Solar Energy Materials and Solar Cells 170 (2017) 287–294

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

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

Optimization of post-deposition annealing in Cu_2ZnSnS_4 thin film solar cells and its impact on device performance

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ARTICLE INFO

Keywords:
Kesterites
Cu_2ZnSnS_4
Thin film solar cells
Post-deposition annealing
Device performance

ABSTRACT

In this work we present an optimization of the post-deposition annealing, in Cu_2ZnSnS_4 (CZTS) thin film solar cells, applied at different stages of the solar cell preparation, namely, bare CZTS absorber, CZTS/CdS heterojunction and CZTS/CdS/i-ZnO/ITO complete solar cell. We performed current-density measurements, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), Raman scattering, photoluminescence (PL) and X-ray photoelectron spectroscopy (XPS) studies to enlighten the mechanisms by which solar cells performance improvement comes about. As a result, we concluded that the optimum post-deposition annealing for CZTS is at 300 °C for 15 min and at atmospheric pressure. The highest efficiency gain was obtained when the absorber layer composition is close to the ideal one and when a single annealing step is performed on complete solar cells, where, we obtained efficiency improvements from below 1% to over 6.6%. Despite the observed improvement in device performance for annealing at intermediate stages it is, however, less pronounced than for full cell annealing. In this process we demonstrate very substantial cell performance improvements. XRD results show a shift of all Bragg peaks to lower diffraction angle values, after post-deposition annealing. Also, the intensity of the peaks decreases and their full width at half maximum increases. PL measurements show that, post-deposition annealing, leads to a clear reduction of the non-radiative recombination channels and that the electronic structure is dominated by fluctuating potentials. XPS measurements reveal an interdiffusion of Cu, Zn and possibly Cd across the interface between buffer and CZTS absorber layers as the source of the significant observed cell performance enhancement.

1. Introduction

Cu_2ZnSnS_4 (CZTS) has been object of intense research due to its nearly ideal band gap of about 1.5 eV, a high absorption coefficient and containing only earth abundant and non-toxic elements [1,2]. The efficiency of CZTS thin film solar cells is known to depend strongly on the concentration of Cu on Zn antisites, Cu vacancies and defect clusters in the kesterite-type structure. However, the relationship of order-disorder, point defects and their influence on device performance is not yet clearly understood [3]. Calculations according to the Shockley-Queisser photon balance have estimated the theoretical conversion efficiency limit of single-junction CZTS solar cells to be as high as 32.2% [4]. Significant developments have been made on CZTS based thin film photovoltaic (PV) solar cells in the past few years, reporting solar cells with 9.2% efficiency [5]. However, CZTS PV technology requires extensive research to become marketable in the near future. So far, high efficiency CZTS based solar cells were found to have slightly Cu-poor and Zn-rich composition [6], which corresponds to a composition ratio of 0.8–0.9 for Cu/(Zn + Sn) and 1.1–1.2 for Zn/Sn, irrespective of the deposition technique or absorber preparation method. During the absorber layer fabrication process, secondary phases may form and depending on their fraction, have a big impact on the characteristics of the cell. Nagoya et al. [7] and Maeda et al. [8] have theoretically predicted ZnS to be the predominant secondary phase under the Cu-poor and Zn-rich growth condition with Cu_{Zn} antisite being the most stable defect in the stability region of CZTS [9]. ZnS has a wider bandgap and is usually less conductive. Therefore is not considered to be responsible for reduced open-circuit voltage (V_{OC}) or reduced shunt resistance, but can lead to high series resistance and reduced charge carrier collection efficiency depending on its location in the solar cell [10,11]. Other secondary phases such as Cu-Sn sulfides, SnS_x or CuS_x are considered to be more detrimental because of their lower bandgap and high conductivity, which can significantly reduce the open-circuit voltage and decrease the shunt resistance leading to much inferior photovoltaic

