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Boosting the kesterite Cu2ZnSnS4 solar cells performance by diode laser annealing

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ABSTRACT

In this work, a novel diode laser annealing was performed as a post-sulfurization heat treatment on pure-sulfide Cu_2ZnSnS_4 thin film solar cells fabricated by sputtering deposition. The effect on both film quality and device performance after annealing at various laser doses was investigated. After receiving an ultra-fast laser scan treatment, the crystallinity of the CZTS film can be improved and the Cu/Zn disordering is reduced. The power conversion efficiency of the laser annealed device was boosted to 7.33%, compared with the reference cell efficiency of 6.72%. The major increase in the short circuit current is driving force of such improvement, from 18 mA/cm^2 to 19.31 mA/cm^2 after laser treatment. These results indicate that the quality of CZTS thin films and the device performance can be effectively improved by the diode laser annealing.

1. Introduction

Cu_2ZnSnS_4 (CZTS) has been regarded as an environment-friendly and cost-effective material for photovoltaic applications and has recently attracted considerable attention. Significant progress has been made over the past few years, with the highest recorded power conversion efficiency (PCE) reaching 11% for CZTS [1] and 12.7% for Se-incorporated CZTS (CZTSSe) [2] solar cells achieved. This demonstrates the substantial commercial potential of this solar technology. According to previous simulation and experimental work, there are two key requirements for high efficiency kesterite CZTS solar cells, i) high crystalline quality in the absorber and ii) effectively passivated interfaces, including grain boundaries, and interfaces of the CZTSe/CdS heterojunction and the CZTSe/Mo [3]. One approach to enhance the material quality and cell performance is the application of a post-sulfurization treatment. Recently, it has been reported that post-annealing of the CZTS/CdS heterojunction at an appropriate temperature (~ 573 K) improved the efficiency of CZTS cells and an appropriate post-annealing temperature improved the J_{sc} of the CZTS cells [4,5]. Diode laser annealing has also been reported to be employed as an alternative for sulfurization annealing to improve the quality of epitaxial CZTS films grown by magnetron sputtering [6]. However, the finished device performance of the laser annealed sample has not been investigated. In this work, laser annealing has been applied as a novel approach of post-annealing treatment and its effect on both material quality and device performance has been investigated. The line-focused scanning diode laser annealing utilized in this work is a super-fast annealing process which dramatically reduces the annealing duration from several tens of minutes to a few microseconds. Moreover, for the wavelength of 808 nm, more than 90% of the laser power will be absorbed by the CZTS absorber within very short exposure time. With the reduction of structure defects and the improvement of material quality led to an improvement in the performance of CZTS thin film soar cells.

2. Experiment

2.1. Film synthesis

A magnetron sputtering system (AJA International, Inc., model ATC-2200) was used to co-sputter Cu/ZnS/SnS precursors on Mo-coated soda lime glass substrate. Specifically, the Cu/Zn/Sn ratios were controlled by adjusting the applied power to the gun for each target: Cu (3 in. target), ZnS (3 in. target), SnS (3 in. target) to obtain a ~ 420 nm Cu/SnS/ZnS mixture precursor. The precursors were sulfurized using Rapid Thermal Processor (AS-One 100) within a combined sulfur and SnS atmosphere at 560 ^{0}C for 5 min. The composition of the precursor was Cu-poor and Zn-rich (Cu/Sn = 1.8, Zn/Sn = 1.3, or (Zn + Cd)/Sn = 1.3, Cd/(Cd + Zn) = 0.4).

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2.2. Laser annealing

The laser annealing process is achieved by scanning an 808 nm line-focused CW diode laser beam with the dimension of 12 × 0.27 mm^2 (FWHM). A fixed scan speed of 6.7 mm/s was used for all samples and the laser power density was changed by modifying the output power.

2.3. Device fabrication

The conventional cadmium sulfide buffer layer was deposited by CBD method. Next, a thin i-ZnO (~ 50 nm) and ITO (~ 220 nm) layer was deposited using the AJA RF power sputtering. Evaporated Al patterns were applied as the top contact for the device. Finally, a ~ 91 nm MgF_2 was evaporated as the Anti-reflection coating (ARC). The total area of the final cells was ~ 0.22 cm^2, as defined by mechanical scribing.

2.4. Characterization

The microstructure and elemental distribution across the CZTS and buffer interface were carefully examined using JEOL JEM-ARM200F (200 kV) aberration-corrected scanning transmission electron microscope (STEM), equipped with an energy dispersive X-ray spectroscopy (EDAX) system. Photoluminescence (PL) spectra were measured using a 1/4 m monochromator (CornerstoneTM 260) equipped with a silicon charge-coupled device (CCD) camera. The continuous wave (CW) laser (405 nm, 50 mW) was used as the excitation source and the luminescence was detected by the CCD. Raman spectra are acquired with the Renishaw in via Raman Microscope using a 785 nm laser. The J-V curves were performed using a solar simulator (Newport) with AM1.5G illumination (100 mW/cm^2) calibrated with a standard Si reference. External quantum efficiency (EQE) measurements were conducted by utilizing a QEX10 spectral response system (PV measurements, Inc.) calibrated by the National Institute of Standards and Technology (NIST)-certified reference Si and Ge photodiodes.

