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Cu_2ZnSnS_4-based thin films and solar cells by rapid thermal annealing processing

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ABSTRACT

In this study, kesterite Cu_2ZnSnS_4 (CZTS) absorber layers were fabricated by DC magnetron sputtering deposition of metallic Cu-Zn-Sn precursors, followed by an annealing treatment in sulfur vapor atmosphere at 600 °C for 3 min using rapid thermal processing (RTP). Three types of stacked metallic films were prepared and included pre-annealing of Cu-Sn stacks in order to induce preferential Cu-Sn alloying. The chemical composition of the sulfurized films was obtained by X-ray fluorescence (XRF) before and after etching the samples in KCN solution. All CZTS thin films are found to be Cu-poor and Zn-rich. Structural characterizations were performed by X-ray diffraction (XRD) and Raman spectroscopy to investigate the impact of pre-annealing on the structural properties of the precursors and final CZTS films. Glow discharge optical emission spectroscopy (GDOES) shows that pre-annealing of the precursors can improve depth homogeneity of the CZTS films. Photoluminescence spectra and the optical band gap energy values are compatible with literature. Selected samples were processed to solar cells and characterized.

1. Introduction

Thin film solar cells are promising candidates for sustainable and inexpensive energy conversion in the future. Three thin film materials so far have been brought into commercial production of solar cells: thin film Si, Cu(In,Ga)Se_2 (CIGS), and CdTe [1,2]. Rare elements such as In and Ga may restrict the further development of CIGS based solar cell, despite the achievement of >21% conversion efficiency [3]. Also, the toxicity of Cd and limited supply of Te constrain the usage of CdTe-based solar cells.

Cu_2ZnSnS_4 (CZTS) has been studied as an alternative photovoltaic material, sharing a similar crystal structure with CIGS and containing abundant, environmentally friendly raw materials. The most stable structure of CZTS is kesterite which has a direct band gap of about 1.5 eV and a high absorption coefficient of over 10^4 cm^{-1} in the visible spectrum range [4]. Many different methods were developed for the growth of CZTS absorber layers. The fabrication processes can be classified in two parts: deposition of metallic precursors followed by annealing in a sulfur atmosphere. In the first part, deposition methods can be categorized as vacuum and non-vacuum techniques. Vacuum methods are for example pulsed laser deposition [5], thermal evaporation [6,7], e-beam evaporation [8], and magnetron sputtering [9–12]. The most commonly used non-vacuum methods are electrodeposition [13–15], spray pyrolysis [16,17], sol-gel deposition [18], doctor-blading or spin-coating of nanoparticles [19,20], or spin-coating or spray-deposition of molecular precursors [21]. In the second part of the fabrication, the annealing process can be performed using conventional thermal processing or using a rapid thermal processing (RTP) system, the latter allowing faster temperature ramping rates. This procedure can be performed using elemental sulfur vapor or an H_2S gas atmosphere. The maximum sulfurization temperature generally varies from 500 °C to 600 °C. The champion conversion efficiencies of around 8.4% for pure sulfide kesterite Cu_2ZnSnS_4 was achieved by Shin et al. [7] at first and later of around 9.6% by Kato et al. [22], which is still far from the theoretical Shockley-Queisser limit of about 32% for the conversion efficiency of CZTS thin film based solar cells [23]. It is difficult to find the best material growth parameters for absorber layers of high quality, in particular due to the possible formation of secondary phases [24]. High growth temperatures (>500 °C) are preferable for grain growth, however, these temperatures may lead to decomposition and loss of volatile elements and compounds such as metallic Zn and Sn-S. Unlike conventional thermal processing, RTP allows high ramp rates up to 50 K/s and shorter processing times, which may minimize decomposition reactions [25]. Also, rapid thermal processing is attractive for industrial fabrication due to its higher throughput and lower energy consumption.

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Table 1
Prepared metallic films for CZTS.

Sample	Complete stacked films	Pre-annealing of Mo/Cu/Sn	Sulfurization temperature
I		–	
II	Mo/Cu/Sn/Zn/Cu	200 °C, 3 min	600 °C
III		380 °C, 6 min	

In this work it was tried to find a promising metallic precursor with and without a pre-annealing step of the Cu-Sn metallic layers, suitable for sulfurization with a RTP system. Using stacked Mo/Cu/Sn/Zn/Cu metallic films and RTP sulfurization at 600 °C for 3 min, we investigate and compare the impact of the pre-annealing treatment of Mo/Cu/Sn on the structural, optical and optoelectronic properties of the CZTS thin film absorber layers.

2. Experimental

Three types of stacked Mo/Cu/Sn/Zn/Cu films were fabricated using DC magnetron sputtering. The first type of film (I) was prepared by sequential deposition of the metallic precursor Mo/Cu/Sn/Zn/Cu. The thickness values targeted were in the range of 175, 230, and 165 nm for the Cu, Zn, and Sn layers, respectively. 70% of the Cu thickness was deposited on top of the Mo layer, and 30% on top of the Zn layer. The second type of film (II) was exposed to a pre-annealing treatment at 200 °C in vacuum after the deposition of Mo/Cu/Sn layers. The metal layer thicknesses were chosen in order to obtain a [Cu]/[Sn] ratio of 1.2 in the precursor film. The last type of film (III) was annealed at 380 °C in vacuum after deposition of the Mo/Cu/Sn layers ([Cu] / [Sn] = 1.2), to yield Cu-Sn alloys on Mo on which Zn and the final Cu was deposited afterwards. For comparing of the pre-annealing treatment and temperatures, these three kinds of films were prepared and denoted as I, II, and III type films (Table 1).

