

Photovoltaic Properties of Bulk-Heterojunction Organic Solar Cell with Ultrathin Titanium Oxide Nanosheet as an Electron Selective Layer

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1. Introduction

Bulk-heterojunction (BHJ) devices based on a mixture of pi-conjugated polymer/ fullerene derivatives are considered as one of the promising candidates for low-cost, flexible, lightweight solar cells because of their simple, solution-processable, and low-temperature fabrication on glass or flexible substrates. Recent advances in the fabrication of polymer-and-fullerene-based materials have improved the power conversion efficiency of BHJ to up to 5% in conventional device structures consisting of poly(3,4- ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS) as the anodic buffer layer, a poly (3-hexylthiophene)(P3HT): phenyl-C61-butyric acid methylester(PCBM) mixture as the active layer, and cathodes[1-4]. Solution-processable n-type wide-gap semiconductors such as titanium oxide and zinc oxide should be preferentially used as the cathode buffer layer because of their excellent electron extracting and transport properties, optical transmittance, and exciton- and hole-blocking nature.

Since crystalline TiO₂ (anatase phase) and ZnO films require high-temperature (~500 °C) processes, an inverted structure consisting of a transparent conducting oxide (TCO)/ electron-extracting buffer layer/ active layer/ hole extracting buffer layer/ electrode is preferable for the fabrication of BHJ cells with crystalline titanium oxide. Efficient and stable BHJ cells have recently been developed using inverted structures [5-8]. However, the requirement of a high-temperature process is a severe disadvantage for the fabrication of flexible organic solar cells on plastic substrates. In our previous study, we have newly developed the inverted bulk-heterojunction cell with ultra-thin crystalline titania nanosheet (TN) as an electron selective layer. Here, the TN layer is deposited onto ITO electrode by the layer-by-layer (LBL) deposition of a diluted dispersed anionic nanosheet and a cationic poly(diallyldimethyl- ammonium chloride) (PDDA), which is suitable for the fabrication of uniform, nano-controlled TN ultrathin films at low temperature[9]. Only a few nanometer thick TN/PDDA multilayers markedly suppressed the leakage current, and the open circuit voltage V_{OC} and efficiency was increased nearly two-fold. However, the potential barrier at the ITO/TN interface caused the S-shaped curves around V_{OC} in current-voltage characteristics. Therefore, the reduction of contact resistance across the TN layer is an effective way to improve the photovoltaic properties of our cells.

In this study, we have investigated the photovoltaic properties of the inverted BHJ cell in the transparent conducting

oxide (ITO, gallium doped zinc oxide (GZO), or ITO covered with thin anatase TiO₂ film)/ TN/ P3HT: PCBM active layer/ MoO₃/ Ag multilayered structure in order to control the potential barrier at TCO/ TN interface. It is also expected that the potential barrier should be further reduced at the TN/ low work-function metal electrode interface, such as Al or Mg etc. Therefore, we also investigated the photovoltaic properties of conventional BHJ cell in the ITO/ MoO₃/ P3HT: PCBM active layer/ TN/ Al multilayered structure.

2. Experimental procedure

The devices were fabricated on 150-nm-thick ITO or GZO electrodes patterned to be 2 mm in width and pre-coated on glass substrates. After routine cleaning with detergent, deionized water, and ultrapure water (with ultrasonication, 2-3 times), the titanium oxide layers were deposited onto the ITO electrode in the case of the inverted BHJ cell. The TN was fabricated by LBL deposition of cationic PDDA (immersed in 2 wt% PDDA in water for 10 min) and TN (immersed in 1 mmol/l for 20 min). 19-23) For ITO/ anatase TiO₂ electrode, a smooth and dense TiO₂ anatase film (~100 nm thick) was prepared on the ITO-coated glass substrate using the sol-gel technique followed by heat treatment at a temperature of 450 °C. The details of the film preparation technique using anatase TiO₂ were discussed elsewhere.14-16) The TN films were then fabricated by the LBL deposition technique. After the heat treatment of TN at 120 °C for 30 min, a P3HT/PCBM mixture (10 and 8 g/l) dissolved in chlorobenzene was spin-coated onto the TN-coated substrate. The sample was then heated at 150 °C for 5 min in nitrogen to induce the microphase separation of the crystalline P3HT/ PCBM film. Finally, the MoO₃ (20 nm) and Ag (>30 nm) layers were evaporated. Their effective area was 4 mm².

In the case of the conventional BHJ cell, 10 nm-thick MoO₃ was thermally evaporated, or PEDOT-PSS was spin-coated on ITO. The active layer, TN layer and Al top electrode were then deposited in a same manner.

Electrical properties were characterized using a glove box filled with pure argon at ambient temperature with an electrometer (Keithley 6847) under 1 sun global AM 1.5 illumination using a calibrated solar simulator (SAN-EL Electric XES-40S1).

