Tailoring Mo(S,Se)$_2$ structure for high efficient Cu$_2$ZnSn(S,Se)$_4$ solar cells

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ABSTRACT

The direction of Se-Mo-Se sheets to the Mo film is crucial for the thickness of Mo(S,Se)$_2$ and the electrical conductivity, so as the back contact of Cu$_2$ZnSn(S,Se)$_4$ solar cells. In this study, the preferred orientation of Mo(S,Se)$_2$ film changes from (100) peak to (103) peak, i.e. from perpendicular to the substrate to tilted to the substrate for Se-Mo-Se sheets as the roughness decrease of Mo back contact layer. The Se vapor can easily diffuse through the channels between Se-Mo-Se sheets when the formed Mo(S,Se)$_2$ layer is (100) peak preferred with Se-Mo-Se sheets perpendicular to the substrate, and thus excessively thick Mo(S,Se)$_2$ will be formed. Whereas, the Se-Mo-Se sheets are tilted to substrate when the preferred orientation of Mo(S,Se)$_2$ is (103) peak. The tilted Se-Mo-Se sheets can act as a natural Se diffusion barrier to suppress the Se vapor diffusion through the already formed Mo(S,Se)$_2$ layer to further selenize the remaining Mo film, and also can provide a good electrical conductivity. As a result, the thickness of Mo(S,Se)$_2$ sharply decreased from 1500 nm to 200 nm with the surface morphology change of Mo back contact, which resulting in the decrease of series resistance of Cu$_2$ZnSn(S,Se)$_4$ solar cells from 2.94 Ω cm^2 to 0.49 Ω cm^2, and the increase of conversion efficiency of Cu$_2$ZnSn(S,Se)$_4$ solar cells from 6.98% to 9.04%.

1. Introduction

Cu(In,Ga)Se$_2$ (CIGS) solar cells are one of the most promising thin film photovoltaic devices and the best efficiency has reached 22.6% [1]. However, In and Ga are rare elements, thus the maximum power production capacity of CIGS solar cells will be limited to $\sim$ 100 GW per year [2]. Kesterite structure Cu$_2$ZnSn(S,Se)$_4$ (CZTSSe) is a suitable alternative material with the more earth-abundant and low-cost elements Zn and Sn to replace the rare elements In and Ga [3,4]. Thus, CZTSSe solar cells will be much cheaper. In the past few years, CZTSSe solar cells have attracted much attention and the highest efficiency of CZTSSe solar cells is 12.6% [5,6].

Like CIGS solar cells, Mo film is served as back contact in CZTSSe solar cells. Generally, a Mo(S,Se)$_2$ interfacial layer can be formed between CIGS or CZTSSe absorber and Mo back contact during the growth of CIGS or CZTSSe film [7,8]. It is well known that a thin Mo(S,Se)$_2$ layer can act as a buffer layer to convert the Schottky contact to a quasi-ohmic contact, which is beneficial to the transportation of charge carriers [9–11]. However, an over thick Mo(S,Se)$_2$ layer will block the transportation of charge carriers, which is detrimental to the performance of devices [7,9,12]. Generally, to promote the growth of grains, suppress the surface decomposition, and avoid the formation of V$_{Se}$ or

V$_S$ defects, CZTSSe films are often prepared at high temperature under high Se or S partial pressure [8,12–15]. As a consequence, an over thick Mo(S,Se)$_2$ layer will be formed, which will increase the contact resistance between CZTSSe absorber layer and Mo back contact electrode [8,12]. Thus, it is crucial to control the thickness of Mo(S,Se)$_2$ interfacial layer for high efficient CZTSSe solar cells. Shin et al. indicated that the formation of MoSe$_2$ during selenization process under Se ambient can be divided into three step processes: diffusion of Se through Cu$_2$ZnSnSe$_4$ (CZTSe), diffusion of Se through MoSe$_2$ which is growing with continued annealing, and reaction between Se and Mo [8]. Thus, the formation of Mo(S,Se)$_2$ can be suppressed by such processes. For example, an intermediate layer, such as TiN, TiB$_2$, ZnO, and MoO$_2$, deposited between CZTSSe absorber and Mo back contact acts as a Se diffusion barrier to inhibit the formation of Mo(S,Se)$_2$ [12,16–19]. However, these intermediate layers may induce a rather high series resistance in the device and degrade the device performance [16,17]. Lopez-Marino et al. and Schnabel et al. indicated that a direct contact between CZTSSe and Mo(S,Se)$_2$ is necessary for achieving high device performance, though a thin MoO$_2$ or TiN intermediate layer can effectively suppress the formation of Mo(S,Se)$_2$ [18,19]. Thus, a top sacrificial Mo cap layer was deposited on MoO$_2$ or TiN layer to control the thickness of Mo(S,Se)$_2$ layer, and thereby the performance parameters

