Solar Energy Materials & Solar Cells 117 (2013) 81–86

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

One-step deposition of Cu_2ZnSnS_4 thin films for solar cells

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ARTICLE INFO

Article history:
Received 23 January 2013
Received in revised form
2 May 2013
Accepted 19 May 2013
Available online 11 June 2013

Keywords:
Cu_2ZnSnS_4
Chemical bath deposition
Raman spectra
Solar cells

ABSTRACT

A simple one-step chemical bath process was developed to fabricate Cu_2ZnSnS_4 (CZTS) thin films. Effects of pH value and $ZnCl_2$ precursor content on the formation of CZTS were investigated. The best process parameters were a pH value of 3.5–4 and a $ZnCl_2$ content of 1.75 mmoL for deposition of high quality of CZTS films. The films consist of kesterite phase CZTS nanocrystals and exhibit a band-gap of ~1.48 eV. A conversion efficiency of 0.30% was achieved in one of the CZTS thin film solar cells. The route developed here may provide an alternative approach to produce low-cost and large area solar cells.

1. Introduction

Cu_2ZnSnS_4 (CZTS) possesses numerous advantages, such as rare-metal-free, nontoxicity, direct band-gap (1.45–1.50 eV), and high absorption coefficient ($> 10^4$ cm^{-1}), etc. In recent years, it has been studied extensively as an excellent optical absorber [1–6]. Power efficiency of CZTS thin film solar cells fabricated by vacuum physical deposition has reached as high as 8.4% [7]. To reduce manufacturing cost, several solution-based routes have been proposed. For example, the $Cu_2ZnSn(S,Se)_4$ (CZTSSe) cell derived from precursor containing hydrazine has yielded a maximum efficiency beyond 11%. [8] However, specially designed equipment is required due to hydrazine toxicity and easy explosivity. Another solution approach based on nanocrystals has been suggested for CZTSSe cells, and ~7.2% conversion efficiency has been achieved [9]. Yet many issues need to be overcome in this method, such as organic residue, phase segregation and unexpected intermediate products, weak adhesion between substrate and films, and so on. [10] Although the sol–gel method is a simple liquid phase process, stabilizers such as monoethanolamine are usually used, and these stabilizers are toxic and will decrease electric performance of CZTS thin films [11]. Furthermore, the grains in CZTS films fabricated by spray pyrolysis have a large dispersivity in sizes, resulting in a very poor PN junction [12]. The four-step screen printing technology is a relatively complicated one and it is very difficult to obtain high quality CZTS thin films with a small thickness [13].

Recently, the chemical bath deposition (CBD) technique has been extensively used to fabricate semiconductor quantum dots and thin films. For instance, with photo-chemical reaction CZTS thin films were obtained by an aqueous solution containing $CuSO_4$, $ZnSO_4$, $SnSO_4$ and $Na_2S_2O_3$ [14]. CZTS films were also fabricated by combining CBD with ion exchange and sulfurization treatment [15]. C. Gao and H. L. Shen described another three-step process for growth of CZTS films, including ionic-adsorption deposition of (Cu,Sn)S layer, CBD deposition of ZnS layer, and sulfurization treatment. However, the prepared CZTS films either were poor in crystal quality, or deviated from their stoichiometry, or were coarse and loose [16]. In this work we developed a CBD technique for fabricating CZTS thin films. Comparing with the processes reported in Refs. [14–16], our method only involves CBD and sulfurization treatment, and has advantages, such as process simplicity, no need of special equipment and ultraviolet irradiation, compact and dense thin films with uniform grain sizes, easy control of composition and easily obtaining large area of films, etc. The fabricated CZTS thin films exhibit a high crystal quality, nearly perfect stoichiometry and high absorption coefficient.

