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10% Efficiency $Cu_2ZnSn(S,Se)_4$ thin film solar cells fabricated by magnetron sputtering with enlarged depletion region width

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ABSTRACT

High performance $Cu_2ZnSn(S,Se)_4$ (CZTSSe) solar cells are fabricated by selenization of the precursor films of Mo/Sn/Cu/ZnS/Sn/ZnS/Cu deposited by magnetron sputtering. The investigation of the solar cells with different Zn/Sn ratio in CZTSSe film discloses that the charge carrier concentration and depletion region width of the device is very sensitive to Zn/Sn ratio of CZTSSe layer. The CZTSSe film with Zn/Sn = 1.05 has lower carrier density (5.0×10^{15} cm^{-3}), which is half of the cell with Zn/Sn = 1.12, whereas the depletion region at the CdS/CZTSSe hetero-junction interface of the former (200–250 nm) is 100 nm longer than the latter. As a result, better collection of photo-generated charge carrier is found with the cell with longer W_d in the longer wavelength region above 800 nm. Therefore, the average power conversion efficiency is increased from 6.53% to 9.16% with enlarged depletion region width, and the best performance with 10.2% efficiency is achieved.

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1. Introduction

Solar energy is considered to be the most promising renewable energy source to displace conventional fossil fuels which are not only limited in earth-crust but also causing green-house effect due to CO_2 emission. To make solar electricity cost-effective, it is tremendously needed to reduce the cost of the source materials and simplify the fabrication process for preparation of high performance solar cells in large-scale production. Thin film solar cells based on $Cu_2ZnSn(S,Se)_4$ (CZTSSe) light absorbing materials continue to attract attention from both scientific and industrial community owing to their advantage of using earth abundant and low cost source elements [1,2]. The remarkable performance enhancement of CZTSSe solar cells to over 12% has indicated the huge potential of this type of new PV technology to deliver cost-effective solar electricity to meet the demand of rapidly increasing electricity usage in today's world [3]. To date, most of the reported high performance CZTSSe solar cells with efficiency above 10% were fabricated by solution-based process [4–10], including the 12.7% champion device [8]. However, the extremely toxic and explosive hydrazine may cause practical issues that can restrict the large scale production of CZTS solar cells by this method in the future. Thus development of safe method for fabrication of high performance CZTS solar cells is of highly importance for this new PV technology to fulfill its mission in the future.

Fundamentally, it is known that charge carrier depletion width at the hetero-junction interface is one of the key parameters that affect the performance of thin film solar cells. The relative dielectric constant of kesterite $Cu_2ZnSn(S_x,Se_{1-x})_4$ varies from 6.8 to 8.6 as x changes from 1 to 0 according to theoretical calculation and experimental results [11,12]. Based on this result, the carrier density of CZTSSe absorber is generally in the range of 5×10^{15}–1×10^{16} cm^{-3}, and the depletion region width (W_d) is typically in the range of 150–220 nm [7,13]. Generally speaking, a narrow depletion region is not only adverse to the photo-generated charge carrier collection in thin film solar cell, especially for the charge generated at the long wavelength region close to band edge, but also may lead to increased interface recombination and tunnel recombination, which result in significant open circuit voltage (V_{oc}) loss. Hence, increase of the depletion region width of CZTSSe solar cells is crucial to push the performance of CZTSSe solar cells to a higher level.

Herein, we present the study of fabrication of high performance CZTSSe thin film solar cells with efficiency above 10% using

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magnetron sputtering deposition. We investigated the influence of Zn content on the carrier density of CZTSSe absorber and the depletion region width (W_d) of CZTSSe solar cell as well as on device performance. The results have shown that the depletion region width at the hetero-junction interface of CZTSSe/CdS is very sensitive to the relative content of Zn in the film. A slight increase of Zn/Sn ratio from 1.05 to 1.12 led to a significant decrease of W_d by around 100 nm. As a consequence, the average performance of the CZTSSe solar cells decreased from 9.16% to 6.53% under one sun illumination.

2. Experimental details

2.1. Precursor fabrication

The precursor for the growth of CZTSSe light absorber film was made by sputtering a stacking layer of metal and metal sulfide with controlled thickness on Mo substrate. The stacking sequence of the precursor was Mo/Sn/Cu/ZnS/Sn/ZnS/Cu deposited using 99.99% pure metal targets and 99.99% ZnS target. Sn and Cu layers were sputtered by a DC-magnetron sputtering system with power of 0.46 W cm^{-2} and 0.39 W cm^{-2} in an atmosphere of 1.0 Pa Ar, respectively. ZnS layers were sputtered by a RF-magnetron sputtering system with power of 1.63 W cm^{-2} in 5 Pa Ar atmosphere. The background pressure of the sputtering chamber was controlled as 3.0×10^{-3} Pa. The thickness of each layer is shown in the inset of Fig. 1(a). Mo back contact with a bi-layer structure was deposited by DC magnetron sputtering on clean soda lime glass which was washed using deionized water under ultrasonication. The bi-layer structure of Mo was fabricated by deposition the first layer (thickness about 300 nm) with power density of 0.93 W cm^{-2} in 1.5 Pa Ar atmosphere and then the second layer (thickness about 500 nm) with power density of 1.10 W/cm^2 in 0.1 Pa Ar atmosphere. The substrate was not heated during the sputtering process.

