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Fabrication of efficient PbS colloidal quantum dot solar cell with low temperature sputter-deposited ZnO electron transport layer

Shuaipu Zang, Yinglin Wang*, Meiying Li, Wei Su, Hancheng Zhu, Xintong Zhang*, Yichun Liu*

Center for Advanced Optoelectronic Materials Research, School of Physics, and Key Laboratory of UV-Emitting Materials and Technology of Chinese Ministry of Education, Northeast Normal University, 5268 Renmin Street, Changchun 130024, People's Republic of China

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ABSTRACT

Preparation of electron transport layer (ETL) with high uniformity by convenient and low-temperature process is of essential importance for the future development of colloidal quantum dot solar cells (CQDSCs) into large-area and flexible devices. Herein we utilized magnetron sputtering technique to deposit ZnO thin film as the ETL of PbS CQDSCs. The ZnO film deposited at ambient temperature displayed preferential growth along (001) direction, pinhole free morphology, and good optical transmittance. On rigid SnO_2:F (FTO) conductive glass substrates, PbS CQDSCs with sputtered ZnO ETL achieved a power conversion efficiency of 6.47% under AM 1.5 G simulated solar irradiation, which was higher than the 6.02% efficiency of the CQDSC fabricated on the benchmarked ZnO nanocrystals ETL. The good uniformity of sputtered ZnO film also facilitated the consistency of photovoltaic parameters of big-sized CQDSCs, as demonstrated by the similar output of four series-connected CQDSC units fabricated in one batch with a total active area of 14.4 cm^2. Flexible PbS CQDSCs was also fabricated on the sputtered ZnO ETL, using In_2O_3:Sn-coated polyethylene terephthalate (ITO-PET) as the substrate, which achieved a power conversion efficiency of 3.87% and displayed negligible decline of the photovoltaic parameters after 100-time bending treatment. Our research demonstrates that the magnetron-sputtered ZnO film, with favorable features of low-temperature process, large-area continuity, and high bending tolerance, presents promising potential for the future development of PbS CQDSCs.

1. Introduction

Colloidal quantum dots solar cells (CQDSCs) have become promising candidates for the high-efficiency and low-cost generation of solar electricity [1–3], due to many advantages of light-harvesting lead chalcogenide (PbX, X = S, Se, Te) quantum dots, such as size-tunable bandgap, scalable synthesis, multiple exciton generation and solution-based deposition technology, etc. [4–6]. During the past decade, the power conversion efficiency (PCE) of CQDSCs was dramatically improved through surface passivation of CQDs and device engineering of cells [7–20]. Meanwhile, it was also reported that CQDSCs without any encapsulation presented respectable air-stability for a period of over 5 months [8], which is encouraging for the practical applications of CQDSCs. However, it is still challenged to develop universal fabrication technologies for CQDSCs, satisfying various requirements of commercial applications, such as large-scale production and flexible devices.

There have been several advanced methods for fabricating large-scale PbS QDs film suitable for CQDSCs [21–24]. The PbS nano-ink was explored to upgrade the multi-step fabrication of PbS QDs film based on the layer-by-layer spin-coating to a single-step process [21]. A process-controlled spray-coating technology, which simulated the roll-to-roll method, successfully achieved a considerable fabrication rate of 1 m/s for PbS film [23]. Besides the PbS QDs layer, the electron transport layer (ETL) is another key component of CQDSCs. It was usually prepared by spin coating the dispersed solution of pre-synthesized ZnO nanocrystals (NCs) [8], which is not applicable in the large-scale production of ETL. Among the general techniques for preparing metal oxide films, such as magnetron sputtering [25], spray pyrolysis [26], sol-gel methods [27], and electrodeposition [28], etc., magnetron sputtering has been well applied in the existing photonics and electronics industries, since it enjoys several favorite advantages, such as easy control, high reproducibility, large scale-up and moderate processing temperature [29]. Consequently, magnetron-sputtered ZnO film could facilitate the fabrication of CQDSCs with diverse sizes and substrates.

Herein, we demonstrated that the low-temperature magnetron-sputtered ZnO served as more reasonable ETL in PbS CQDSCs compared with the benchmarked ZnO NC_s film. High continuity of magnetron-sputtered ZnO film brought favorable consistency of photovoltaic

* Corresponding authors.
E-mail addresses: wangyl100@nenu.edu.cn (Y. Wang), xtzhang@nenu.edu.cn (X. Zhang), ycliu@nenu.edu.cn (Y. Liu).

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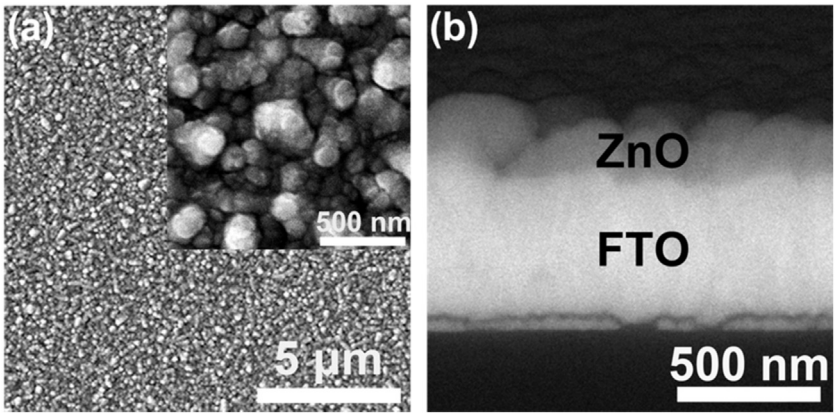

Fig. 1. (a) Top-view and (b) cross-sectional SEM images of sputtered ZnO film on glass/FTO substrate.

performance to each series unit of a cascade system, which generated a maximum output power of 12.58 mW from an active area of 14.4 cm^2. We also incorporated this low-temperature magnetron-sputtered ZnO film into the flexible CQDSCs, and proved its outstanding tolerance against bending treatment by the ignorable variation in the photovoltaic parameters of CQDSCs.