of fill factor (*FF*) and open voltage circuit (V_{OC}) are increased. On the other hand, Li et al. proposed a new method to suppress the formation of $MoSe_2$ by a dense temporary alloy layer formed during a low temperature annealing process under Ar atmosphere [20]. As further selenizing the samples under high Se pressure, the thickness of $MoSe_2$ interfacial layer was tailored to less than 10 nm and the conversion efficiency was improved from 5.6% to 8.7%. However, this process cannot work well in some other processes, such as selenizing the precursors prepared by sol-gel method. Though preparation of CZTSSe films under low Se pressure can prevent the formation of $Mo(S,Se)_2$ layer and a CZTSe solar cells with the efficiency of 8.2% was fabricated under low Se pressure [21], the CZTSe surface may decompose and more defects exist in the absorber layer. Thus, it is necessary to find a way to easily control the thickness of $Mo(S,Se)_2$ interfacial layer while selenizing the precursors at high temperature under high Se pressure.

In this study, we present an effectively and easily controlled way to tailor the preferred orientation and thus tailoring the thickness of $Mo(S,Se)_2$ by modifying the surface morphology of Mo back contact. Though Shin et al. indicated that the preferred orientation of CIGS film can be changed by the modification of Mo morphology [22], they didn't disclose the influence on the formation of $MoSe_2$ with different orientation by other factors, such as thickness of $MoSe_2$. This paper makes detail analysis to the influence of preferred orientation of $Mo(S,Se)_2$ on the thickness of $Mo(S,Se)_2$ and thereby the influence on the device performances. In other work, such as work done by Lin et al., they also proposed a method to decrease the thickness of $MoSe_2$ in CIGS solar cells [23]. They attribute this decrease to the increase of Na content in the CIGS absorber with the increase of thickness of Mo barrier layer prepared at higher working pressure, which will promote the formation of Na_2Se_X at grain boundaries during selenization. Thus, the dense of CIGS absorber is increased and the grain boundary diffusion of Se is reduced, which will reduce the growth rate of $MoSe_2$. In our study, however, we found the decrease of thickness of $Mo(S,Se)_2$ is because of the change of the preferred orientation of $Mo(S,Se)_2$, which is introduced by the different morphologies of Mo films. As a consequence, the thickness of $Mo(S,Se)_2$ was tailored from 1500 nm to 200 nm, the series resistance of CZTSSe solar cells was reduced to a low level ($\sim$ 0.49 Ω cm^2), and thereby the conversion efficiency of CZTSSe solar cells was increased from 6.98% to 9.04%.

2. Experimental

Soda-lime glasses (SLG) were used as substrates. The SLG were cleaned by electronic cleaning agent followed by ultrasonic cleaning, and then the SLG were dried with a nitrogen flux. Mo films were deposited on the cleaned SLG by DC-magnetron sputtering Mo target. One-layer-structured and two-layer-structured Mo films with different surface morphologies were prepared at different deposition conditions, respectively, as shown as Fig. 1(a)-(c). First, a one-layer-structured Mo film named as Mo-1 was prepared at a higher working power of 2.5 W/cm^2 under a lower working pressure of 0.2 Pa as shown in Fig. 1(a). The thickness of sample Mo-1 is about 1200 nm and the square resistance is about 0.26 Ω/□. To modify the surface morphology, two-layer structured Mo films were induced as shown in Fig. 1(b) and (c). The thick bottom layer (ca. 1200 nm) was deposited with the same conditions as sample Mo-1, and the thin top layer (ca. 100 nm) was deposited at working power of 2.5 or 0.5 W/cm^2 under a higher working pressure of 1.5 Pa, which were named as Mo-2 and Mo-3 (Fig. 1(b) and (c)), respectively.