2.2. CZTSSe film and device fabrication

The sputtering-deposited precursors were firstly annealed at 300 °C for 20 min in Ar atmosphere under the pressure of 10^4 Pa. After that, a selenization process at 570 °C for 15 min was used to synthesize CZTSSe film in an atmosphere containing sufficient Se vapor and 10^4 Pa Ar atmosphere [14]. Se vapor was achieved by heating sufficient solid Se material at 450 °C which was put in a molybdenum barrel with a 1.5 mm spout. The heating rate for the substrates and Se source was 40 °C/min.

CZTSSe thin film solar cells were fabricated by deposition of a 50 nm CdS buffer layer at 83 °C for 12 min by chemical bath deposition method (CBD) on top of the prepared CZTSSe absorber film, followed by deposition of 50 nm i-ZnO and 500 nm ZnO:Al layers by sputtering and a Ni/Al grid contact by electron beam evaporation. The active area of each CZTSSe solar cell was 0.345 cm^2 determined by mechanical scribing. It is worth to mention that no etching was used in the device fabrication in this work.

2.3. Film characterization

The compositions of the films were determined by a MagixPW2403 X-ray Fluorescent spectrometer with an Rh-anode, which was calibrated using inductively coupled plasma spectroscopy to ensure its accuracy. The structural properties of the precursors and the selenized samples were analyzed by a Philips X-pert pro X-ray diffractometer with Cu Kα as the radiation source. A RenishawinVia Raman spectroscopy with 514 nm excitation laser was used to analyze the material phases of the selenized samples. A scanning electron microscope (SEM, Hitachi S-4800) was used to characterize the morphology of as-prepared CZTSSe films. The thickness of the films was determined by an AMBIOS XP-2 stylus profiler. The depth profiles showing the distribution of the elements in deposited film were recorded by secondary ion mass spectroscopy (SIMS; IMS-4F, CAMECA, Nancy, France).

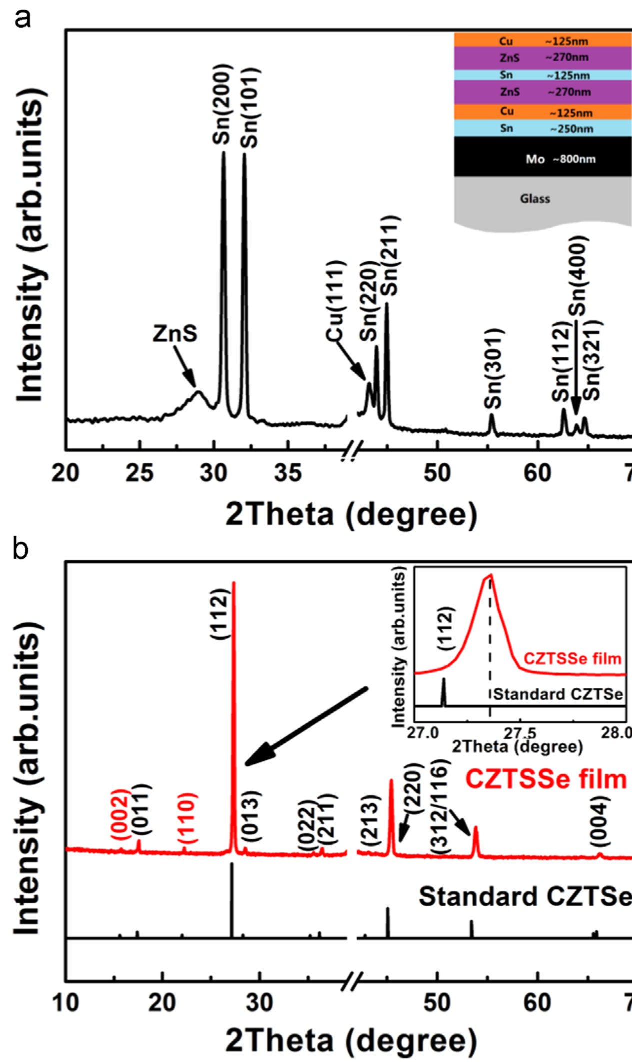

Fig. 1. (a) The XRD pattern of as-sputtered precursors. Inset: the stacking structure of as-sputtered precursors and the thickness of each layer. (b) XRD pattern of the selenized CZTSSe films with the diffraction pattern of standard CZTSe material based on JCPDS #00-052-0868. Inset: enlarged (112) peak of the CZTSSe films.

2.4. Device performance characterization

The current density–voltage (*J*–*V*) characteristics of the CZTSSe solar cells were measured by a solar simulator under the standard AM1.5 spectrum with illumination intensity of 1000 W m^{-2} at room temperature using a Keithley 2420 source meter unit. The light intensity of the solar simulator was calibrated with a standard mono crystalline Si reference solar cell. External quantum efficiency (EQE) measurements were performed by measuring the short-circuit current with spectrally resolved monochromatic beam and locked-in amplifier, using calibrated Si and InGaAs photodiodes as references. Measurements of photoluminescence (PL) spectroscopy and time resolved PL spectroscopy (TRPL) were carried out on the finished device by using Hamamatsu single-photon counting system and an 800 nm solid state laser with

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