



# Effect of UV light irradiation on photovoltaic characteristics of inverted polymer solar cells containing sol–gel zinc oxide electron collection layer

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## ABSTRACT

An inverted organic bulk-heterojunction solar cell containing a zinc oxide (ZnO) based electron collection layer with a structure of ITO/ZnO/[6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (PCBM): regioregular poly(3-hexylthiophene) (P3HT)/poly(3,4-ethylenedioxythiophene): poly(4-styrene sulfonic acid)/Au (ZnO cell) was fabricated. We examined the relationship between the heating temperature of the ZnO layer and the device performance under irradiation by simulated sunlight while cutting the UV light. The effects of the UV light contained in simulated sunlight were investigated by photocurrent–voltage (*I*–*V*) and alternating current impedance spectroscopy (IS) measurements. When the ZnO cells were irradiated with simulated sunlight, they exhibited a maximum power conversion efficiency (PCE) of over 3%, which hardly varied with the heating temperature of ZnO layers treated at 250 °C, 350 °C, and 450 °C. In contrast, when the ZnO cells were irradiated with simulated sunlight without UV content, their photovoltaic characteristics were very different. In the case of the cell with ZnO prepared by heating at 250 °C, PCE of 2.7% was maintained even under continuous irradiation with simulated sunlight without UV. However, for the cells with ZnO prepared by heating at 350 °C and 450 °C, the shapes of the *I*–*V* curves changed with the UV-cut light irradiation time, accompanying an increase in their series resistance. Overall, after UV-cut light irradiation for 1 h, the PCE of the cell with ZnO prepared by heating at 350 °C decreased to 1.80%, while that of the cell with ZnO prepared by heating at 450 °C fell to 1.35%. The photo IS investigations suggested that this performance change was responsible for the formation of charge-trapping sites at the ZnO/PCBM:P3HT interface which act as recombination centers for photo-produced charges in the PCBM:P3HT layer.

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## 1. Introduction

Bulk heterojunction polymer solar cells have attracted considerable attention because of their advantages in being low-cost, lightweight, flexible and environmentally friendly [1–7]. The organic active layer of these cells typically consists of a *p*-conjugated polymer as an electron donor and a fullerene derivative as an electron acceptor, and the power conversion efficiency (PCE) of polymer

solar cells has recently approached 10% following the development of new organic materials [8–14].

The device structures have two groups: conventional and inverted types. The active layer of the conventional structure is generally sandwiched by transparent indium tin oxide (ITO) and Al electrodes. The back Al electrode collects electrons because of its low work function. However, the conventional structure is sensitive to oxygen and humidity because the low work function Al layer is easily oxidized unless the cell is completely sealed from the atmosphere under an ultrahigh vacuum. When the organic active layer is sandwiched by an ITO electrode coated with a chemically stable n-type metal oxide and a non-corrosive electrode such as Au or Ag, the photo-generated electrons in the active layer are collected by the modified ITO, while the photo-generated holes are collected by the high-work function metal. These organic solar cells are called “inverted solar cells” because the electrons flow in the reverse direction to those in conventional solar cells. This inverted structure has the advantage of long-term stability, because the electrode compositions are insensitive to both oxygen and humidity [15–20].

We have previously studied electron collection layers such as titanium oxide ( $\text{TiO}_x$  and  $\text{TiO}_2$ ) [21–23], zinc oxide (ZnO) [24], and zinc sulfide [25] for inverted polymer solar cells. We reported a novel fabrication method and the performance of inverted cells formed with chemical bath deposited  $\text{TiO}_x$  and sol–gel ZnO layers. We also reported that an inverted organic solar cell with a novel ZnO layer can be prepared on a polyethylene terephthalate substrate in air [26]. This flexible and air-stable device provides highly advantageous features for commercial viability. Several research groups have reported the fabrication and characterization of polymer solar cells with various ZnO electron collection layers, including nanoparticles [27,28], nanorods [29,30], and uniform films [31]. Krebs et al. investigated the effects of UV irradiation on the performance of inverted cells with ZnO nanoparticles as electron collection layer [32,33]. They performed photo  $I$ – $V$  measurements with and without UV light under various conditions to explain the disappearance and the re-appearance of the inflection point of the  $I$ – $V$  curves.

