Solar Energy Materials and Solar Cells 178 (2018) 200–207

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

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

Stoichiometry control of sputtered zinc oxide films by adjusting Ar/O_2 gas ratios as electron transport layers for efficient planar perovskite solar cells

Wenjing Zhao[a,b,c], Kang Wang[a,b,c], Hua Li[a,b,c], Zhou Yang[a,b,c], Zhike Liu[a,b,c], Jie Sun[a,b,c], Dapeng Wang[a,b,c,*], Shengzhong (Frank) Liu[a,b,c,*]

[a] Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710119, China

[b] Shaanxi Key Laboratory for Advanced Energy Devices, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710119, China

[c] Shaanxi Engineering Lab for Advanced Energy Technology, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710119, China

ARTICLE INFO

Keywords:
Magnetron sputtering
Gas ratio
ZnO film
Electron transport layer
Perovskite solar cells

ABSTRACT

To modify the stoichiometry and enhance electronic transportation of electron transport layers (ETLs) potentially for the large-scale high performance planar perovskite solar cells (PSCs) on the flexible substrate, ZnO films as ETLs with controlled stoichiometry are fabricated by magnetron sputtering method under a mixture working gases of Ar and O_2 at room temperature. The impact of Ar/O_2 ratios on the structural, electrical, and optical properties of ZnO films is systematically investigated. The X-ray photoelectron spectroscopy results indicate that the sputtered ZnO films with controlled stoichiometry are successfully achieved. For the proper deposition condition with Ar/O_2 ratio of 1:4, ZnO film exhibits large-size grains, low defect states density, and good optical crystalline quality. Furthermore, the sputtered ZnO films deposited under various Ar/O_2 ratios are introduced into the PSCs as ETLs. The photovoltaic performance of the PSCs is strongly dependent on the properties of the sputtered ZnO ETLs. Compared with the ZnO ETLs prepared under various Ar/O_2 ratios, the PSCs based on the ZnO ETL deposited under the Ar/O_2 ratio of 1:4 demonstrate the improved short-circuit current and fill factor, contributing to a maximum power conversion efficiency of 16.60%. This study highlights that the sputtered ZnO film is one of promising ETLs for high-efficiency PSCs under low-temperature processing.

1. Introduction

Recently, perovskite solar cells (PSCs), as an outstanding representative of the third-generation solar cells, have attracted the global attentions due to their advantages of noticeable photovoltaic performance, low-cost, simple-processing, and high-flexibility [1–3]. In less than a decade, the certified power conversion efficiency (PCE) of PSCs has rapidly increased from 3.8% in 2009–22.1% now under 1 sun conditions (100 mW/cm^{-2} AM 1.5 G) [4,5], which is approaching the PCE of commercial monocrystalline silicon solar cells. Such a significant boosting performance in the PCE is mainly attributed to the superior intrinsic properties of the perovskite materials, including ambipolar charge transport [6], tunable bandgaps (direct optical bandgap of $CH_3NH_3PbI_3$ is ~ 1.5 eV) [7], high absorption coefficients (~ 10^4 cm^{-1}) [8], long charge carrier diffusion lengths ($CH_3NH_3PbI_3$ > 1 μm) [9], small exciton binding energies (2–55 meV) [10], and low charge recombination rates. Therefore, combined these impressive properties with simple fabrication processes through the mature solution- or vacuum-based techniques [11,12], the high-quality perovskite films are desirably fabricated according to the practical requirements, which accelerates the development and applications of perovskite photovoltaic devices.

In addition to a perovskite absorber layer, a typical PSC device architecture consists two electrodes, an electron transport layer (ETL), and a hole transport layer (HTL). There are several literatures on improving the performance of PSCs without any ETLs [13,14]. However, to obtain a high-efficiency PSC, the ETL still plays an indispensable role in blocking holes and transporting electrons. The ETL also can prevent the perovskite absorber layer from directly contacting the electrode to reduce the recombination of photocarriers. In terms of the electron transport materials, TiO_2 is one of most robust and stable metal oxide based ETLs for the state-of-the-art PSCs. However, to obtain high-quality TiO_2-based ETL with sufficient conductivity, a high-temperature treatment at 450–500 °C is always required [15,16]. Such a high temperature treatment introduces the extra production costs and constrains the flexible substrate used in roll-to-roll technique. Comparing with

* Corresponding authors at: Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710119, China.