2. Experimental

2.1. Solution preparation

All the chemicals used in our experiments were analytical grade. Firstly, $CuSO_4.5H_2O$ (0.1 M, 10 mL), $ZnCl_2.2H_2O$ (0.1–

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http://dx.doi.org/10.1016/j.solmat.2013.05.039

0.22 M, 10 mL), $SnCl_2$ (0.08 M, 10 mL), and deionized water (120 mL) were mixed and stirred for 5–8 min to get clear and homogeneous solutions, followed by adding C_2H_5NS (1 M, 20 mL), Na_2EDTA (0.05 M, 10 mL) and H_2NCONH_2 (5 M, 20 mL) into the above solutions. Finally, the pH value of the solutions was adjusted by adding diluted HCl or NaOH.

2.2. Fabrication of CZTS thin films

To deposit CZTS films, the cleaned Mo/glasses were directly immersed into the fresh solutions and the depositing temperature was kept at 85 °C by means of water bath heat. The depositing times were 4 and 20 h, for the films with a thickness of about 0.18–0.22 μm and 1.1 μm, respectively. The sulfurization process was performed in the Ar/H_2S (5%) atmosphere with a pressure of ~9 Torr. The as-deposited films were initially treated at 150 °C for 20 min to ensure sufficient reaction between films and H_2S gas, and then annealed at 500 °Cfor 1 h to form the CZTS phase.

2.3. Fabrication of the prototype CZTS thin film solar cell

To grow 50 nm thick N-type CdS layer, a piece of 2×3 cm^2 Mo/glass coated a layer of 1.1 μm CZTS thin film was dipped in the alkaline CdS solution for 10 min at 80 °C. A PN heterojunction would be formed between the P-type CZTS and N-type CdS due to different electric properties. A ~50 nm i-ZnO layer and a ~250 nm ZnO:Al layer were orderly sputtered on the CdS/CZTS/Mo/glass through an aperture mask by sputtering deposition. Each photovoltaic device has an area of ~0.25 cm^2.

2.4. Physical measurements

X-ray diffraction (XRD) patterns of all the samples were taken on a Rigaku D/max 220 kV X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The surface morphologies of the films were examined using a Scanning Electronic Microscope (SEM, FEI Sirion 200) and Transmission Electron Microscopy (TEM, JEOL 2010F at 200 KV). Chemical composition of each film was analyzed by Energy Dispersive Spectrometry (EDS). For Raman analysis, a 325 nm He–Cd laser was used as the excitation source (JY-HR800) and the absorption spectra were recorded using a Jasco UV-570 spectrophotometer. Current–voltage (*J–V*) properties of the devices were characterized using a digital source meter (2400, Keithley) under AM 1.5 simulated solar spectrum with an irradiation of 1000 Wm^{-2}. External quantum efficiency (EQE) was measured by a single source illumination system