The IS measurement is possible to observe electric properties of a bulk and an interface that we cannot observe by a direct current (dc) method because the electric response speed for each component is different on the microscopic time scale. We previously investigated inverted solar cells containing metal oxide as an electron collection electrode by IS [24,25,34]. In this paper, we discussed the UV effects based on the results of the IS measurements in addition to the  $I$ – $V$  measurements. We examined the relationship between the heating temperature of the ZnO electron collection layer and the device performance under simulated sunlight irradiation while cutting the UV light. An increase in the crystallinity of the ZnO layer caused the decreased device performance under the irradiation of simulated sunlight without UV.

## 2. Experimental section

### 2.1. Materials

Zinc acetate ( $\text{Zn}(\text{OAc})_2$ ), monoethanolamine (MEA), 2-methoxyethanol, regioregular P3HT (molecular weight  $M_w = 87,000$ ), Triton-X 100, and chlorobenzene (CB) were purchased from Sigma–Aldrich Chemical Co., Inc. PCBM was purchased from Frontier Carbon Corporation. PEDOT:PSS (Clevios® P) was purchased from H.C. Starck GmbH. All chemicals were used as received. Glass-FTO (fluorine-doped tin oxide) substrates (A110U80, sheet resistance =  $12 \Omega/\text{sq.}$ ) were purchased from the AGC Fubritech Co., Ltd. Au wires were purchased from the Furuuchi Chemical Corporation.

### 2.2. Fabrication of inverted polymer solar cells

The glass-FTO electrodes were cleaned by sonication in 2-propanol, washed in boiling 2-propanol, and then dried in air. The fabrication was carried out in air, with the relative humidity controlled at less than 35%. A ZnO solid film with thickness of about 60 nm was prepared on the clean FTO substrate using the sol–gel method described in our previous work [24,26]. The ZnO precursor solutions were prepared in 2-methoxyethanol, which contained  $\text{Zn}(\text{OAc})_2$  as the Zn source and MEA as a stabilizer. The solutions were spin-coated onto the FTO, and the precursor films were heated at 250 °C, 350 °C or 450 °C for 1 h in an electric furnace. A mixed CB solution containing P3HT and PCBM (weight ratio = 5:4) was spin-coated onto the FTO/ZnO surface. A PEDOT:PSS dispersion in water containing 0.5 wt.% of Triton-X 100 was spin-coated onto the PCBM:P3HT layer. The film thicknesses were about 250 nm for the PCBM:P3HT layer and approximately 80 nm for PEDOT:PSS. The Au back electrode with a thickness of about 150 nm was vacuum deposited at  $2 \times 10^{-5}$  torr on the PEDOT:PSS layer. Finally, the cells were annealed at 150 °C for 5 min on a hot plate. The effective area of the solar cells was restricted to  $1 \text{ cm}^2$  by depositing the Au electrode with a shadow mask.

### 2.3. Measurements

The  $I$ – $V$  curves of the solar cells were measured by linear sweep voltammetry at a scan rate of  $5 \text{ V min}^{-1}$  under AM 1.5G simulated sunlight irradiation. The light source was a SAN-EI Electric XES-502S solar simulator, which was calibrated using an EKO MS-601 pyranometer. When the simulated sunlight intensity was measured again using a standard silicon photovoltaic detector, the correct value was  $78.5 \text{ mW cm}^{-2}$ . All DC electric measurements were made using a Hokuto Denko HZ-5000 electrochemical analyzer. The IS measurements were obtained using a Hewlett–Packard precision LCR meter (4284A) in the dark and under simulated sunlight irradiation. The frequency range was from 20 Hz to 1 MHz, the alternating signal magnitude was 5 mV and DC bias was 0 V. The data obtained were fitted with Scribner Associates Z-VIEW software v3.1 using the appropriate equivalent circuits. X-ray diffraction

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