

Performance improvement of inverted polymer solar cells thermally evaporating nickel oxide as an anode buffer layer

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ABSTRACT

Nickel oxide (NiO) was thermally evaporated between the active layer and the top anode in inverted polymer solar cells. We demonstrate that NiO behaves as an anode buffer layer. The NiO thin film can modulate the Schottky barrier and form an ohmic contact at the organic/metal interface, which make it a great holes transport layer. The device performance with NiO of different thicknesses are investigated and compared. The results show that the power conversion efficiency (PCE) increases by fivefold with 2 nm NiO compared to the control cell without NiO. The optimum device performance with 2 nm NiO shows the J_{sc} of 7.92 mA/cm², V_{oc} of 0.46 V, FF of 39.8%, and thus the PCE of 1.45% under AM1.5G illumination of 100 mW/cm².

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1. Introduction

During the past decade, there has been an extensive research for polymer solar cells, which are fabricated by conjugated polymer and fullerene derivative. It has the advantage of solution processing capability, low-cost, large area device, and flexibility [1–4]. For the conventional device architecture, solar cells based on glass/indium tin oxide (ITO)/poly (3,4-ethylenedioxythiophene):poly (styrene-sulfonate) (PEDOT:PSS)/RR-P3HT:PCBM/LiF/Al, power conversion efficiencies in the range of 4%–5% have been reported. However, PEDOT:PSS is hygroscopic so extensive exposure to moisture can reduce its conductivity [5]. In addition, recent research has shown that PEDOT:PSS degraded the performance of device due to its corrosion to ITO [6]. The ITO/PEDOT:PSS interface is known to be rather unstable [7], as well as the usual Al top electrode [8]. The low work function metals that are typically employed as cathodes in conventional polymer solar cells are susceptible to oxidation [9]. For these reasons, inverted polymer solar cells are employed to replace PEDOT:PSS and Al. The inverted device structure is usually ITO/TiO₂/RR-P3HT:PCBM/buffer layers/Ag. TiO₂ acts as an electron transport layer with a lower work function (–4.2 eV). We have recently shown three kinds of metal oxide such as MoO₃ [10], WO₃ [11], and V₂O₅ [12] could improve device performance as anode buffer layers. Irwin et al. [13] have reported that p-type

semiconducting nickel oxide is an efficiency-enhancing anode interfacial layer in polymer solar cells, and insertion of the NiO layer affords PCE as high as 5.2%. However, thin films of p-NiO were deposited by pulsed laser deposition (PLD) on patterned ITO anodes. Films patterned by shadow mask were used in the fabrication of solar cells. The manufacture craft is relatively complicated. In this paper, we will demonstrate an enhancement in polymer solar cell performance by just evaporating a thin NiO as a buffer layer. The device performance with NiO of different thicknesses is investigated and compared.

2. Experimental

The photovoltaic device has a structure of ITO/nc-TiO₂/RR-P3HT:PCBM/NiO/Ag, as shown schematically in Fig. 1(a). The ITO-conducting glass substrate (a sheet resistance of 15 Ω/□) was pre-cleaned by acetone, ethanol, and de-ionized water for 15 min. Anatase TiO₂ thin films were prepared as described in our previous papers [14,15]. P3HT (Lumtec Corp, used as received) was dissolved in 1,2-dichlorobenzene to produce 18 mg/ml solution, followed by blending with PCBM (Lumtec Corp, used as received) in 1:1 weight ratio [16]. The blend was stirred for 72 h in the air before spin coating on top of TiO₂ film surface. Then the samples were baked in low vacuum (vacuum oven) at ~160 °C for 20 min. The typical film thickness of P3HT:PCBM is about 200 nm. Finally the devices were completed with thermal evaporation of NiO and 100 nm Ag in sequence under a high vacuum (5×10^{-4} Pa) without disrupting the vacuum. The deposition rate was about 0.02 nm/s, which was monitored with a quartz-oscillating

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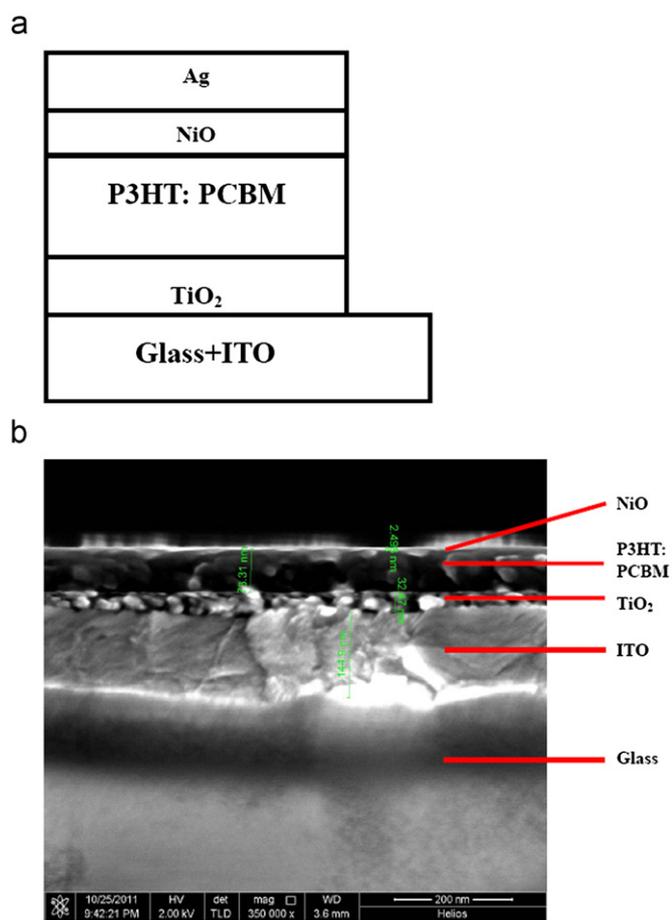


Fig. 1. (a) Schematic structure drawing of the inverted polymer solar cells. (b) The cross sectional scanning electron microscope (SEM) images of the device except Ag anode.

thickness monitor (ULVAC, CRTM-9000). The active area of the device was about 6.4 mm^2 . Fig. 1(b) shows the cross sectional scanning electron microscope (SEM) images of the device except Ag anode. It can be seen that each interface is distinct, and the thickness of each layer is about 145 nm (ITO), 32 nm (TiO_2), 73 nm (P3HT:PCBM), and 2 nm (NiO).