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http://dx.doi.org/10.1016/j.solmat.2017.05.065
Received 7 September 2016; Received in revised form 18 March 2017; Accepted 27 May 2017
Available online 20 June 2017

performance of the cell [12]. New concepts for further increasing the performance and reducing the costs by, for example, improved solar cell architectures and processing, are needed. In this work, development, optimization and understanding the effects of post-deposition annealing in Cu_2ZnSnS_4 thin film solar cells and its impact on device performance are presented. The main goal is to improve the efficiency of the Cu_2ZnSnS_4 thin film solar cells produced by rapid thermal processing (RTP) [13], in an atmosphere containing H_2S, of multi-period precursor layers deposited on Mo coated soda-lime glass (SLG) by RF magnetron sputtering. Two types of precursors were prepared with the following structures: ($ZnS/SnS_2/Cu$) and $(ZnS/SnS_2/Cu)_{(8\_periods)}$. For each type of precursors two sets of absorbers have been prepared and subjected to post-deposition annealing at various stages of the cell preparation. The effects of this post-deposition annealing were studied.

2. Experimental

In this work, the method employed for the growth of Cu_2ZnSnS_4 thin films consisted on the annealing of RF-magnetron sputtered precursors deposited on Mo coated SLG. Two types of precursors were prepared with the following structures: ($ZnS/SnS_2/Cu$) and $(ZnS/SnS_2/Cu)_{(8\_periods)}$. For each type, two sets of absorbers have been prepared, one with excess Zn and another with the ideal composition [6]. With the resulting absorbers, sets of cells have been prepared and subjected to the post-deposition annealing at various stages of the cell preparation, namely, bare CZTS absorber, CZTS/CdS heterojunction and CZTS/CdS/i-ZnO/ITO complete solar cells. The resulting final cell structure was SLG/Mo/absorber/CdS/i-ZnO/ITO. A DC-magnetron sputtered single layer Mo film with a thickness around 0.5 μm was used as standard back contact. The precursor stacks were annealed in a rapid thermal processing (RTP) furnace with an atmosphere of 95% N_2 + 5% H_2S at a pressure of 1 atm and at 520 °C for 30 mins. The p-type CZTS absorber layer had a thickness ranging from 1 to 1.5 μm. Before the buffer layer deposition, potassium cyanide (KCN) etching was employed to remove possible unwanted CuS secondary phases formed on the absorber surface. A thin n-type CdS layer of 70 nm thick was deposited on the p-type CZTS film by chemical bath deposition (CBD). Subsequently, the device structure was completed by depositing a 60 nm highly resistive intrinsic ZnO (*i*-ZnO) layer followed by the deposition of an indium tin oxide (ITO) layer with a thickness around 0.3 μm. The sheet resistance of the window layer control sample was ~ 23 Ω. The optimum post-deposition annealing was carried out on a hot plate at atmospheric pressure, in an atmosphere of N_2 and at 300 °C for 15 mins. The top surface, cross-sectional morphology and average composition of the absorber layers were analysed by SEM/EDS using a TESCAN Vega3 SBH SEM microscope, operated at an acceleration voltage of 15.0 kV for image acquisition and 25 kV for chemical analysis. The crystalline structure was analysed by X-ray diffraction (XRD) with a Philips PW 3710 system, in the Bragg-Brentano configuration (θ-2θ), using the CuKα line (λ ~ 1.54060 Å) and the generator settings were 50 mA and 40 kV. A LabRam Horiba, HR800UV spectrometer, equipped with a solid state laser oscillating at 532 nm was used for Raman scattering measurements. Raman spectra were calibrated using a single crystal Si reference sample, before the actual measurements, by setting the position of the dominant Si peak at 520 cm^{-1}. The photoluminescence (PL) measurements were performed with a Bruker Vertex 80v Fourier transform infrared (FTIR) spectrometer, equipped with an InGaAs photodetector. The samples were inserted in a helium gas flow cryostat and the measurements were performed at 70 K. The 514.5 nm line of an Ar^+ ion laser was used as the excitation source and the excitation power was measured at the front of the spectrometer entrance window. The PL spectra are presented as measured. For these PL measurements, a CdS thin film reference sample was deposited by CBD on SLG, using the same conditions as those for the deposition of the buffer layer on the solar cells. X-ray photoelectron spectroscopy (XPS) measurements were performed in an Ultra High Vacuum (UHV) system with a base pressure of 2×10^{-10} mbar. The system is equipped with a hemispherical electron energy analyser (SPECS Phoibos 150), a delay-line detector and a monochromatic AlKα ($h\nu \sim 1486.74$ eV) X-ray source. High resolution spectra were recorded at normal emission take-off angle and with a pass-energy of 20 eV, which provides an overall instrumental peak broadening of 0.5 eV. Ar^+ ions (1.5 kV), with an incidence angle of 45°, were used for XPS depth profiling. The solar cell performance was characterized through current-voltage (J-V) measurements under simulated standard test conditions in which the light source consisted of a tungsten-halogen lamp combined with an infrared filter for spectrum conditioning.

