Current Applied Physics 16 (2016) 1353–1363

Contents lists available at ScienceDirect

Current Applied Physics

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

The interface and its role in carrier transfer/recombination dynamics for the planar perovskite solar cells prepared under fully open air conditions

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A R T I C L E I N F O

Article history:
Received 16 May 2016
Received in revised form
9 July 2016
Accepted 1 August 2016
Available online 3 August 2016

Keywords:
Planar perovskite solar cells
Open air conditions
Interfaces
Transport/recombination kinetics
Dynamic IMVS model

A B S T R A C T

The planar heterojunction perovskite solar cells, where the perovskite film is deposited directly onto a flat hole blocking layer, have recently attracted a great deal of attention owing to their high performance and ease of processing. However, the interface and its underlying role in carrier transport/recombination kinetics for such perovskite devices prepared under ambient air is still obscure. Herein, we addressed this issue by a dynamic intensity modulated photovoltage spectroscopy (IMVS) model using a continuity equation. The interface and its role in charge-carrier transport/recombination kinetics have been explored and discussed as an approach to understand the origin of the photovoltaic properties for the devices prepared under ambient air. The experimental IMVS responses were measured and satisfactorily fitted to the analytical results. Compared to the typical IMVS model based on dye-sensitized solar cells (DSSCs), the better IMVS fitting results presented in this study indicated that there was a discrepancy between the planar perovskite devices and those of DSSCs in electron transport/recombination properties, because carrier transfer across the TiO_2/liquid electrolyte interface in DSSCs has been modified. That is, the Schottky interface in DSSCs needs to be replaced by the semiconductor heterojunction interface in perovskite solar cells (PSCs). Besides, the interface exhibits a more significant role in determining the carrier transport/recombination process by influencing the boundary conditions in a continuity equation. Furthermore, the intensity modulated photocurrent/photovoltage spectroscopy responses demonstrated that the carrier recombination characteristic is ultimately related with the surface and defect density in the interface. Interfacial modification, such as air-annealing, resulting in crystallographic changes, oxygen passivation, and variation in grain domain size, could suppress carrier recombination and prolong charge lifetime, which can yield more photo-generated electrons to be collected by anode, subsequently resulting in strikingly improving photovoltaic performance of the devices. In short, the dynamic IMVS model would help in elucidating the role of interface and the importance of interfacial modification or even interface design in order to obtain a highly efficient solar cell. The study can not only pave the way to construct the current–voltage curve using a continuity equation model, but also provide new insights into the performance-improving steps for the PSCs prepared under fully open air conditions, which is of great importance for their future commercialization.

1. Introduction

Derived from dye-sensitized solar cells (DSSCs), hybrid organic–inorganic perovskite (e.g., $CH_3NH_3PbI_3$) solar cells (PSCs) have been a hot area of research during the past three years due to their high efficiency, low production cost, and simple preparing process [1–8]. Since the first reported perovskite device [4], PSCs fabricated via a solution process have reached a power conversion efficiency (PCE) as high as 19.3% reported by Y. Yang and co-workers [7], which indicates that organometal halide perovskite is a very promising solar cell material.

To date, PSCs have evolved into two different structures with some discrepancies within them. The first uses a microporous oxide

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http://dx.doi.org/10.1016/j.cap.2016.08.002
1567-1739/

layer as the scaffold in PSCs, such as TiO_2, ZnO, Al_2O_3, ZrO_2 and etc., typically for the purpose of maximization the interfacial area between the scaffold and the perovskite film. The second architecture is the planar heterojunction structure without the scaffold, similar to that of a simple n-i-p solar cell. Up to now, the highest efficient planar devices have been obtained using a wide variety of approaches and were able to surpass PCEs of 10% [9–16]. Thus, the planar structure we employed is the simplification of the PSCs on account of its advantage for large-scale manufacturing.

For a perovskite solar cell, the combined factors such as carrier generation, transport, recombination and collection are often intertwined, producing several different interfaces. Attributed to interfacial defects and the specific charge-carrier distribution, the carrier recombination usually occurs at the interfaces, which can play a very significant role in the carrier transfer and recombination processes. Thus, in order to develop a high-performance solar cell, interfaces become the key issue beside the appropriate materials, a high-quality film and proper device structures.

Based on the knowledge gained from DSSCs, several reports have showed that charge transport and recombination properties in solid-state mesostructured/planar perovskite solar cells are similar to those of solid-state DSSCs [17–19]. However, perovskite in PSCs not only acts as an absorber analogous to dyes in DSSCs, but also behaves ambipolar diffusion (electron and hole) with long diffusion lengths [20,21]. The interface and its role in carrier transport and recombination process have not been completely investigated, due to our limited knowledge about the working principles in such devices. Small-perturbation techniques, which can measure the electric response under bias voltage or illumination, are proved to be an effective approach to investigate the interfacial carrier transfer and recombination properties in a photoanode. Therefore, to elucidate the roles of interfaces in such planar devices, we reported charge-carrier transport/recombination properties characterized by intensity-modulated photocurrent/photovoltage spectroscopies (IMPS/IMVS), one of the small-perturbation techniques.