2. Experimental

2.1. Materials

Zinc acetate dehydrate (99%), methanol (99.9%), potassium hydroxide (90%), lead oxide (99%), 1,2-ethanedithiol (EDT, 97%) and acetonitrile (99%) were purchased from Aladdin. Tetrabutylammonium iodide (TBAI, 98%), oleic acid (OA, 99%), hexamethyldisilathiane (TMS, 99%) and 1-octadecene (ODE, 90%) were purchased from Aldrich. All chemicals were used as received without purification. SnO2:F (FTO) conductive substrates (15 Ω/sq) were purchased from Nippon Sheet Glass. ITO-PET conductive substrates (45 Ω/sq) were purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. These substrates (20 mm × 20 mm, 50 mm × 50 mm) were firstly cleaned sequentially by ultrasonication in, deionized water, acetone and isopropanol and then exposed to UV-ozone for 15 min for further use.

2.2. Solar cell fabrication

ZnO films were deposited on various substrates with a custom design magneton-sputtering equipment at ambient temperature. Typically, ZnO target (99.99%) was bombarded in argon atmosphere under a given power density of 2.7 W/cm^2. The system pressure was maintained at 1.5×10^{-2} Torr, and the deposition time was 40 min. The sputter-deposited ZnO films (~150 nm thick) were directly used for characterizations and device fabrication without any annealing treatment.

CQDSCs were fabricated using the sputter-deposited ZnO films as ETL and PbS QDs film as the light harvesting layer. PbS QDs with the first exciton absorption peak at 940 nm (Fig. S1) were prepared by the reported method [30]. The PbS QDs, dispersed in octane solvent, were deposited on ZnO ETL by the layer-by-layer spin-coating method adopted from the literature [8]. All spin-coating steps were performed under ambient condition at room temperature. Lastly, Au electrodes were thermally evaporated onto the PbS QD layer through shadow mask at a base pressure of 10^{-6} Torr to finish cell fabrication. The active area of cells was 2.6 mm in diameter defined by the apertures of shadow mask.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 X-ray diffractometer. UV-vis absorption spectra were collected on a UH4150 spectrophotometer. The morphology of ZnO films was observed with a FEI Quanta 250 scanning electron microscope (SEM). Photoluminescence measurement was conducted on a J-Y Horiba UV-lamb micro-Raman spectrometer in a back-scattering configuration, using a 325 nm He-Cd laser for excitation. Current density–voltage (*J-V*) characteristics were recorded on a Keithley 2400 A source meter under AM 1.5 G irradiation supplied by a Sun 2000 solar simulator (ABET Technology). Open-circuit photovoltage decay measurements is carried out with Modulab XM PhotoEchem Station (Solartron Analytical) and a 680 nm diode light (M680L4 Thorlabs) as the excitation source. All measurements were performed in air. Cells were stored in ambient air between each measurement without encapsulation.

3. Result and discussion

Fig. 1 shows the top-view and cross-sectional SEM images of the sputtered ZnO films. The ZnO films displayed a rough but continuous morphology without pinhole in different magnifications (Fig. 1a). By contrast, numerous pinholes exist on the surface of ZnO NCs film (Fig. S2a), which might be induced by the fast volatilization of chloroform solvent during the spin-coating process and be detrimental to the photovoltaic performance of solar cells fabricated on it.

The X-ray diffraction (XRD) pattern of magnetron-sputtered ZnO film (Fig. 2a) shows a strong (002) peak, indicating the preferential growth of ZnO along the (001) direction. The optical properties of the sputtered ZnO film were further investigated for its photovoltaic application. The exciton absorption difference between the sputtered ZnO and the ZnO NCs film (Fig. 2b and Fig. S2b) led to the unavoidable transmittance loss from 300 to 450 nm (Fig. 2c). Furthermore, the transmittance loss of magnetron-sputtered ZnO film in the range from 450 to 800 nm was a bit higher than that of ZnO NCs film, which was associated with enhanced scattering induced from its rough surface as depicted in Fig. 1a. In the photoluminescence (PL) spectrum of the sputtered ZnO film (Fig. 2d), the peak appeared around 380 nm was generated by intrinsic luminescence of ZnO, and the broad peak from 500 to 650 nm was usually deemed as the luminescence of surface defects of ZnO caused by the oxygen vacancies [31]. Such defects may impact the carrier recombination and photovoltaic performance of solar cells.

PbS CQDSCs with planar heterojunction structure were then fabricated with magnetron-sputtered ZnO and ZnO NCs ETL (Fig. S3). Photocurrent density-voltage (*J-V*) curves of these cells (Fig. 3a) were measured under AM 1.5 G solar irradiation (100 mW/cm^2) and atmo-