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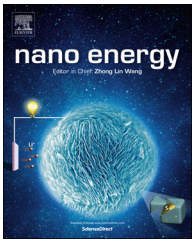

RAPID COMMUNICATION

High efficiency organic/silicon hybrid solar cells with doping-free selective emitter structure induced by a WO_3 thin interlayer

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Abstract
Organic/silicon hybrid solar cell has recently received intensive interest due to its simple and low-cost fabrication process, which could be potentially used in photovoltaics. However, the efficiency of organic/silicon solar cell needs further improvement. Here, we have introduced a WO_3 thin layer between the Ag front electrodes and poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate)(PEDOT:PSS) film in the PEDOT:PSS/silicon solar cell to form a doping-free selective emitter (SE) structure. The carrier recombination is suppressed at the interface of silicon and electrodes, and meanwhile, the contact resistance between the Ag electrodes and PEDOT:PSS film is largely reduced. Therefore, the open-circuit voltage and fill factor of solar cell is significantly improved. As a result, the solar cell with a SE structure displays the power conversion efficiency (*PCE*) of 11.65%, which is much higher than the one without a WO_3 thin layer. These results pave a new way for the fabrication of high efficiency organic/silicon hybrid solar cells.

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Introduction

Crystalline silicon solar cell is dominant in the photovoltaic market due to its excellent properties such as stability and high power conversion efficiency (*PCE*) [1]. However, the fabrication of crystalline silicon solar cell is quite complicated, with high cost, since it is based on the formation of p-n junction by a high temperature process [2]. Therefore, various technologies involving heterojunction perovskite solar cells [3], carbon nanotube/silicon heterojunction solar cells [4], bulk-heterojunction solar cells [5] and graphene/silicon heterojunction solar cells [6] have been explored to develop solar cells by simplifying the cells' fabrication process at low temperatures. Recently, the silicon/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) hybrid solar cell which combines the advantages of both organic and inorganic has been intensively studied [7]. It has been reported that common planar-PEDOT:PSS/silicon solar cells usually can achieve an efficiency about 10% [8-10]. By interface organic passivation [11,12], cathode modification [13] and inorganic doping [14], a *PCE* over 11% can be achieved. The PEDOT:PSS/silicon hybrid solar cell is generally assumed to be a Schottky junction solar cell [15], and PEDOT:PSS serves as the metallic contact. However, it was recently reported that an inversion layer should be formed at the interface of silicon and PEDOT:PSS, which suggests that the PEDOT:PSS/silicon solar cell actually acts like a p-n junction [16]. In this case, the *p*-type inversion layer acts as the emitter in the solar cell to generate electric field for the separation of electron–hole pairs, and the PEDOT:PSS only works as transparent electrodes. Nevertheless, according to the simulation results, an ultimate *PCE* above 20% is theoretically possible for PEDOT:PSS/silicon solar cells [17]. Therefore, there still exists much room for the improvement of PEDOT:PSS/silicon solar cell performance.

The transition metal oxide (TMO) including MoO_3 and WO_3, with the properties of their non-toxicity and high work function, have been recognized as an excellent hole transport layer in organic photovoltaic (OPV) devices for efficiency improvement [18,19]. In our previous research, we have used the MoO_3 to significantly improve the performances of PEDOT:PSS/silicon solar cells [20]. However, it must be noted that the accurate control of TMO film thickness and uniformity is rather important for the fabrication of PV device, especially in the case of TMO film with nanometer thickness. It is better to prepare a thin TMO film at a relatively low growth rate. Since the TMO film is generally formed by thermal evaporation, its growth rate is strongly associated with the melting point and evaporation rate of the TMO materials. Compared to the MoO_3, the WO_3 has much higher melting point and smaller evaporation rate [21], and therefore should easily be grown at a low rate, which will be beneficial for the formation of a thin and uniform TMO film.

Here, we have chosen WO_3 as a thin interlayer between the PEDOT:PSS film and Ag electrodes to improve the performances of solar cells for the first time. It is found that the introduction of WO_3 thin film can generate a selective emitter (SE) structure with high carrier concentration beneath the electrodes. The formation of SE structure can effectively reduce series resistance and improve the open-circuit voltage (V_{oc}) of solar cells. A power conversion efficiency (*PCE*) of 11.65% can be achieved for the PEDOT:PSS/silicon solar cell with the SE structure, which is much higher than that of the conventional one.

Experimental section

Device fabrication

300 μm thick, n-type single-side polished (100)-oriented crystalline silicon wafers with a resistivity of 0.1 Ω cm were used for experiments. The samples with a size of $1.4 \times 1.4\ cm^2$ were ultrasonically cleaned in deionized (DI) water for 15 min, followed by immersing into 15% HF solution for 10 min. Then, the samples were immediately transferred into a glove box. Highly conductive PEDOT:PSS (Heraeus PH 1000) solution mixed with 5% (wt) dimethyl sulfoxide (DMSO) and 1% (wt) Triton (Sigma Aldrich) was spin-coated onto the samples using a speed of 3000 r/min, followed by 125 °C/15 min annealing in N_2 atmosphere. Subsequently, 2-8 nm thick WO_3 films were thermally deposited onto the PEDOT:PSS layer, followed by 200-nm-thick Ag electrode grid deposition using a shadow mask. Finally, In:Ga eutectic layer was used to form an ohmic contact at the silicon backsides.

Material and device characterization

The morphologies of the PEDOT:PSS film and PEDOT:PSS/WO_3 film were measured using an atomic force microscope (AFM, Dimension Edge, Bruker). UV photoemission spectrum (UPS) measurements were collected on a Thermo ESCALAB 250 in an ultra-high vacuum chamber with a vacuum of $<10^{-10}$ Torr using He I (21.22 eV) radiation line from a discharge lamp. The evolution in the minority carrier lifetime of samples was recorded by a microwave photoconductance decay (μ-PCD) technique (WT-2000PVN, Semilab). After slicing the samples by focus ion beam (FIB) method, a transmission electron microscope (TEM, Tecnai G2 F20S-TWIN) was used to observe the cross-section of the solar cells. The capacitance versus voltage (*C-V*) was measured by a Keithley 4200-SCS (100 kHz) for the determination of the built-in potential barrier at the interface of PEDOT:PSS and silicon. The current density versus voltage (*J-V*) characteristics of the solar cell were measured by a Keithley 2400 source meter with a solar simulator (94022A, Newport) under AM 1.5 G conditions at an illumination intensity of $100\ mW/cm^2$, calibrated by a standard Si solar cell (PVM937, Newport).

Results and discussion

Figure 1(a) illustrates the schematic diagram of our PEDOT:PSS/silicon hybrid solar cell. One can see that there exists a WO_3 interlayer introduced between the Ag electrodes and PEDOT:PSS film. The optical image of real device is shown in Figure S1. Figure 1(b) shows the TEM cross-sectional micrograph of the solar cell and its local enlarged views. The interfaces of PEDOT:PSS/silicon and PEDOT:PSS/WO_3/Ag are indicated by the blue dashed lines for clarity. It can be seen that PEDOT:PSS film has a thickness of ~50 nm, and there