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Influence of stabilizing agent on dip coating of Cu_2ZnSnS_4 thin film

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ABSTRACT

In the present study, Cu_2ZnSnS_4 (CZTS) thin films with different amount of Triethanolamine (0 μl, 30 μl, 150 μl and 300 μl) as a stabilizing agent in 200 ml precursor solution have been synthesized on glass substrate using a simple dip coating technique followed by annealing in nitrogen atmosphere at 300 °C for 1 h with 10 °C/min ramping rate. The influence of different amounts of Triethanolamine (TEA) on CZTS films are assessed through studies on phase formation, structural information, morphology, compositions and band gap energy which are obtained using X-Ray Diffraction, Raman Spectroscopy, Scanning Electron Microscopy, Energy Dispersive Spectroscopy and UV–Vis spectroscopy respectively. 30 μl of TEA addition is found to generate void free evenly spread stoichiometric CZTS film with a narrow Raman CZTS vibrational mode at 329 cm^{-1} and energy band gap of 1.47 eV.

1. Introduction

$CuIn_xGa_{(1-x)}Se_2$ (CIGS) has been in use as absorber material in thin film solar cell from last decade and achieved highest efficiency beyond 20% [1]. Now, Cu_2ZnSnS_4 (CZTS) is researched as an alternative to CIGS for next generation low cost solar cell as it consists of low cost, earth abundant and non-toxic elements. CZTS films can be deposited by several methods such as sputtering [2], e-beam [3], spray pyrolysis [4], electrodeposition [5] and dip coating [6,7], etc. Till now, CZTS solar cells are reported with a maximum power conversion efficiency of 12.6% so far through solution based method using hydrazine hydrate through spin coating [8]. But due to the toxic and explosive nature of hydrazine hydrate, alternative way to synthesize CZTS is needed. Among all these techniques, dip coating is a non-vacuum based technique which has a potential to produce low manufacturing cost thin film solar cells at industrial level. Rajesh et al. proposed the synthesis of CZTS using monoethanolamine (MEA) as stabilizing agent through dip coating technique [9]. Later on Cao et al. fabricated CZTS thin film by dipping the substrate into the precursor solution containing metal salts and thioacetamide with Na_2EDTA and H_2NCONH_2 followed by annealing in Ar + H_2S atmosphere and they investigated the effects of pH and $ZnCl_2$ precursor content on the formation of CZTS [10]. Afterwards, the effect of copper precursor on physical properties of CZTS is also studied by Ferhat Aslan et al. [11]. At the same time, Renato D' Angelo et al. [12] proposed the reaction route for the formation of pure kesterite CZTS by annealing the dip coated film in inert atmosphere without sulfurization. Recently, in our previous work [13] the authors have studied the effect of annealing parameters on phase formation of CZTS (without adding stabilizing agents or any additives in the precursor solution) where five plunges were found necessary for uniform coating and found that annealing at 300 °C for 1 h at a ramping rate of 10 °C/min in N_2 atmosphere is the optimum condition for the formation of phase pure CZTS film.

As per our knowledge till now, there is no study available in the literature on the effect of amount of stabilizing agent on the formation of CZTS through dip coating technique.

In authors' previous work [6], Triethanolamine (TEA) is used as stabilizing agent in the precursor solution instead of Monoethanolamine (MEA) which is earlier reported by Rajesh et al. [9]. K. Majid et al. [14] has reported the ease of non-conducting complex formation of copper salt with MEA, DEA and TEA and found that Cu:ligand ratio in case of MEA and TEA is same but uncharged complex formed can't react further in case of MEA, whereas in case of TEA it can react further, which is essential need for the formation of CZTS. Complexation of copper with the TEA shows that it acts as a multidentate ligand and coordinates via N and O atoms, forming a five membered ring while as MEA and DEA act as bidentate ligand via N and O atoms. Thus, complex formation is more favorable in case of TEA than MEA.

