.8}\text{Cd}_{0.2}\text{SnS}_4\) pentrary alloy nanostructure were prepared and deposited on glass substrates with different copper concentrations (0.3, 0.5, 0.7 and 0.9 mol/L) using Sol gel – spin coating method. Morphological and analytical studies were investigated by Field Emission-Scanning Electron Microscope (FE-SEM), atomic force microscopy (AFM). It is found that the average grain size of \(\text{Cu}_2\text{Zn}_{0.8}\text{Cd}_{0.2}\text{SnS}_4\) pentrary alloy nanostructure is 51.92 to 76.43 nm for the thin films prepared at 0.3, 0.5, 0.7 and 0.9 mol/L respectively.

Introduction

To meet the increasing demand for energy and overcome to materials the limited availability of fossil, photovoltaic solar energy production, will become increasingly important. Among different types of solar cells, the \(\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2\) (CIGS) thin-film solar cell have attracted much attention in this regard due to its high power conversion efficiency and stability[1,2]. But this compound contains expensive materials such as (In)) and (Ga) and toxic element such as (Se) [3]. This could impede further development in the field of thin-film solar cells. To overcome these limitations made some efforts to find low-cost, non-toxic and earth-abundant elements. \(\text{Cu}_2\text{CdSnS}_4\) (CCTS) and \(\text{Cu}_2\text{ZnSnS}_4\) (CZTS), as a potential material to substitute CIGS, has attracted great interest due to its direct band gap (\(\text{E}_g=1.4-1.5\ \text{eV}\)) with high absorption coefficient of \(10^4\ \text{cm}^{-1}\), show P-type conductivity and abundant in the earth’s crust [4]. From these unique features, CZTS is expected to be one of the promising materials for thin film solar cell. Therefore, if we can use CZTS film as absorber of solar cells, we will be free from both of the resource saving problem and the environmental pollution [5].

Many experimental techniques have been employed for preparing CZTS thin films for absorber layers, such as pulsed laser deposition technique [6], fast co-evaporation [7], sputtering-sulfurization method [8], sputtering [9], thermal evaporation [10], electrodeposition [11,12], spray pyrolysis [13] and hot injection method [14].

Yeh et al.[15] used sol-gel method to deposit CZTS film on glass sodium substrate Without sulfurization treatment, thin film annealed at 280 °C. The CZTS films was observed to be grown well with good crystalline. Kumar et al [16] prepared CZTS absorber layers by pyrolysis deposition onto soda-lime glass (SLG) substrate at (643-683) °C their results showed that a polycrystalline CZTS films. The band gap of the film was in the range of (1.40-1.45) eV. Kasim Uthman Isah el.al.[17] prepared CZTS by sulfurization of thermally evaporated metallic precursors on glass substrates. The Zn and Sn thicknesses were constant at 300nm and 200nm respectively. while the Cu thicknesses were 100, 150 and 200 nm. The energy gap increased with increasing copper content from (1.49 -1.51 )eV. Showed X-ray diffraction that polycrystalline films exhibiting Kesterite structures with preferential orientation along (112) direction. Grain size increases with increasing Cu/(Zn + Sn) ratio.

Experimental

All chemicals of analytical grade were received from Sigma-Aldrich Company and prepared at Institute of Nano Electronic Engineering (INEE) in University Malaysia Perlis (UniMAP). The
Cu$_2$Zn$_{0.8}$Cd$_{0.2}$SnS$_4$ pentryary alloy nanostructures were deposited on the glass substrates by the sol-gel spin coating methods. The solution of the Cu$_2$Zn$_{0.8}$Cd$_{0.2}$SnS$_4$ precursors were prepared from different molarity copper (II) chloride monohydrate 0.3, 0.5, 0.7, and 0.9 mol/L and zinc (II) acetate dehydrate (0.3mol/L), tin (II) chloride dehydrate (0.3), cadmium (II) chloride (0.3mol/L), thiourea (0.3mol/L), 2-methoxyethanol (2-metho), and monoethanolamine (MEA). The 2-metho and MEA were used as the solvent and the stabilizer, respectively. The solution was stirred at 50°C to completely dissolve the metal compounds, during stirring the milk solution became a yellow. After that, the solution was dropped onto the glass substrate that was rotating at 2500rpm for 30s. After deposition by spin coating, the films were dried at 250°C for 80min on a hot plate. The coating and drying processes were repeated for seven times to obtain ~1 µm thick films.