3. Results and discussion

The work reported in this paper consisted on a systematic study of the effect of the post-deposition annealing on the performance of CZTS based thin film solar cells, applied at different stages of cell preparation. For both types of precursors, ($ZnS/SnS_2/Cu$) and $(ZnS/SnS_2/Cu)_{(8\_periods)}$, the maximum temperature and the dwelling time at maximum temperature for the post-deposition annealing were varied from 200 to 400 °C and from 15 to 20 mins, respectively. The application of the post-deposition annealing to the full cells based on the first type of precursors ($ZnS/SnS_2/Cu$) has shown that annealing at 200 °C leads to an improvement of the solar cell efficiency by a factor of 2 while a post-deposition annealing at 300 °C leads to an efficiency improvement by a factor of 11. The changes in the solar cell performance parameters are shown in Table 1. Annealing at temperatures lower than 300 °C also improves cell performance, however, in a less pronounced way, while, annealing at 400 °C is detrimental for the solar cell and leads to a clear degradation of the performance possibly due to CZTS decomposition and deterioration of the CdS layer. For the annealing time, in the interval considered, no significant changes have been observed. The results have shown that the optimum post-deposition annealing, for the CZTS case, should be performed at 300 °C for 15 mins. In an effort to improve beyond the best results and realizing that the open circuit voltage (V_{OC}) was still too low we decided to test precursors with 8 periods of ($ZnS/SnS_2/Cu$) in order to reduce undesired phase segregation. For this type of precursors the effect of Zn content was also studied. While the solar cell performance results, with this new type of precursors, did not show significant gains before post-deposition annealing, after the annealing major gains were obtained. The highest efficiency gain was obtained when the absorber layer composition is close to the ideal one and when a single annealing step is performed on complete solar cells (Table 2). However, in all the cases, the post-deposition annealing on full cells promotes an improvement of all device parameters, such as, open circuit voltage (V_{OC}), short circuit current

Table 1
Comparison of performance, before and after the post-deposition annealing, at 200 °C and 300 °C for 15 mins, on complete solar cells (CZTS/CdS/i-ZnO/ITO) with ideal composition absorbers. The ratios of all device parameters corresponds to CZTS/CdS/i-ZnO/ITO 200 °C or 300 °C annealed divided by CZTS/CdS/i-ZnO/ITO not annealed.

Complete cells		V_{OC} (mV)	V_{OC} ratio	I_{SC} (mA cm^{-2})	I_{SC} ratio	FF (%)	FF ratio	Eff. (%)	Eff. ratio
CZTS/CdS/i-ZnO/ITO	Not annealed	174.8	**1.04**	4.6	**1.4**	26.3	**1.5**	0.21	**2.1**
	200 °C annealed	182.6		6.4		38.6		0.45	
	300 °C annealed	399.2	**2.3**	12.8	**2.8**	45.8	**1.7**	2.35	**11.2**