Inverted polymer solar cells integrated with small molecular electron collection layer

CrossMark

Ai-Li Shi [a], Yan-Qing Li [a,*], Zai-Quan Xu [a], Fu-Zhou Sun [a], Jian Li [a], Xiao-Bo Shi [a], Huai-Xin Wei [a], Shuit-Tong Lee [a], Satoshi Kera [b], Nobuo Ueno [b,*], Jian-Xin Tang [a,*]

[a] Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou 215123, China
[b] Graduate School of Advanced Integration Science, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

ARTICLE INFO

ABSTRACT

An efficient inverted polymer solar cell (PSC) is reported by integrating a small molecular electron collection layer (ECL) between indium tin oxide (ITO) cathode and the photoactive layer of blended poly(3-hexylthiophene) and [6,6]-phenyl C61 butyric acid methyl ester (P3HT:PCBM). The ECL is composed of a cesium carbonate-doped tris(8-hydroxyquinolinato) aluminum (Cs_2CO_3:Alq_3) layer. As determined by photoelectron spectroscopy and electrical measurements, the Cs_2CO_3 doping induces suitable energy level alignment at the ITO/Cs_2CO_3:Alq_3/PCBM interface and the increase in bulk conductivity of organic ECL, which are favorable to electron extraction through Cs_2CO_3:Alq_3 to ITO cathode. In addition, optical simulation indicates that the Cs_2CO_3:Alq_3 layer can act as an optical spacer to modulate the region of highest incident light intensity within the photoactive layer, where absorption and charge dissociation are efficient. The inverted PSC with an optimized Cs_2CO_3:Alq_3 ECL exhibits a power conversion efficiency of 4.83%. The method reported here provides a facile approach to achieve high-performance inverted PSCs at low processing temperature.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) are considered as an alternative approach for renewable energy sources because of the fabrication possibility by low-cost and large-area roll-to-roll manufacturing technologies [1–8]. In the past years, tremendous efforts have been devoted to improving the power conversion efficiency (PCE) and long-term air stability of PSCs via the synthesis of low band-gap materials [6–8], interface engineering of electrical contacts [9,10], optimization of morphologies by advanced processing methods [1–5], and the development of new device architecture [4,5,11,12]. In particular, inverted-structure with transparent indium tin oxide (ITO)

as the bottom cathode for electron extraction has been proposed for high-efficiency PSCs to avoid the oxidation of metallic cathodes in regular-structure devices and match the vertical phase separation in polymer BHJs [2,13–18].

It is known that the important factor to cell performance of inverted PSCs is the selection of electron collection layers (ECLs) between ITO cathode and the photoactive layer for efficient electron extraction. Previously, various inorganic compound films, such as titanium oxide [14–16], zinc oxide [10,17–20], cesium carbonate (Cs_2CO_3) [21–23], aluminum oxide [24], or cadmium sulfide [13], have been incorporated as an ECL for inverted PSCs, due to their large band gaps, relatively high electron mobility, and good environmental stability. However, for inorganic compound films, a relatively high-temperature annealing process is usually necessary to remove the residual organic compounds for well-controlled morphological and structural properties [14–20]. In addition, inorganic ECLs with a relatively thick

* Corresponding authors. Tel.: +86 512 65880941; fax: +86 512 65882846 (Y.Q. Li).
E-mail addresses: yqli@suda.edu.cn (Y.-Q. Li), uenon@faculty.chiba-u.jp (N. Ueno), jxtang@suda.edu.cn (J.-X. Tang).

film thickness exhibit the brittle nature, which may inhibits their application with flexible substrates [25]. Recently, some attempts have been explored for using small molecules or conjugated polymers as an ECL for inverted PSCs, which can be easily fabricated with controlled film morphology and chemical composition at low processing temperature [2,26–29]. However, high conductivity and Ohmic contact with ITO cathode are requisite for efficient electron extraction with the use of small molecular ECLs.

It has been demonstrated alkali metal compounds, including cesium carbonate (Cs_2CO_3), cesium fluoride (CsF), or cesium azide (CsN_3), can be incorporated in organic devices as an n-type dopant to facilitate electron injection/extraction and transport with a wide range of electrodes and to reduce the Ohmic loss [27,30–33], and their roles in the electron-transport enhancement has been elucidated [34,35]. However, there is few effort to explore the possibility of using small molecular layer with n-type alkali metal compound dopants for electron extraction in PSCs.

