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Influence of pH on structural, optical and electrical properties of solution processed Cu_2ZnSnS_4 thin film absorbers

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ABSTRACT

Cu_2ZnSnS_4 (CZTS) films were obtained by the dip-coating method. The effect of different pH values 4.0, 4.5, and 5.0 on the structural, morphological, optical and electrical properties of samples was investigated by XRD, SEM, UV–vis and Hall Effect measurements. The XRD spectra showed that the characteristic peak intensity of CZTS semiconductor increased with increasing pH value of the precursor solution. It was also observed that increased pH values resulted in a significant reduction in the amount of impurity phases of the films. The UV–vis studies revealed a significant increase in the optical absorption of thin films in the visible region as the pH value of the solution was increased. The band gap of the samples shifted from 2.0 to 1.38 eV by increasing the pH value. The electrical resistivity of the films was found to vary from 2.8×10^{-2} to 3.1 Ω cm, depending on its pH value.

1. Introduction

Currently, non toxic indium free CZTS is the most advantageous low cost thin film material for the solar cell applications due to its optimal energy band gap of ~1.5 eV [1]. A record conversion efficiency of 12.6% was obtained for CZTS based thin film solar cell [2].

Many conventional film preparation techniques have been adopted to obtain CZTS such as electro-deposition, spray pyrolysis, radio-frequency (RF) and direct-current (DC) magnetron sputtering, evaporation, pulsed laser deposition, solvothermal, and sol–gel [3–10]. However, the most appealing one is the solution-based sol–gel method to fabricate the thin films because of being a simple and low cost film preparation technique, being coated readily by large area substrates, having easily applicable additives, and being prepared under non-vacuum conditions by spin cast or dip coating. Particularly, for the last property, an example of the CZTS thin films with conversion efficiencies of 3.01 and 5.6% makes non-vacuum solution based methods a choice of our interest [10,11].

Great research effort has been made to improve the physical properties of the CZTS by optimizing the various growth conditions, such as Na-doping concentration and metal salt ratio [12–13]. However, it is still needed to investigate the solution based CZTS thin films. For instance, the pH of solution can affect the physical properties of Mn-doped zinc oxide ($Zn_{1-x}Mn_xO$), copper sulfide (Cu_xS), and zinc sulfide (ZnS) thin films [14–16].

In this study, we report the effects of different pH values of solutions on the structural, optical and electrical properties CZTS thin films, which were deposited by the sol–gel dip coating method.

2. Experimental

2.1. Preparation of CZTS films

Copper (III) nitrate hemipentahydrate ($Cu(NO_3)_2\cdot2.5H_2O$), zinc acetate dihydrate ($Zn(CH_3COO)_2\cdot2H_2O$), tin (II) ethylhexanoate ($(CH_3(CH_2)_3CH(C_2H_5)CO_2)_2Sn$), and thiourea ($CH_4N_2S$) were separately dissolved in a mixture of ethanol and glacial acetic acid. These prepared solutions were mixed at room temperature. To regulate pH values, it was adjusted by adding a few drops of triethanolamine to the final solutions. The molar ratios of the Cu/Zn/Sn/S elements in the solutions were 2/1/1/4. Three different solutions with the pH values of 4.0, 4.5, and 5.0 were obtained in that way. Detail of the solution and film preparation can be found in the previous work [17]. The tentative reaction mechanism for the formation of CZTS thin films during the annealing process can be written as follows.

$$Cu(NO_3)_2\cdot2.5H_2O\rightarrow Cu^{2+}+2NO_3^{-} \quad (1)$$

$$Zn(CH_3COO)_2\cdot2H_2O\rightarrow Zn^{2+}+2CH_3COO^{-} \quad (2)$$

$$CH_3(CH_2)_3CH(C_2H_5)CO_2)_2Sn\rightarrow Sn^{2+}+2CH_3(CH_2)_3CH(C_2H_5)COO^{-} \quad (3)$$

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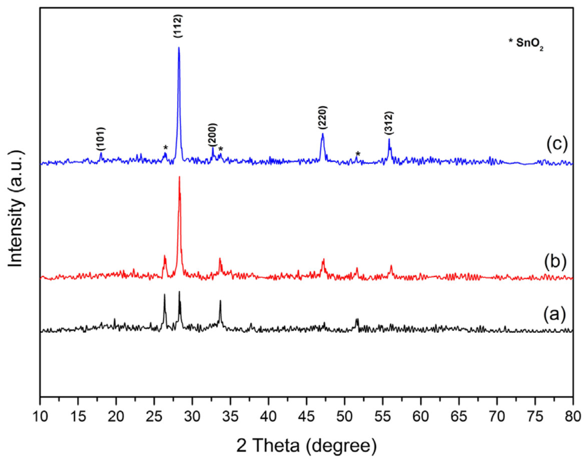
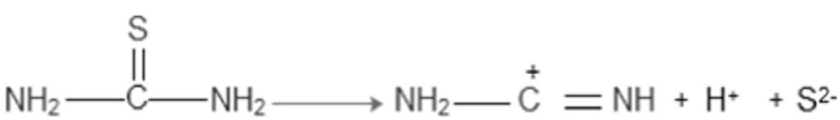