In our previous work, formation mechanism of CZTS is proposed in which formation of CZT complex from individual metallic complexes is needed for the formation of phase pure CZTS. The possible formation mechanism of methanol based CZTS precursor complex can be formulated as follows: [6]

$$Cu^{2+} + Sn^{2+} \overset{Redox}{\rightarrow} Cu^{+} + Sn^{4+}$$

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$$Cu^{+} + n[(NH_2)_2CS] \xrightarrow{\text{Coordination}} [Cu((NH_2)_2CS)_n]^{+}$$

$$Sn^{4+} + n[(NH_2)_2CS] \xrightarrow{\text{Coordination}} [Sn((NH_2)_2CS)_n]^{4+}$$

$$Zn^{2+} + n[(NH_2)_2CS] \xrightarrow{\text{Coordination}} [Zn((NH_2)_2CS)_n]^{2+}$$

$$[Cu((NH_2)_2CS)_n]^{+} + [Sn((NH_2)_2CS)_n]^{4+} + [Zn((NH_2)_2CS)_n]^{2+} \rightarrow [CuZnSn((NH_2)_2CS)_n]^{m+}$$

$$(NH_2)_2CS_{(s)} \xrightarrow{\Delta} NH_4SCN_{(s)} \rightarrow CS_{2\,(g)} + H_2S_{\,(g)} + NH_{3\,(g)}$$

The prime objective of this work is to study the influence of stabilizing agent (Triethanolamine) on phase formation of CZTS through single-plunge dip coating with hydrazine free precursor solution of metal chlorides and thiourea mixed in methanol solvent followed by annealing in nitrogen atmosphere at 300 °C for 1 h with 10 °C/min ramping rate.

2. Experimental

In the present study, dip coating technique is used to synthesize Cu_2ZnSnS_4 (CZTS) films. Precursor solution for the synthesis of CZTS is prepared by dissolving 2:1:1 M ratio of $CuCl_2$ (0.1 M), $SnCl_2$ (0.05 M), and $ZnCl_2$ (0.05 M), separately in methanol. To each of these solutions, TEA (Triethanolamine) is added and stirred well. For comparison purpose with TEA-free CZTS film, one set of above stated three solutions are prepared without TEA. The individual solutions are then mixed together followed by addition of thiourea (0.5 M) and the mixture is stirred well to give a transparent pale yellow solution. The final volume of precursor solution used for the dip coating is 200 ml. This pale yellow solution (precursor solution) is used for forming the CZTS films. To study the influence of the stabilizing agent on the properties of the film, varied TEA quantities are added by keeping the concentrations of all others precursors constant. Different quantity of TEA (0 μl (TEA-free), 10 μl, 50 μl and 100 μl) have been added in each of the chloride solution, and mixed, making the final solution as 0 μl (TEA-free), 30 μl, 150 μl, and 300 μl (0 mM (TEA-free), 1.13 mM, 5.65 mM and 11.3 mM) respectively. In each of these solutions, the succeeding steps are followed accordingly. Glass substrates are cleaned with acetone, ethanol, methanol and deionized water respectively in an ultrasonicator bath for 20 min each. For dip coating, cleaned glass substrates are dipped into the precursor solution for 5 min and then annealed in tubular furnace at 300 °C for 1 h in N_2 atmosphere with 10 °C/min ramping rate in order to study the effect of concentration of TEA on the formation of CZTS film. This optimized annealing parameter is reported earlier [13]. Graphic representation of formation of CZTS is shown in Fig. 1.