In this work, we present a comprehensive study of an efficient inverted PSC integrated with an n-type doped small molecular ECL, which is formed by a Cs_2CO_3-doped tris(8-hydroxyquinolinato) aluminum (Cs_2CO_3:Alq_3) film. The selection of Alq_3 is based on its advantageous properties in terms of band gap, electron mobility, and environmental stability, and Cs_2CO_3 is incorporated as an n-type dopant to enhance the electrical conductivity of Alq_3-based ECL. A correlation between cell response parameters and film properties is investigated to analyze the functionality of the Cs_2CO_3:Alq_3 ECL. Using data on interface energetics and electrical properties determined by photoelectron spectroscopy and electron-only devices, it is shown that the optimal doping of Cs_2CO_3 results in suitable energy level alignment and increased bulk conductivity, which is favorable for electron extraction through Cs_2CO_3:Alq_3 to ITO cathode. In addition, optical device simulation indicates that the Cs_2CO_3:Alq_3 layer can act as an optical spacer to modulate the region of highest incident light intensity within the photoactive layer for efficient absorption.

2. Experimental section

2.1. Device fabrication

Inverted PSCs were fabricated on ITO-coated glass substrates with a sheet resistance of 20 Ω per sq. Prior to device fabrication, the ITO glass substrates were ultrasonic cleaned with Decon 90, rinsed in de-ionized water, and subsequently dried in an oven. The substrates were then transferred into a vacuum deposition chamber with a base pressure of 2 (10^{-6} Torr for thermal evaporation of Cs_2CO_3-doped Alq_3 layers with various host-dopant compositions and film thicknesses, which were produced by co-evaporation from individual Cs_2CO_3 and Alq_3 sources. Deposition rates and thicknesses of different layers were monitored with quartz oscillating crystals, which were calibrated initially. After thermal deposition of Cs_2CO_3:Alq_3, the resulting samples were transferred into an interconnected nitrogen (N_2)-filled glove box for spin-coating the blend of poly(3-hexylthiophene):[6,6]-phenyl C61 butyric acid methyl ester (P3HT:PCBM) with a 1:0.8 weight ratio (10 mg mL^{-1}, dissolved in dichlorobenzene) at 600 rpm for 1 min. The wet film was subjected to a thermal annealing on a hot plate at 110 °C for 10 min inside the glove box. The thickness of the resultant P3HT:PCBM blend film was determined to be approximately 120 nm by the alpha-SE™ Spectroscopic Ellipsometer. Finally, to complete the device fabrication, the samples were transferred back to the vacuum deposition chamber, in which a MoO_3 layer as a hole collection layer and a 100 nm-thick Al anode were thermally evaporated through shadow masks. The active device area was estimated to be 0.1 cm^2 as determined by the overlap of ITO cathode and Al anode.

2.2. Characterization of photovoltaic cells and thin films

Photovoltaic measurements of inverted PSCs were conducted at room temperature in air without any device encapsulation under illumination of a 150 W Newport 91160 solar simulator using an air mass (AM) 1.5G filter. The simulated light intensity was adjusted to be 100 mW cm^{-2}, which was calibrated with a standard Si optical power meter. Current density–voltage (J–V) characteristics were examined using a programmable Keithley 2612 source measurement unit. The incident photon to current conversion efficiency (IPCE) spectra were measured with a photo-modulation spectroscopic setup (Newport monochromator). Surface morphology and roughness were characterized with atomic force microscopy (AFM) (Veeco MultiMode V) in tapping mode. Absorption spectra were measured using an UV/vis/near-IR spectrometer (Perkin Elmer Lambda 750). The film thickness was measured by the alpha-SE™ Spectroscopic Ellipsometer. Elemental composition and the electronic structures of the films were determined by ultraviolet and X-ray photoelectron spectroscopies (UPS and XPS) in a Kratos AXIS Ultra-DLD ultra-high vacuum system (a base pressure of 3×10^{-10} Torr) with HeI excitation (21.2 eV for UPS) and monochromatic Al Kα source (1486.6 eV for XPS). Details of the experimental setup for UPS and XPS measurements have been given elsewhere [27]. All spectra were measured at room temperature. Fermi level (E_F) was referred as the zero binding energy in XPS and UPS spectra.

2.3. Theoretical calculation

The one-dimensional transfer matrix formalism is applied to model the electromagnetic field distribution inside inverted PSCs. Optical constants (n and k) and film thicknesses for different layers in the cell were experimentally derived from ellipsometry measurements and used as input parameters in the software to get the optical field profile. The local energy dissipated at a constant wavelength was simulated inside the active area by taking into account optical interference effects.

3. Results and discussions

Fig. 1a plots the J–V characteristics of inverted PSCs with a blended P3HT:PCBM photoactive layer under AM