Fig. 1. XRD pattern of the CZTS films obtained with solutions having different pH value.

peaks corresponding to reflections from (101), (112), (200), (220), and (312) planes indicating that the films have kesterite CZTS structure (JCPDS card no. is 26-0575). The observed results are in a good agreement with the previous works [18–19]. According to the XRD results, the peak intensity of (112) plane increases with increasing pH values of the solution from 4.0 to 5.0. This characteristic feature of the peak intensity can also be clearly observed for the (220) and (312) planes as shown in Fig. 1, which means that the crystallization of the films rises as the pH value is increased. It is a fact that the increase in OH^- ions in the solution results in higher pH values. This increase then affects the growth rate. The solution with more OH^- ions than H^+ will accelerate the hydrolysis of CH_4N_2S which then releases sulfur ions to form CZTS composite. Previously, Umnuay et al. [15] were investigated the growth kinetics of Cu_xS thin films by the chemical bath deposition. They later reported that the growth rate of films increases by increasing the pH value. A similar result was also observed for the ZnS thin films by chemical bath deposition [16]. Therefore, one could say that the pH value affects the hydrolysis and condensation behavior of the sol–gel process during gel formation. Besides, the diffraction peaks corresponding to the (110), (101), and (200) planes were also observed. These are belong to the SnO_2 phase (JCPDS card no. is 70-6153). The presence of the SnO_2 impurity phase in CZTS films was also observed elsewhere [17]. The peak intensities of the SnO_2 phase decrease with rising pH values in contrast to the CZTS phase as seen in Fig. 1.



(4)

The overall ionic reaction is as

$$2Cu^{2+} + Zn^{2+} + Sn^{2+} + 4S^{2-} \rightarrow Cu_2ZnSnS_4 \quad (5)$$

2.2. Characterization

A Rigaku Ultima III (Cu Kα, 40 kV, 30 mA, 1.54 Å) X-ray diffraction (XRD) unit was used to determine the phase purity of the film structure. The optical measurements including the absorption spectra of the films were performed in Perkin Elmer 45 UV–vis dual beam spectrometer. Scanning electron microscope (SEM) observations were performed on Zeiss Evo 50 system with an EDX spectrometer (Bruker AXS Microanalysis GmbH), operating at 20 kV. The Hall measurements were performed using the van der Pauw method at room temperature with Ecopia HMS-3000 Hall effect measurement system.

3. Results and discussion

3.1. Structural properties

The different pH values dependent XRD pattern for the CZTS films is shown in Fig. 1. As can be seen in this figure, the diffraction

The EDX measurement was recorded in order to better understanding of structural and compositional properties of CZTS films. The detail of compositional ratios of samples is presented in Table 1. According to the EDX results as given in Table 1, Cu/(Sn+Zn) and Zn/Sn ratios of the prepared samples increase with increasing pH value. The film prepared with a pH value of 5.0 exhibits nearly stoichiometry with 0.93 and 0.94 ratios of Cu/(Sn+Zn) and Zn/Sn, respectively. When the Zn/Sn ratio is below 1 all CZTS films indicate Sn-rich. However, the Zn/Sn ratio found to be increased substantially as the pH value increases. This result is consisted with the XRD results.

As observed in Fig.1, the characteristic peak of SnO_2 phase decreases with increasing the pH value of the solution. The amount of Sn element in the films comparatively determines the formation of SnO_2 phase. Thus, decreasing in the intensity of SnO_2 phase with increasing the pH value can be attributed to the Zn/Sn ratio of the films. The EDX results are also indicated that the sulfur ratio of the films increases by increasing the pH value (see Table 1).

Table 1
EDX results of the CZTS thin films deposited at different pH.

pH of solution	Cu/Zn/Sn/S (at%) in the solution	Cu/Zn/Sn/S (at%) in the film					
		Cu	Zn	Sn	S	Cu/(Zn+Sn)	Zn/Sn
4.0	2/1/1/4	19.22	12.34	32.68	35.76	0.43	0.37
4.5	2/1/1/4	24.68	14.87	20.12	40.33	0.70	0.74
5.0	2/1/1/4	26.13	13.58	14.43	45.86	0.93	0.94