To the best of the authors' knowledge, this manuscript describes the first dynamic IMVS model based on a continuity equation, strongly correlating to the unique planar configuration. The results exhibit that the measured IMVS responses were successfully fitted to our mathematical IMVS model. In order to investigate the discrepancy between DSSCs and planar PSCs in carrier recombination mechanism, we compared two different mathematical IMVS models based on PSC and DSSC, respectively. The IMVS fitting results suggested that the discrepancy can be originated from the semiconductor heterojunction formed at the solid-state interfaces. Additionally, the different boundary conditions can determine the varied carrier distribution and transport. Therefore, the interface in PSCs, including carrier recombination dynamics have been explored and discussed as an approach to understand the origin of the photovoltaic properties for the devices prepared under open air conditions. Moreover, the dynamic IMVS model would help in paving the way to construct the current–voltage curve using a continuity equation model for the structure-related charge generation and transport kinetics.

Since charge recombination mainly occurs at the interfaces, trap-induced recombination mechanism has a higher rate than the electron–hole recombination and Auger recombination. We explored the influence of air-annealing on the interface, carrier transport/recombination properties and subsequently device performance. Several reports have researched the influence of moisture in air on $CH_3NH_3PbI_3$ film growth and find that air is better than N_2 for high-performance solar cells in the annealing process, attributed to crystallographic changes, oxygen passivation, and variation in grain domain size [22,23]. Moreover, the studies of defect trapping states of $CH3NH_3PbI_3$ perovskite film and the photoexcited carrier dynamics indicate that the carrier recombination dynamics is ultimately related with both the defect density and the relaxation rate of the carriers in defects [24]. Air-annealing can suppress surface recombination, due to the decrease of not only interfacial contacts and grain boundaries, but also the densities of surface and defect states in perovskite film.

In short, the probable mechanism of recombination is interfacial recombination, via surface/defect states, therefore, interfacial modification and even careful interface design could be the key approaches to obtain highly efficient PSCs. We hope that the report will help clarifying the role of the interface in carrier transport/recombination mechanism for such planar devices as well as shedding light on the efficiency-improving steps in the future.

2. Experimental section

2.1. Device fabrication

Firstly, fluorine-doped tin oxide (FTO)-coated glass was patterned by etching with 2 M HCl and Zn metal powders. Then the etched substrates were cleaned in detergent water, deionized water, acetone and ethanol in ultrasonic bath, successively. A c-TiO_2 was prepared by spin-coating an acidic solution of titanium isopropoxide in isopropano at 2000 rpm for 60 s, followed by annealing at 550 °C for 60 min in air.

PbI_2 was deposited on the c-TiO_2/FTO/glass substrate by spin coating a *N,N*-dimethylformamide (DMF) solution of PbI_2 (462 mg mL^{-1}) at 4000 rpm for 30s. The PbI_2 film was then dried on the hot plate at 70 °C to remove the remaining solvent.

CH_3NH_3I was synthesized by the method reported in the literature [25]. We fixed PbI_2-coated substrates one by one on both sides of CH_3NH_3I powders with PbI_2-coated side facing downward. Subsequently, the whole tube is heated to 150 °C and allowed to react for 3 h. After cooling to room temperature, the perovskite film was washed by isopropanol and air-annealed on the hot plate at 110 °C for 10 min in ambient environment.

The hole-transportation layers were deposited by spin coating a solution of 2,2′,7,7′-tetrakis-(N,N-di-*p*-methoxyphenyl-amine) 9,9′-spirobifluotenec (spiro-OMeTAD) (72.3 mg), 28.8 μL of 4- tert-butylpyridine and 17.5 μL of lithium-bis(trifluoromethanesulfonyl) imide (Li-TFSI) solution (520 mg of Li-TFSI in 1 mL of acetonitrile) all dissolved in 1 mL of chlorobenzene at 4000 rpm for 40 s on the perovskite substrate. Finally, a silver electrode was deposited by thermal evaporation onto hole transport material (HTM) layer under high vacuum. The perovskite layer and hole-transportation layer were fabricated under fully open air conditions with humidity over 50%.

2.2. Device characterization

The surface and cross-sectional morphology were characterized by a field emission scanning electron microscope (FE-SEM, SU8020). X-ray diffraction was measured by D/MAX2500V from 10° to 60°, with a scanning speed of 5° per minute. Ultraviolet–visible absorbance spectra were measured by CARY 5000 (Agilent, Australia) from 380 to 900 nm. Steady-state photoluminescence (PL) was carried on F-4500 Fluorescence Spectrophotometer with an excitation wavelength of 370 nm and detection at 770 nm. The photovoltaic performance was measured by Keithley 4200 source meter under AM 1.5 irradiation generated by a solar simulator (XES-301S) in air. J–V curves were measured by scanning from short circuit to open circuit. X-Ray photoemission spectroscopy (XPS) was carried out on a VG ESCALAB250 Xi (Thermo, USA) surface analysis system equipped with a monochromatic Al Kα X-ray