Thermal-evaporated selenium as a hole-transporting material for planar perovskite solar cells

Yunxiang Di[a], Qiang Zeng[a], Chun Huang[b], Ding Tang[d], Kaiwen Sun[c], Chang Yan[c], Ying Wang[a], Shanming Ke[b,*], Liangxing Jiang[a], Xiaojing Hao[c], Yanqing Lai[a], Fangyang Liu[a,c,**]

[a] School of Metallurgy and Environment, Central South University, Changsha 410083, PR China
[b] College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, PR China
[c] Australian Centre for Advanced Photovoltaics, School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, NSW 2052, Australia
[d] College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, PR China

ABSTRACT

A hole-transporting layer is essential for effective operation of planar perovskite solar cells. Hole-transporting materials (HTMs) used so far are mainly based on organic semiconductors, which are usually expensive and relatively instable compared with inorganic materials. In this article, crystalline selenium (c-Se) prepared by thermal evaporation followed by annealing at low temperature was used as the hole-transporting layer for the planar perovskite solar cells in the device structure of fluorine-doped tin oxide (FTO)/SnO$_2$/perovskite/selenium/Au. The device employing c-Se as HTM displayed enhanced long-term stability, keeping 80% of the original efficiency after 40 days in ambient environment. However, the power conversion efficiency of 8.3% remains low compared with the device based on spiroOMeTAD, which results from higher recombination in the c-Se device as determined by impedance spectroscopy. Thermal-evaporated selenium could be a low-cost and easy-fabrication HTM for efficient and stable perovskite solar cells after reducing the recombination in devices.

1. Introduction

Perovskite solar cells (PSCs) employing organo-lead halide perovskite absorber materials have rapidly become the focus of emerging photovoltaic techniques in recent years. Their excellent properties, such as high optical coefficient [1,2], high charge carrier mobility [3], and long diffusion lengths [4,5] enable the rapid development of the power conversion efficiency (PCEs) from 3% to over 20% within few years [1,2,6–8].

Despite the excellent photovoltaic performance, PSCs are susceptible to degradation in moisture and air because of the low formation energy of perovskite, which further hinders their development and deployment [9]. Therefore, it is important to find a suitable top charge-transporting layer of the device to defend against moisture ingress [10]. For the regular n-i-p configuration PSCs, p-type organic hole-transporting materials (HTM), such as 2,2′,7,7′-tetrakis (N, N-p-dimethoxyphenylamino)-9,9′-spirobifluorene (spiroOMeTAD), have been widely used [11]. Although the incorporation of organic hole-transporting layers can obtain high efficiency, the relatively prohibitive cost and poor stability of these organic hole-transporting layers limit the

utilization and commercialization of these PSCs. Moreover, additives (such as 4-tert-butylpyrifine (TBP) and Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI)) are usually needed to improve the conductivity of organic HTM, which can dramatically decrease the chemical stability of perovskite [12]. Thus, it is necessary to develop new HTMs with low cost and high stability.

Recently, many studies have focused on inorganic hole-transporting layers. CuSCN [13,14], CuI [15,16], CuGaO$_2$ [17], MoO$_2$ [18], CuInS$_2$ [19], CZTS [20] and CIGS [21] have been employed in regular configuration PSCs. Although these inorganic hole-transporting layers can improve the stability of PSCs, the efficiency of regular configuration PSCs based on most of them (~ 10%) is still lower than that of spiroOMeTAD devices. In addition, most of them are solution-processed nanocrystals, which makes the fabrication of PSCs more difficult and complex. Discovering efficient, stable and low-cost inorganic HTMs has remained a challenge.

In this work, we report the use of thermal-evaporated selenium as HTM in the regular configuration PSCs. Crystalline selenium (c-Se) has been investigated as absorber in thin film solar cells [22–26] due to the high absorption coefficient over 10^4 cm^{-1}. Moreover, c-Se is low cost

and has proper low-lying valence band maximum (-5.64 eV) [26] as well as high hole mobility (~ 60 cm^2 V^{-1} s^{-1}) [27], which makes it a promising HTM candidate. We demonstrate PSCs based on c-Se HTM that show 8.3% efficiency and significantly improved stability compared with PSCs based on spiroOMeTAD.

2. Method

2.1. Materials

Spiro-OMeTAD (Shenzhen Feiming Science and Technology Crop.), TBP (Sigma Aldrich, 99%), Li-TFSI (Sigma Aldrich, 97%), PbI$_2$ (Sigma Aldrich, 99.999%), PbBr$_2$ (Sigma Aldrich, 99.999%), CH(NH$_2$)$_2$I (dyesol), CH$_3$NH$_3$Br (dyesol), dimethylformamide (DMF, Sigma Aldrich, 99%), dimethyl sulfoxide (DMF, Sigma Aldrich, 99%), selenium (Aladdin, 99.999%).

2.2. Fabrication of PSCs

The 15 Ω/sq patterned FTO glass (Nippon) was washed sequentially with 2% Micro-90 solution, ethanol, and deionized water. SnO$_2$ compact layer was prepared using a previously published protocol by Qi et al.[28]. The SnO$_2$ colloid precursor obtained from Alfa Aesar (tin (IV) oxide, 15% in H$_2$O colloidal dispersion) was diluted by H$_2$O to 3% and then filtered by 0.45 μm PTFE filters. After that, the solution was spin-coated onto the patterned FTO substrate at 3000 rpm for 30 s, followed by annealing at 150 °C for 30 min in ambient air. The perovskite films were deposited from a precursor solution containing CH(NH$_2$)$_2$I (1 M), PbI$_2$ (1.1 M), CH$_3$NH$_3$Br (0.2 M) and PbBr$_2$ (0.2 M) in anhydrous DMF : DMSO 4:1 (v/v) according to a previous report [29]. The perovskite solution was spin-coated in a two-step program; first at 1000 rpm for 10 s and then at 4000 rpm for 30 s. During the second step, 200 μl of chlorobenzene were poured on the spinning substrate 15 s prior to the end of the program. The substrates were then annealed at 100 °C for 1 h in a nitrogen filled glove box.