3. Results and Discussion

Figure 1 shows the current density-voltage (J-V) characteristics of TCO/TN (0, 2, and 4 layer) / P3HT:PCBM/

MoO₃/Ag devices under white light illumination. The J_{SC} , V_{OC} , fill factor (FF) and power conversion efficiency η of each device. The J_{SC} , V_{OC} , FF, and η of the device without TN are 8.04 mA/cm², 0.31 V, 0.39, and 0.97%, respectively. The V_{OC} , FF, and η of the device with one or two TN layers are improved without a marked decrease in J_{SC} , and η is increased nearly twofold by the insertion of two TN layers onto ITO electrode. That is, the ITO electrode was fully covered by the two TN layers (~2nm thick). However, an S-shaped curve is clearly observed and the current decreases in the J-V curves above V_{OC} in the device with a thicker TN layer. Both FF and J_{SC} decrease with increasing number of TN layers in the device with thicker TN layers, presumably owing to the suppression of electron injection at the ITO/TN interface and the increment of series resistance across TN multi-layers. On the other hand, this abnormal S-shaped curve disappeared by the use of GZO and ITO/anatase TiO₂ as the TCO. The conduction band edge of TN locates at about 4.0 eV below vacuum level, whereas the work-function of ITO, GZO and ITO/TiO₂ are estimated at 4.8, 4.5, and 4.2 eV, respectively. We therefore concluded that the reduction of potential barrier at TCO/ TN interface is very important for the further improvement of the photovoltaic properties of our proposed devices.

Figure 2 shows the J-V characteristics of ITO/PEDOT-PSS/ active layer/ TN/ Al and ITO/MoO₃/ active layer/ TN/ Al devices under white light illumination. Here, 3 layers of TN multilayer were required for the full coverage of active layer because the hydrophobic active layer repels the first PDDA and TN layer deposition. Since the potential barrier at Al/ TN interface is negligibly small, no S-shaped curves were observed in Fig. 2. Although the active layers were immersed in pure water under the atmosphere during the deposition of TN layers, and higher FF of about 0.6 were successfully obtained owing to the lower series resistance compared with the devices in Fig. 2. The V_{OC} was improved from 0.35 V to 0.6 V by the insertion of TN layers probably due to the reduction of leakage current and improved contact at the cathode/ active layer interface. Although the J_{SC} observed in Fig. 2 is smaller than those in Fig. 1, the improved FF and V_{OC} contribute the improvement of the power conversion efficiency of about 3 %.

4. Conclusions

In this study, we have investigated the photovoltaic properties of the inverted BHJ cell in an TCO/ TN/ P3HT:PCBM active layer/ MoO₃/ Ag multilayered structure, and the conventional type BHJ cell in an ITO/PEDOT-PSS (or MoO₃) / P3HT:PCBM active layer/ TN/ Al multi-layered structure. Only two layers of PDDA and TN multilayered film effectively decrease the leakage current and improved the cell performance. And series resistance across the ITO/TN interface was successfully reduced by the reduction of potential barrier at TCO/ TN interface in inverted devices. The series resistance was further reduced in the conventional structure with the TN films as the electron selective layers.

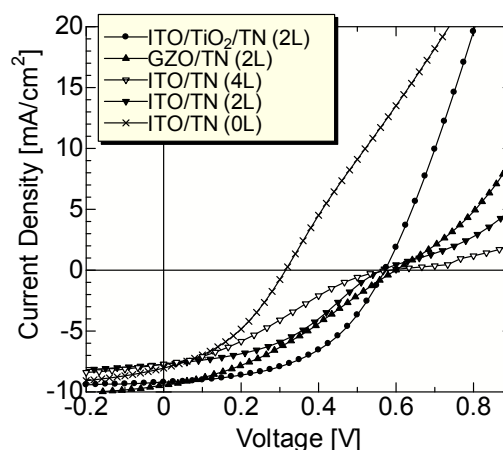


Fig. 1 Photovoltaic properties of TCO/TN (0, 2, and 4L) / P3HT:PCBM/ MoO₃/Ag devices under AM1.5 light illumination.

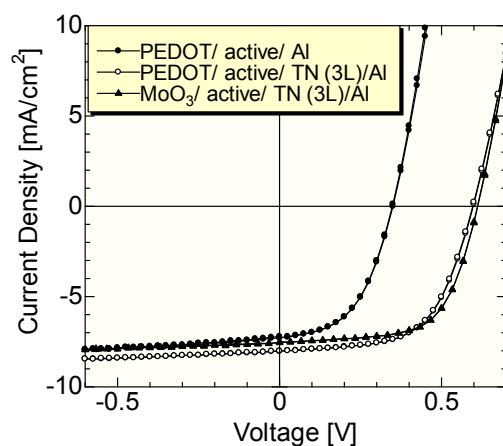


Fig. 1 Photovoltaic properties of ITO/PEDOT-PSS (or MoO₃) / P3HT:PCBM/ TN/Al devices under AM1.5 light illumination.

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