E-mail addresses: dpwang@snnu.edu.cn (D. Wang), liusz@snnu.edu.cn (S.F. Liu).

https://doi.org/10.1016/j.solmat.2018.01.027
Received 13 December 2017; Received in revised form 16 January 2018; Accepted 21 January 2018

TiO_2, zinc oxide (ZnO) is a very competitive candidate for the ETL due to its suitable energy levels and high electron mobility [17]. Moreover, ZnO can be easily fabricated by various processing approaches at a low temperature, which caters to the development trend in large-scale production and low-energy consumption of solar cells. Kumar et al. reported the PSCs with the PCE of 8.90% employing the ZnO contact layer grown by chemical bath deposition as the ETL [18]. Guo et al. have obtained the high-quality spin-coating processed ZnO/$CH_3NH_3PbI_3$ bilayer for high-performance PSCs under ambient conditions [19]. Zhao et al. have investigated the charge extraction and transportation properties of ZnO films made through sol-gel and hydrolysis methods as ETLs in perovskite solar cells [20]. Qin et al. reported the surface engineering to enhance thermochemical stability of $CH_3NH_3PbI_3$ perovskite films on the solution-processed ZnO film [21]. It is found that the morphology and structure of ZnO film depends on the processing methods, which affect the charge extraction and transportation from perovskite layer into ZnO film, determining the efficiency and stability of the PSCs.

Compared with various solution-processing methods for ZnO ETLs, magnetron sputtering technique, one of the promising physical vapour deposition technologies, is considered as the most convenient method to deposit reproducible and homogeneous ZnO films over a large-area substrate at a lower deposition temperature [22]. In addition, the structural, electrical, and optical properties of sputtered ZnO film with controllable stoichiometry can be easily modified by adjusting sputtering parameters, such as working gas Ar/O_2 ratio, which may have a great impact on the performance of the PSCs.

In this study, ZnO films are fabricated by magnetron sputtering method under a mixture working gases of Ar and O_2 at room temperature. We have systematically investigated the impact of Ar/O_2 ratios on the structural, electrical, and optical properties of ZnO films. The X-ray photoelectron spectroscopy (XPS) results indicate that the stoichiometry of sputtered ZnO films could be modified even deposited by various Ar/O_2 ratios at room temperature. When the Ar/O_2 ratio is 1:4, ZnO film exhibits larger grains, lower bulk defect states density, and better optical crystalline quality in comparison to ZnO films prepared with the other Ar/O_2 ratios. The PSCs based on a ZnO ETL deposited under the proper Ar/O_2 ratio of 1:4 demonstrate the improved short-circuit current (J_{sc}) and fill factor (FF), contributing to a maximum PCE of 16.60%.

2. Experimental

ZnO films were deposited on FTO substrate by a radio frequency (RF) magnetron sputtering system. Firstly, the FTO glass substrate was sequentially washed by acetone, isopropanol, and ethanol in an ultrasonic processing for 30 min, respectively. The substrate was then fixed on the substrate holder and was transferred to the anode side in the chamber. During the sputtering processing, the RF power was set consistently at 200 W and deposition pressure was kept at 7 Pa with a turbo molecular pump. Noticeably, the deposition temperature was controlled at room temperature for all films. To evaluate the impact of the working gas on the properties of ZnO films, a mixture gas of argon and oxygen with the total flow rate of 50 sccm was introduced. The Ar/O_2 ratios of 5:0, 3:2, 1:1, 1:4, and 0:5 were adjusted by mass flow controllers, respectively. Finally, the uniform ZnO films with a thickness of ~ 80 nm were obtained.