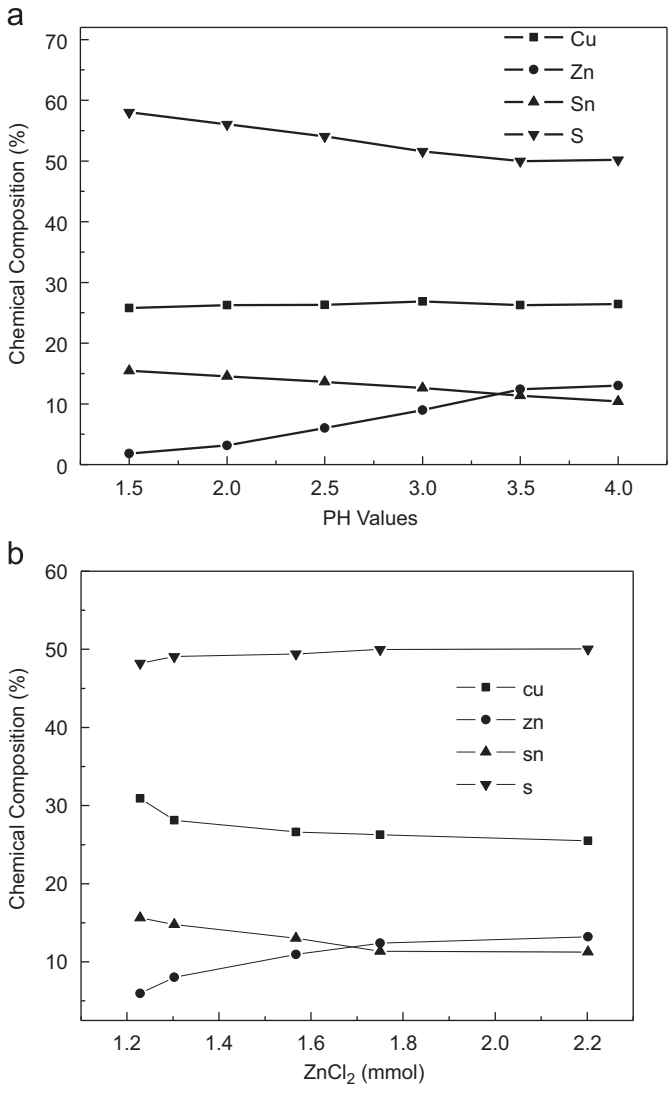

Fig. 1. The EDX spectra of the thin films deposited at different pH values (a), and with different contents of $ZnCl_2$ precursor at pH 3.5 (b).

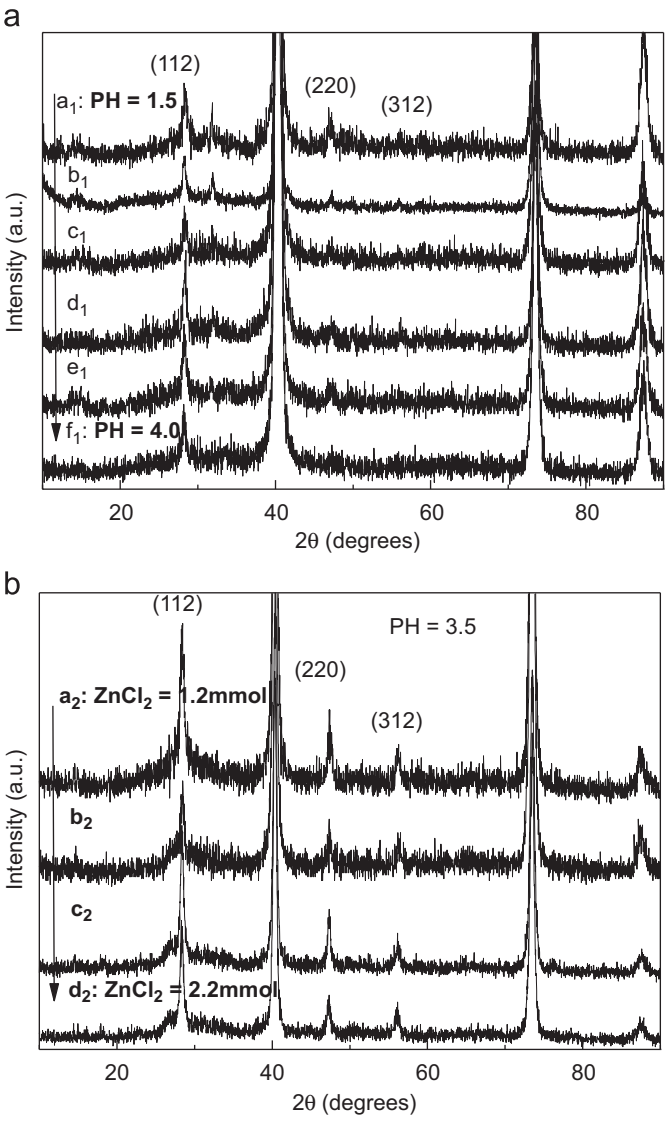

Fig. 2. The XRD patterns for the thin films deposited at various pH values (a):1.5 (a_1), 2.0 (b_1), 2.5 (c_1), 3.0 (d_1), 3.5 (e_1), and 4.0 (f_1), and with different amounts of $ZnCl_2$ precursor at pH 3.5 (b): 1.2 (a_2), 1.3 (b_2), 1.75 (c_2), and 2.2 mmol (d_2).