Surface morphologies of Cu$_2$Zn$_{0.8}$Cd$_{0.2}$SnS$_4$ thin films were investigated using Field Emission-Scanning Electron Microscope (FE-SEM) system (NOVA NANO SEM 450). Thin films morphology was analyzed by atomic force microscope (AFM).

**Result and discussion**

**Analysis and characterization.** We have investigated the morphology of Cu$_2$Zn$_{0.8}$Cd$_{0.2}$SnS$_4$ nanostructure at various copper concentrations using FE-SEM. The FE-SEM images in Fig. 1 (a) and (b) The films uniformly covered the substrate and the observable small grains involved in the crystal formation confirm the nanostructure nature of the Cu$_2$Zn$_{0.8}$Cd$_{0.2}$SnS$_4$ films. Fig. 1(c) and (d) show surface FE-SEM images. The grain sizes appear spherical in shape and voids and pores of a few. Also we find that the grain sizes and the densities of the Cu$_2$Zn$_{0.8}$Cd$_{0.2}$SnS$_4$ films increase with the increase in Cu$_{2+}$ concentration in the solution from 0.3 to 0.9 mol/L and this agree with reported earlier for copper variation in spray deposited CZTS films [18]. It is well known that the conversion efficiency of polycrystalline solar cells increases with increasing grain size in the absorber materials, so large grain size is advantageous to improving the performance of photovoltaic devices [19].

![Fig. 2 FE-SEM images of Cu$_2$Zn$_{0.8}$Cd$_{0.2}$SnS$_4$ pentryary alloy nanostructure at various copper concentrations a(0.3 mol/L) b(0.5 mol/L), c(0.7mol/L), d(0.9 mol/L)](image)

The Cu$_2$Zn$_{0.8}$Cd$_{0.2}$SnS$_4$ thin films were morphologically characterized using atomic force microscopy. Figure 2 shows three dimensional AFM images for Cu$_2$Zn$_{0.8}$Cd$_{0.2}$SnS$_4$ thin films. These thin films were deposited at different molarity copper 0.3, 0.5, 0.7, and 0.9 mol/L. The AFM images prove that the films have a smooth surface, good adherence to the substrate, and narrow particles size distribution. The images also demonstrated that the surface roughness increases with increased molarity copper with increased root mean square (rms) roughness, due to increased crystal sizes (Table 2). The results also indicate that the surface quality of the Cu$_2$Zn$_{0.8}$Cd$_{0.2}$SnS$_4$ nanocrystals improves with molar concentration.
Fig. 3. 3D-AFM images of the surface of the Cu$_2$Zn$_{0.8}$Cd$_{0.2}$SnS$_4$ nanocrystals prepared at various molarity copper 0.3, 0.5, 0.7, and 0.9 mol/L.

Table 2 Average crystal size from AFM (Cs), roughness of Cu$_2$Zn$_{0.8}$Cd$_{0.2}$SnS$_4$ pentary alloy

<table>
<thead>
<tr>
<th>Molar concentration (mol/L)</th>
<th>C$_s$ (nm)</th>
<th>roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>51.92</td>
<td>0.318</td>
</tr>
<tr>
<td>0.5</td>
<td>58.60</td>
<td>1.34</td>
</tr>
<tr>
<td>0.7</td>
<td>65.56</td>
<td>1.43</td>
</tr>
<tr>
<td>0.9</td>
<td>76.43</td>
<td>1.63</td>
</tr>
</tbody>
</table>

Conclusion

The films show an increase in grain size with increase in Cu concentration, which indicates an enhancement of the grain growth under Cu-rich conditions. The images also demonstrated that the surface roughness increases with increased molarity copper with increased root mean square (rms) roughness.

References