The structure of PSC is FTO/ZnO/$CH_3NH_3PbI_3$/spiroMeOTAD/Au. Following by the fabrication of sputtered ZnO ETLs, the $CH_3NH_3PbI_3$ perovskite absorber layer is made as follows. At first, the perovskite precursor solution is prepared at room temperature in glove box according to our previous publication [23], including 1.106 g PbI_2 (99.99%, Alfar Aesar), 0.38 g CH_3NH_3I (synthesized based on our published literature), and 2 mL γ-butyrolactone (GBL). After the filtration, the mixed solution is spin-coated on the ZnO ETLs at 4000 rpm for 30 s and methylbenzene as anti-solvent is dripped into the precursor solution during the spin-coating process. At last, the dark perovskite films are obtained after post-annealing on a hot-plate at 100 °C for 10 min. For the HTL solution, 18 mg spiroMeOTAD, 28.8 μL tert-butylpyridine, and 44 μL lithium bis imide acetonitrile solution (520 mg/mL) are dissolved in 2 mL chlorobenzene. The HTL solution is also spin-coated onto perovskite layer at 5000 rmp for 30 s. Au electrode with a thickness of 80 nm is then deposited by a thermal evaporator.

The surface morphology and roughness images of sputtered ZnO films are characterized by a field-emission scanning electron microscopy (SEM, HITACHI, SU 8020) and an atomic force microscope (AFM, Brooke, Dimension ICON). The chemical properties of the ZnO films are investigated by XPS (ESCALAB250Xi, Thermo Fisher Scientific). Photoluminescence (PL) (excitation at 325 nm) and time-resolved PL (TRPL) (excitation at 405 nm and emission at 760 nm) are carried out with an Edinburgh Instruments Ltd. FLS980 spectrometer. The photocurrent density versus voltage (*J–V*) performance of the PSCs are measured by using a Keithley 2400 source meter under the solar simulator illumination with the light intensity of 100 mW/cm^2 (AM 1.5 G, SAN-EIELECTRIC XES-40S2-CE solar simulator), as calibrated by a NREL-traceable KG5 filtered silicon reference cell. The active area of all solar cells is prepared by a 9 × 9 mm^2 mask. All devices are measured under the standard test procedure at a scan rate of 30 mV/s. Incident photon-to-current conversion efficiency (IPCE) spectra of the PSCs are recorded by a QTest Station 500TI system (Crowntech. Inc., USA). The monochromatic light intensity for IPCE is calibrated using a reference silicon detector.

3. Results and discussion

The top-view SEM images of the sputtered ZnO films, which are deposited on FTO glass under various Ar/O_2 ratios, are shown in Figs. 1**a–1e**. The uniform and compact structures are clearly observed from all films. The statistics distribution of the average grain sizes are determined by image analysis using more than 100 grains per measurement, which are plotted in Figs. 1**f–1j**, respectively. It is found that the Ar/O_2 ratio has a great impact on the surface morphology of ZnO films. For the film deposited under the Ar-rich condition, the typical packed nanoparticles with the average grain size of ~ 106 nm are observed in Fig. 1**a**. When the oxygen is introduced during the deposition even with a low flow rate, great changes have taken place on the surface morphology of the sputtered ZnO films. The large grains with the average diameter of ~ 160 nm are adhered uniformly by the small grains with the diameter of ~ 25 nm. The generation of small grains surrounding the large grains might attribute to the oxidation effect of oxygen during the sputtering process. The ejected species, including the sputtered atoms and ion clusters from the ZnO target [24], contain the amount of zinc dangling bonds and experience the oxidation reaction with the oxygen-containing sputtering gas atoms prior to reaching the substrate, contributing to the generation of ZnO nanoparticle on the large grains. In this study, the substrate temperature is set at room temperature. Such a low temperature cannot provide enough energy for the diffusion and rearrangement of sputtered ZnO nanoparticles on the substrate [25], as shown in Figs. 1**b and** 1**c**. When the Ar/O_2 ratio is 1:4, a large quantity of zinc related species react adequately with the appropriate quantity of oxygen. The small grain ZnO nanoparticles are then combined into the large-size nanoparticles before reaching the substrate. As a result, ZnO nanoparticles with the average grain size of ~ 242 nm are observed in Fig. 1**d**. However, under the O_2 condition, there are still small nanoparticles with the average grain size of ~ 141 nm on the ZnO film surface, as shown in Fig. 1**e**. It is because the ZnO nanoparticles hardly combine together during the whole deposition process owing to the zinc deficiency in the ejected species.

Figs. 1**k–1o** show the AFM images of the sputtered ZnO films deposited under various Ar/O_2 ratios. For the film deposited under the Ar-rich condition, the root-mean-square (RMS) roughness is 18.8 nm. When the oxygen content increases to the Ar/O_2 ratio of 3:2, the RMS