Metallic precursor layers were enclosed in a quartz box with a volume of approximately 200 cm^3. 300 mg sulfur was placed closed to samples and the quartz box was inserted in a RTP chamber. The quartz box was not vacuum tight but it provides sulfur vapor pressure up to 1 mbar. After achieving ~2×10^{-5} mbar base pressure in the RTP chamber the samples were heated by high radiation emitted by tungsten halogen lamps with a ramp rate of 5 °C/s up to a dwell temperature of 600 °C, which was kept for 3 min. The evaporated sulfur reacted with the hot metallic precursor layers. A thermocouple was attached close to the samples for temperature measurements. Cooling of the samples down to 60 °C were performed by turning of the lamps in vacuum before the RTP vented with nitrogen [26]. For removal of possible copper-sulfide phases segregated on the surface, samples were etched for 3 min in a 10% KCN solution. All of the absorber analyses were performed after KCN etching except for the first X-ray fluorescence (XRF) measurements. The compositional ratio of the films was checked by XRF before and after KCN etching to reveal whether copper-sulfide phases formed on the surface or not. The atomic ratio of the films was determined by XRF line scans (100 different points) with a step size of 50 μm. Generator settings were 300 μA and 30 kV and the exposure

Table 2
Atomic ratio of type I, II and III films before and after KCN etching. The precursor composition was estimated from weighing, whereas the processed absorbers (I–III) were measured by XRF.

Sample	Before KCN etching			After KCN etching		
	Cu/(Zn + Sn)	Cu/Sn	Zn/Sn	Cu/(Zn + Sn)	Cu/Sn	Zn/Sn
Precursor	0.77	1.75	1.26			
I	0.81	1.77	1.16	0.81	1.78	1.17
II	0.79	1.65	1.08	0.80	1.68	1.10
III	0.78	1.65	1.10	0.79	1.65	1.09

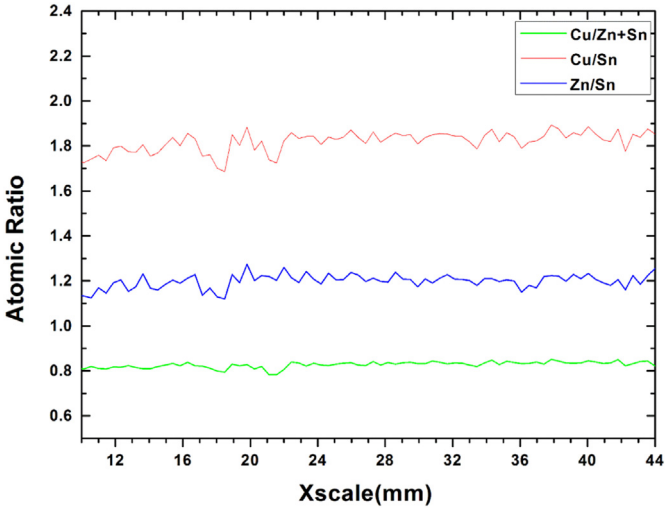

Fig. 1. Atomic ratio of the KCN etched type I kesterite film through the surface of the film.

time of each measurement was 60 s. The crystalline structure of the films was characterized by X-ray diffraction (XRD) using an X'pert Pro System with Bragg Brentano configuration (θ-2θ), using the CuK_α line ($\lambda = 1.54060$ Å) and with generator settings of 30 mA and 40 kV. Raman spectroscopy of the films were taken with a micro-Raman spectrometer (Dilor Labram Micro-Raman), where the wavelength of the excitation light was 633 nm, with a spot size of 3 μm and intensity of 2 W/cm^2. The surface and cross-section morphology of the films were characterized by a Gemini Leo 1530 scanning electron microscope (SEM). Depth profiles of the films were investigated by Glow Discharge Optical Emission Spectroscopy (GDOES, GDA650 Analyzer). The transmittance spectra of the films were obtained by a Dongwoo Optron spectrophotometer using 450 W Xe lamp in the spectral range of 600–1350 nm at room temperature. Optical band gap measurements were achieved by transferring the CZTS thin film layers from Mo-coated glass to pure cleaned glass by a peel-off technique. A similar procedure had been previously used for CIGS materials [27]. Photoluminescence measurements were performed at room temperature using an excitation laser at 670 nm and a 1/4 m spectrograph coupled to an InGaAs diode array. For solar cell applications, chemical bath deposition of a CdS buffer layer was obtained from cadmium acetate/ammonia solution added to thiourea solution at 60 °C for 7 min.

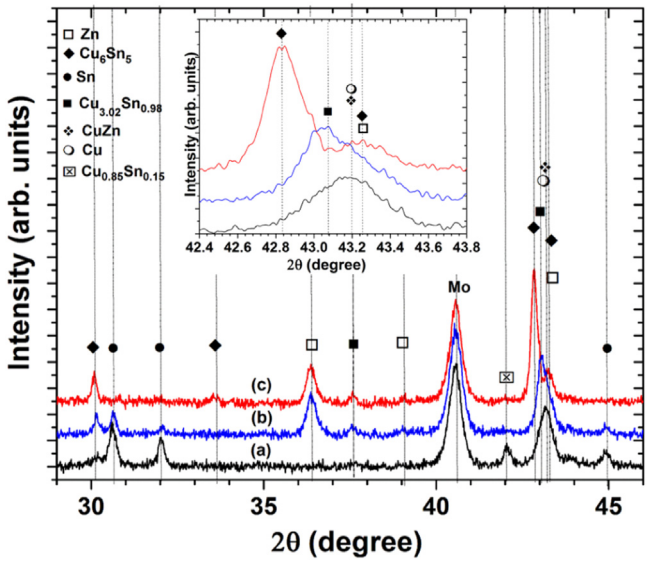

Fig. 2. X-ray diffraction pattern of a) I, b) II, and c) III type metallic precursor films.