2.3. Spiro-OMeTAD deposition

Spiro-OMeTAD solution was spin-coated onto the perovskite layer at a speed of 4000 rpm for 20 s, where 1 ml Spiro-OMeTAD/chlorobenzene (75 mg/ml) solution was employed with the addition of 17.5 μl Li-TFSI/acetonitrile (520 mg/ml) and 28.5 μl TBP. After that, the samples were stored in a desiccator overnight. Then, 100 nm of Au electrode was thermally evaporated under a vacuum of 10^{-4} pa. The spiroOMeTAD based devices need no further annealing.

2.4. Selenium deposition

A 1.5 μm thick layer of selenium was deposited on the perovskite layer using thermal evaporation under a vacuum of 10^{-4} pa at a deposition speed of 1 nm/s. Au electrode was then deposited on the selenium to achieve ohmic contact. After that, the whole device with the structure FTO glass/SnO$_2$/perovskite/c-Se/Au was annealed at 100 °C for 30 min in inert atmosphere to convert amorphous selenium into lower-resistive crystalline form.

2.5. Characterization

The surface and cross-section morphologies of the samples were examined with a scanning electron microscope (SEM, Quanta-200). The UV–Vis absorption spectra of perovskite and selenium films were recorded on a Shimadzu UV-2450 instrument. The crystal structures of selenium films were determined by using X-ray diffraction (Bruker) and Raman scatter spectroscopy (LabRAM HR800) with excitation wavelengths of 532 nm. The ultraviolet photoelectron spectroscopy (UPS) measurements were carried out on an STARPES (SPECS) system with a

SPECS Microwave UV Light Source (He I = 21.2 eV). A total energy resolution of 70 meV was selected for the UPS measurements as determined from the Fermi edge of Au. Current density-voltage (J–V) characterization of PSCs was measured by a Keithley 2400 Source Meter under the illumination of AM 1.5 G simulated solar light (Newport 91160). EQE data was recorded by a QEX10 spectral response system. Steady photoluminescence spectra were measured using a 1/4 m monochromator (Cornerstone TM260) 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. Impedance spectra was recorded over the frequency range of 1 MHz to 1 Hz under 100 mW/cm^2 at AM 1.5 G illumination with a computer-controlled potentiostat (Princeton Applied Research PARSTAT 4000).

3. Results and discussion

Considering that perovskite is sensitive to solution process and temperature, thermal evaporation of materials with low melting point is a simple approach to fabricate high quality HTMs. The X-ray diffraction patterns of thermal-evaporated selenium/FTO/glass before and after annealing at 100 °C for 30 min in inert atmosphere were shown in Fig. 1a. The as grown film displays only the diffraction peaks of FTO which are marked with asterisks (*), indicating the absence of crystalline selenium phase. After annealing, strong diffraction peaks are observed at the angles of 23.5° and 29.7° corresponding to the (100) and (101) crystal planes of trigonal selenium (JCPDF 06–0362). Raman scattering spectrum was performed to further confirm the trigonal phase, as shown in Fig. 1b. The peak located at ~ 236 cm^{-1} consists well with previous report [30]. It is known from the literature that trigonal phase is preferred to be formed from amorphous selenium under low-temperature annealing due to the inner anisotropy [31]. The XRD and Raman scattering results demonstrate that high-purity and well-crystalline trigonal selenium films were produced after low temperature annealing. The XRD results of selenium films annealed at different temperatures along with the SEM images were shown in Fig. S1, and S2, respectively. Trigonal phase could be detected clearly by XRD peaks when the annealing temperature increased to 70 °C or above, which can be further proved by the formation of crystal grains as shown in Fig. S2. Fully crystalline selenium films were successfully achieved by annealing at 100 °C for 30 min. The absorption spectrum of c-Se films as shown in Fig. 1c indicates that the optical band gap of c-Se is 1.8 eV. UV-Vis absorption spectra and corresponding optical band gap calculation of thermal-evaporated selenium annealed at different temperature were presented in Fig. S3. The absorption edge shifts to long wavelength when the annealing temperature increases. The corresponding band gap decreases from 2.1 eV to 1.8 eV, due to the smaller band gap of crystalline Se. The morphology of c-Se deposited on perovskite film was shown in Fig. 1d. The c-Se film is compact with large, micrometer-scale crystalline grains. To identify whether the selenium will react with perovskite during the deposition or annealing process, UV-visible absorbance spectra of glass/perovskite films were compared before and after selenium deposition, as shown in Fig. S4. The absence of absorption edge shift after selenium deposition demonstrates that the reaction between perovskite and selenium can be negligible [16].

The perovskite solar cells were fabricated with the configuration of FTO glass/SnO$_2$/perovskite/c-Se/Au. The solution-progressed perovskite film is smooth and compact as observed in the SEM image (Fig. S5). The cross-sectional SEM image of SnO$_2$/perovskite/c-Se film (Fig. 2a) indicates a perovskite layer with a thickness of ~ 700 nm and a compact c-Se layer with a thickness of ~ 1500 nm. The c-Se layer contacts the perovskite layer directly and covers the perovskite layer uniformly, which is expected to be beneficial for charge extraction. Ultraviolet photoelectron spectroscopy was employed to determine the fermi energy and valance band maximum (VBM) of c-Se, as shown in Fig. S6. The fermi energy of c-Se is determined to be -4.43 eV by