Current density–voltage (J – V) characteristics were measured with a computer-programmed Keithley 2601 source/meter under AM1.5G solar illuminations with an Oriel 300 W solar simulator. The intensity of the solar simulator was 100 mW/cm^2 . The light intensity was measured with a photometer (International light, IL1400), which was corrected by a standard silicon solar cell. The external quantum efficiency (EQE) was measured with Crowntech QTest Station 1000AD. A Hitachi S-4500 scanning electron microscope (SEM) operated at an accelerating voltage of 15 kV was used in order to observe the surface morphology of NiO and estimate the thickness of each layer in the device. Impedance spectroscopy was measured by an impedance analyzer (Wayne Kerr Electronics 6520B) with an ac signal of 1 V in the frequency range of 20 Hz–2 MHz.

3. Results and discussions

The energy levels of the materials used are shown in Fig. 2. It is well known that P3HT and PCBM exist in an interpenetrating network, and could form bulk-heterojunction. The highest occupied molecular orbital (HOMO) level of NiO is -5.0 eV [17], which is very close to the HOMO level of RR-P3HT (-5.2 eV)

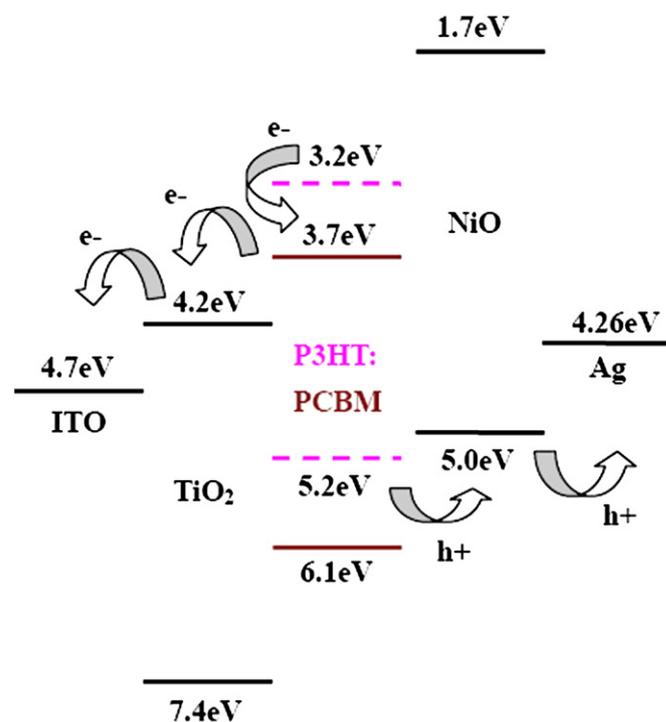


Fig. 2. Energy levels of the materials used in inverted polymer solar cells.

[15]. The energy level match reveals that NiO can extract holes from the active layer. The lowest unoccupied molecular orbital level of NiO is -1.7 eV [17], which is higher than that of PCBM (-3.7 eV) [10]. Introducing a NiO layer will prevent electrons from transferring from PCBM to Ag. Thus, the NiO interlayer effectively prevents the recombination of the charge carriers at the organic/Ag interface. Under illuminations, P3HT absorbs light and generates excitons. Excitons are separated into free electrons and holes by bulk heterojunction. The generated holes are collected by Ag anode through the HOMO level of NiO (-5.0 eV), which ranges between the HOMO level of RR-P3HT (-5.2 eV) and Ag (-4.26 eV) [15]. It plays a part in energy level step, which is favorable for holes transport. Meantime, generated free electrons are collected by ITO cathode by way of the LUMO level of PCBM and conduction band minimum (CBM) of TiO_2 in turn. It is noteworthy that the LUMO of NiO (-1.7 eV) is much higher than that of PCBM (-3.7 eV). The high energy level difference of 2.0 eV can succeed to prevent electrons arriving at Ag. The collection enhancement of electrons and holes will result in the improvement of photocurrent.

Fig. 3 shows the J – V characteristics of inverted polymer solar cells when the thickness of NiO varies from 0 to 5 nm under AM1.5G illumination of 100 mW/cm^2 . The detailed results are given in Table 1. Device without NiO shows short circuit current density (J_{sc}) of 3.83 mA/cm^2 , open circuit voltage (V_{oc}) of 0.23 V , fill factor (FF) of 0.329 , and power conversion efficiency (PCE) of 0.29 . The poor device performance is attributed to direct contact in active layer/Ag. It is possible for PCBM to transfer electrons to the Ag electrode. When evaporating a thin NiO layer, the performance has improved remarkably. When the thickness of NiO is 2 nm, the device has a J_{sc} of 7.92 mA/cm^2 , V_{oc} of 0.46 V , FF of 0.398 , and PCE of 1.45% . The improvement of J_{sc} is explained that the NiO layer can available block electrons and transport holes. The NiO thin film can modulate the Schottky barrier and form an ohmic contact at the organic/metal interface, which make it a great holes' transportation layer. We ascribed the increment of V_{oc} to the enhancement of the built-in potential. It is known that V_{oc}

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