3. Results and discussion

The effect of a capping layer in the laser annealing process has been previously investigated in the study of Excimer-Laser treated Si thin-film [7,8]. The SiO_X capping layer contributes not only to the enhancement of the absorption of the laser beam as an anti-reflection coating (ARC) layer, but also stores some of the heat generated during the laser irradiation and the heat that flows back into the target film which elevates the temperature of the film. Considering the feasibility and the process simplicity, a 50 nm CdS layer was deposited by chemical bath deposition (CBD) as a capping layer for the laser annealing, as well as the buffer layer of the finished device. Varying laser doses were tested by changing the output power of laser beam. Table 1 shows the result of cell performance for the reference cell, as well as for devices which have been laser annealed. Note that the reference sample was fabricated as described in the experimental section, with neither the laser annealing nor any other post treatment. The samples annealed at 24 J/cm^2 and 29.4 J/cm^2 laser annealing achieved higher cell efficiency of 5.6% and 4.93% compared with 4.55% of the reference. The increase in cell efficiency is mainly contributed by the improvement in FF and $J_{sc,}$ despite the lower V_{oc} compared with the reference. All laser annealed samples shows increased J_{sc} compared with the reference, which is more clearly demonstrated by the EQE result, shown in Fig. 1. The better collection efficiency in the long wavelength range of 550–800 nm in the EQE indicates an increase in depletion region and/or diffusion length. The shift of the carrier collection edge in EQE above 800 nm indicates the changing optical property upon laser treatment. A red shift in EQE at the long wavelength suggests a possible decrease of the material bandgap. As the same phenomenon has been observed in CZTS with CdS layer, it is most likely related to the diffusion of Cd into the bulk material during the heat treatment, leading to the formation of Cd alloyed CZTS at the surface region. To investigate such possible change in element distribution, the CZTS/CdS interface is studied by STEM/EDS. Fig. 2 shows the EDS line scan result near the heterojunction, which reveals the inter-diffusion of Cd and Zn at the heterojunction, and the inter-diffusion is more obvious for samples treated with higher laser power. Compared with the reference sample, Cd diffused layers with a thickness of 60–80 nm can be clearly identified for annealing at 29 J/cm^2 and 34 J/cm^2. The concentration of Cd is above 1 at% in this layer and no Cd signal was detected beyond the depth of 100 nm from the interface, which is consistent with the previous study on post-annealing of CdS/CZTS heterojunction by furnace annealing [5].

Table 1
Device parameters of laser annealed samples with CdS capping layer.

Sample No C#	V_{oc} [mV]	FF [%]	J_{sc} (With ARC) [mA/cm^2]	PCE (With ARC) [%]	Laser dose [J/cm^2]
C1	571.60	54%	14.77	4.55%	0.0
C2	535.50	60%	17.44	5.60%	24.5
C3	537.51	56%	16.29	4.93%	29.4
C4	491.41	51%	15.35	3.83%	34.3

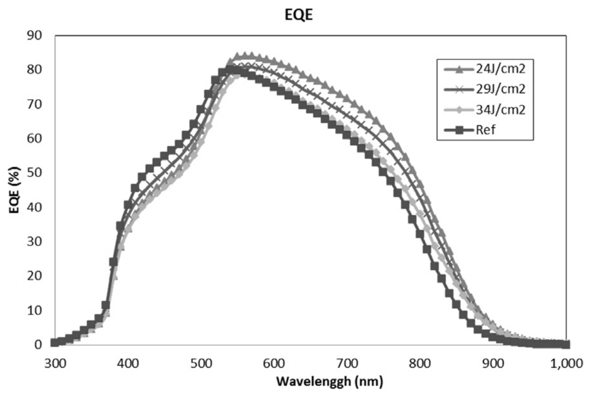

Fig. 1. EQE result of reference and laser annealed CZTS with CdS capping layer.

Steady state photoluminescence has been employed to investigate the effect of laser treatment on recombination properties. Fig. 3(a) shows the linear plot of the steady state PL intensity of each sample against the photon energy. For all samples which received laser annealing treatment, the PL counts/intensities were dramatically increased, compared with the reference sample. The enhanced PL response indicates a better surface passivation after the laser annealing.

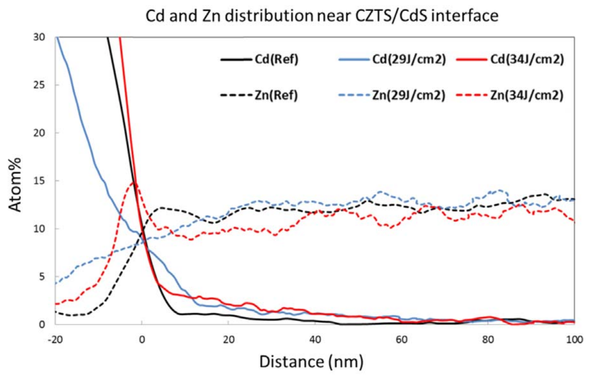

Fig. 2. EDS line-scan result of Cd and Zn distribution at the heterojunction interface of samples with different laser annealing conditions and the reference as a comparison, Cd and Zn inter-diffusion can be observed on laser annealed samples.