Structural characteristics, surface morphology and chemical composition of CZTS films are investigated through X-ray diffraction (XRD) (Bruker Discover D8) with CuK_α radiation ($\lambda = 1.5406$ Å) from 2θ angle 20° to 80° and Field Emission Gun Scanning Electron Microscopy (FEG SEM) (Carl Zeiss Germany, Model Supra-40) equipped with Energy Dispersive X-ray Spectroscopy (EDS) (Oxford Instrument, UK) at an acceleration voltage of 10 KV. Structural information are assessed by Raman Spectrometer (Brucker SENTERRA) with the incident laser light wavelength of 532 nm and band gap calculation of CZTS film is obtained by UV–Vis Spectrophotometer (Perklin Elmer UV–Vis spectrophotometer with integrating sphere) in reflectance and transmittance mode from 500 nm to 1000 nm wavelength range at room temperature.

3. Results and discussion

Dip coating is one of the various wet chemical thin film deposition methods. In this method, substrates are immersed into the precursor solution with certain dwell time and then are withdrawn from the solution. Subsequently, dip coated films are sometimes heat treated in order to evaporate the organic residues and induce crystallization. In

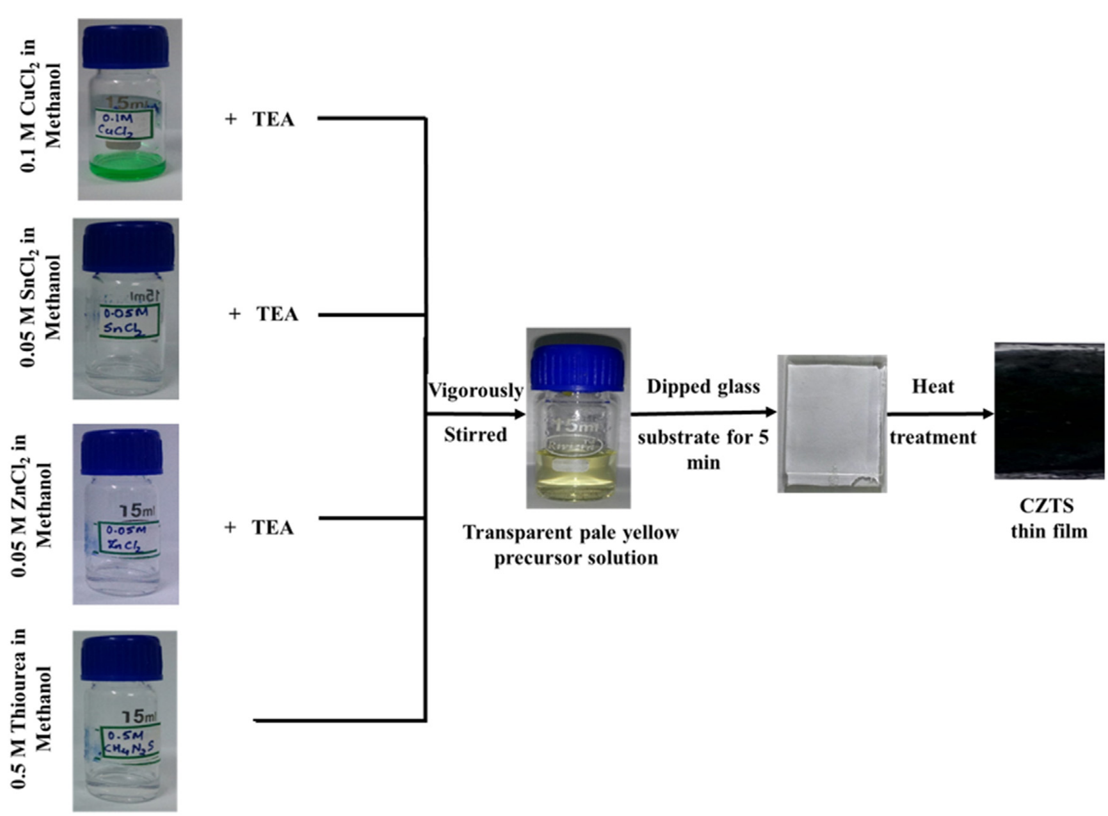

Fig. 1. Graphic representation of formation of CZTS films.