Characterization of Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ nanostructures


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Abstract. Pentary alloys of Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ nanostructures have been grown on glass substrate using sol-gel technique. The concentration of Cd has showed obvious effect for characterization study. Field emission-scanning electron microscope (FE-SEM) and atomic force microscope (AFM) have provide nanostructures of the utilized alloys. Those alloys give good impression about increasing the grain size with Cd concentration increasing, that lead to increasing the surface coarse.

Introduction

Cu$_2$ZnSnS$_4$ (CZTS) compound emerging solar cell material with a suitable band gap of 1.5 eV and an optimal optical absorption coefficient of 10$^4$cm$^{-1}$in the visible region. It is composed of earth-abundant, cheap and non-toxic elements[1,2,3].The structure of CZTS has shown promise as a replacement material for CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS),and CdTe in thin film solar cells by replacing (In) with (Zn), (Ga) with (Sn), and (Se) with (S)[4]. Quaternary CZTS compound crystallizes in the kesterite structure. But possible existence of the structurally similar stannite structure cannot be ruled out, because of kesterite structure of CZTS differs about stannite structure only in the copper and zinc [5,6]. Newly, a metastable wurtzite phase of CZTS has been synthesized in the form of nanocrystals. Crystallizing this material in the form of a wurtzite structure generally offers flexibility over stoichiometry control and also facilitates the nanocrystals to grow in 1D morphology along the anisotropic c-axis direction [7,8]. The CdS film buffer layer is an n-type is invariably made use in the Manufacturing of the solar cells. Rusu et al. used elastic rebound detection analysis to show that the Cd and S spreads into the absorber layer in CdS/CuGaSe$_2$ chalcopyrite solar cells [9]. Cadmium and sulfur concentrations are found to be more than 0.1% in deep inside the absorber layer. Similar spreads of Cd and S into the absorber layer CdS/Cu$_2$ZnSnS$_4$ solar cells can lead to the formation of a compound Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ solid solution in the interface. Depending on the Cd concentration, changes in the drain layer thickness are expected that can alter the charge transport kinetics across the p-n junction. It is important to study the band gap variations, charge transport properties and photoconversion efficiencies of Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ layers in order to increase the rate of the solar cell efficiency.

On other hand, B.S.Pawar et al. [10] have prepared CZTS thin films by using –step electrodeposition method. The estimated optical band gap energy was 2.8eV. M. Altosaar et al [11] have reported the fabrication of Cu$_2$Zn$_{1-x}$Cd$_x$Sn$_4$(Se$_{1-y}$S$_y$)$_4$ solar cells with the Cu$_2$Zn$_{1-x}$Cd$_x$Sn$_4$(Se$_{1-y}$S$_y$)$_4$ absorber layer were prepared from binary compounds in the liquid phase of flux material (KI) in evacuated quartz ampoules. The structure of the solar cell was graphite/Cu$_2$Zn$_{1-x}$Cd$_x$Sn$_4$(Se$_{1-y}$S$_y$)$_4$/CdS/ZnO. N. Kamoun, H. Bouzouita el al. [12] have deposited CZTS thin films by spray pyrolysis technique. Prashant K. Sarswat et al.

Several methods have been used to prepare CZTS thin films for absorber layer, including thermal and electron-beam evaporation[13], electrode deposition [14], pulsed laser...
deposition[15], co-evaporation[16], DC and RF magnetron sputtering[17], thermal evaporation[18], chemical vapor deposition, spray pyrolysis[19].

In this study, we investigate an alternative synthesis route for the preparation of a Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ thin film for a photovoltaic absorber layers by sol-gel spin coating method without sulfurization. For the first time to prepared this Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ thin film using a sol-gel spin coating method on glass substrate and study its characteristics change with the values of x.

**Experimental process**

The Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ alloy thin film were deposited on glass substrate using the sol-gel methods. First solution of the Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ precursors were prepared from copper (II) chloride dehydrate, zinc (II) chloride dehydrate, tin(II) chloride dehydrate, thiourea, 2-methoxyethanol (2-metho) and monoethanolamine (MEA). The 2-metho and MEA were used as the solvent and the stabilizer, respectively. The mole ratios of Cu, (Zn +Cd), Sn, and S in the solution are 2:1:1:4. For obtaining the solution with the different cadmium concentration, the mole ratios of Cd to (Zn +Cd) in the solution vary according to the values of X as 0, 0.2, 0.4, 0.6, 0.8, 1. 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 and measured of the grain size of CCZTS thin films were investigated using Field emission-scanning electron microscope (FE-SEM). Thin films morphology was analyzed by atomic force microscope (AFM).

**Result and discussion**

Figure 1 shows FE-SEM images of sol-gel deposited Cu$_2$Cd$_x$Zn$_{1-x}$SnS$_4$ with the different Cd contents, the mole ratios of Cd to(Cd + Zn) in the solution are varied as( 0, 0.2, 0.4, 0.6, 0.8, 1). The films uniformly covered the substrate and their thickness was around 600nm. Show nanostructure morphology over the entire composition range. The measured grain size of the nanostructure are 26.15nm for Cu$_2$ZnSnS$_4$, 27.37nm for Cu$_2$Cd$_{0.2}$Zn$_{0.8}$SnS$_4$, 35.88nm for Cu$_2$Cd$_{0.4}$Zn$_{0.6}$SnS$_4$, 37.09nm for Cu$_2$Cd$_{0.6}$Zn$_{0.4}$SnS$_4$, 42.62nm for Cu$_2$Cd$_{0.8}$Zn$_{0.2}$SnS$_4$ and 56.18nm for Cu$_2$CdSnS$_4$. The grain size increases with increasing cadmium content this result corresponds with that reported by Karthik Ramasamy et al[20]. A likely explanation for this behaviour is that the enhanced reactivity of cadmium as compared with zinc in more rapid nuclei formation and growth [21]. It is well known that the efficiency of solar cells increases with increasing grain size in the absorber layer, and therefore, the larger grains are required for the fabrication of high efficiency solar cell Refs [22,23]. The rations elements of the prepared films By EDX analysis showing that is copper-poor, zinc-rich and slightly sulphur poor [24,25].The presence of several studies indicates that copper-poor, zinc-rich CZTS films. The have higher p-type conductivity and result increase the efficiency of solar cells [26].

The AFM surface images of a 1 × 1 µm area of nanostructured Cu$_2$Cd$_x$Zn$_{1-x}$SnS$_4$ thin films prepared using the Sol-gel for different cadmium concentration are in shown Figure (2). The images established that the films have a smooth surface. It was observed from the images that roughness increases with increasing cadmium concentration , It was found that the average roughness (Roughness Average) surface of the films is equal to (2.03,2.56,2.70,2.74,3.55,6.75) nm at (x=0,0.2,0.4,0.6,0.8,1) respectively . This result agrees with that reported by Hossain et al. The results also indicate that the surface quality of the Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ thin films improves with increasing cadmium concentration.
Fig. 1: Shows result of FESEM image of Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ at various value x: A(0), B(0.2), C(0.4), D(0.6), E(0.8), f(1).

Fig. 2: Shows 3D- of AFM images for the surface of Cu$_2$Zn$_{1-x}$Cd$_x$SnS$_4$ thin films prepared at various value x: A(0), B(0.2), C(0.4), D(0.6), E(0.8), f(1).
Summary

Cu$_2$ZnSnS$_4$ thin films were successfully formed by sol-gel spin coating technique. The morphological characterization shows that the average roughness value increases with increasing cadmium content. The rations elements of the prepared films by EDX analysis, showing that is copper-poor, zinc-rich and slightly sulphur poor.

References