CZTSSe absorbers were successively fabricated by sol-gel and selenization process. The precursor solutions were prepared by dissolving $Cu(CH_3COO)_2 \cdot H_2O$ (AR), $Zn(CH_3COO)_2 \cdot H_2O$ (AR), $SnCl_2$ (AR), and thiourea (AR) in 2-methoxyethanol (AR), and then ultrasonic stirring for 30 min at room temperature to get colorless transparent solution. Before spin coating, the solution was aged at room temperature for 3 days and proper monoethanolamine (MEA) and triethanolamine (TEA)

were added to avoid cracks during spin coating. All of the chemical reagents were purchased from Aladdin Industrial Corporation. The precursor solutions were spin coated on the above-mentioned Mo-deposited glass substrates at 3000 rpm for 20 s followed by drying in air at 300 °C for 1 min. The coating and drying processes were repeated 8 times to get a Cu_2ZnSnS_4 (CZTS) precursor film with the thickness of $\sim$ 1.5 μm. The compositions of CZTS precursors with different Mo back contacts were almost the same with a Cu-poor and Zn-rich stoichiometry (Cu/(Zn + Sn) = 0.75, Zn/Sn = 1.1, and S/(Cu + Zn + Sn) = 1) measured by X-ray fluorescent spectrometer (XRF). After that, the prepared precursor films were selenized at 550 °C for 40 min under the Se ($\sim$ 10^4 Pa) and Ar ($\sim$ 10^5 Pa) mixed atmosphere to form the CZTSSe absorbers. The XRF results suggest that the ratio of Cu/(Zn + Sn) and Zn/Sn changed little after selenizing, while the ratio of S/(S + Se) was reduced to only 0.01–0.02, which means most of sulfur was replaced by selenium during selenizing process. Se partial pressure is much higher than that of S, whereas, the saturated vapor pressure of S is much higher than that of Se, leading to S escaping from the film and substituted by Se [24]. Besides, the ratios of (S + Se)/(Cu + Zn + Sn) of all selenized samples are greater than 1 due to the formation of $Mo(S,Se)_2$. The ratio of (S + Se)/(Cu + Zn + Sn) increases and the ratio of S/(S + Se) decreases with the increase of the thickness of $Mo(S,Se)_2$ layer, respectively. In addition, $Mo(S,Se)_2$ films named as $Mo(S,Se)_2-1$, $Mo(S,Se)_2-2$, and $Mo(S,Se)_2-3$ were prepared by selenizing sample Mo-1, Mo-2, and Mo-3 directly using the same selenizing process of CZTSSe absorbers, respectively.

CZTSSe thin film solar cells were accomplished by a chemical bath deposited $\sim$ 50 nm CdS buffer layer, a mid-frequency magnetron sputtered $\sim$ 50 nm intrinsic ZnO, a DC-magnetron sputtered $\sim$ 500 nm ZnO:Al transparent conducting layer, and an electron beam evaporated Ni/Al grid contact. The active area of each CZTSSe solar cell was about 0.34 cm^2 defined by mechanical scribing.

The thicknesses of films were measured by a step profiler (Dektak 150). Crystal structures of the films were characterized by a PANalytical X'Pert pro X-ray diffractometer (XRD) with Cu Kα as the radiation ($\lambda_{K\alpha}$ = 1.5416 Å). The compositions of the films were measured by PANalytical MagixPW2403 X-ray fluorescent spectrometer (XRF) with inductively coupled plasma spectroscopy (ICP) calibrated to ensure its accuracy. The morphologies of the films were characterized by a scanning electron microscope (SEM, Hitachi S-4800). Atomic force microscopy (AFM) measurements were conducted with a Dimension Icon AFM (Bruker) via the tapping mode. The current density-voltage (J-V) characteristics were measured by a solar simulator calibrated with a certified Si solar cell under the standard conditions (AM 1.5 G,1000 w/m^2, 25 °C). The external quantum efficiency (EQE) spectra were measured using a chopped white light source (150 W halogen lamp) calibrated with certified Si solar cell (300–900 nm) and InGaAs solar cell (900–1300 nm).

3. Results and discussion

Fig. 1(d) shows the surface morphology of sample Mo-1, which is composed of large worm-like grains with ca. 200 nm long by ca. 100 nm wide (Fig. S1). And Fig. 1(d) shows clearly the presence of voids between grains. To modify the surface morphologies of Mo films, a thin top layer (ca. 100 nm) was deposited at working power of 2.5 and 0.5 W/cm^2 respectively under the same working pressure of 1.5 Pa, which were named as Mo-2 and Mo-3, respectively. Fig. 1(e) and (f) show the selected SEM surface morphologies of sample Mo-2 and Mo-3, and the insets are the enlarged morphology images. We can clearly see that small grains uniformly cover the surface of sample Mo-2 and Mo-3. The films become more compact from Mo-1 to Mo-3, and the grain boundaries of Mo-3 are not as sharp as those in sample Mo-1 and Mo-2. The changes of surface morphologies are also certified by AFM, as shown in Fig. S1. The root mean square roughness of sample Mo-1, Mo-2, and Mo-3 are 13.0 nm, 8.4 nm, and 6.7 nm (Table S1), respectively.