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Spontaneous formation of nanoripples on the surface of ZnO thin films as hole-blocking layer of inverted organic solar cells

Dong Chan Lim [a], Won Hyun Shim [a,c], Kwang-Dae Kim [b], Hyun Ook Seo [b], Jae-Hong Lim [a], Yongsoo Jeong [a], Young Dok Kim [b,*], Kyu Hwan Lee [a,*]

[a] *Materials Processing Division, Korea Institute of Materials Science, Changwon 641-010, Korea*
[b] *Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea*
[c] *School of Materials Science and Engineering, Pusan National University, San 30 Jangjeon-dong Geumjeong-gu, Pusan 609-735, Korea*

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ABSTRACT

A simple method for spontaneous formation of nanoripples on ZnO thin films was developed, and these nanostructured ZnO films were used as hole-blocking layer in inverted organic solar cells. Moreover, the size (height) of nanoripples on ZnO surface could be controlled in the range of several tens of nanometers. Among various ZnO films, surface structures with ~70 nm-high nanoripples resulted in the best photovoltaic performance of the organic solar cell consisting of a stack of indium tin oxide/ ZnO/ regioregular poly (3-hexyl thiophene), phenyl-C_{61}-butyric acid methyl ester/Ag. The power conversion efficiency of inverted organic solar cells consisting of with 70 nm-high ZnO nanoripples (~3.2%) was higher than that of a relatively flat ZnO surface by a factor of ~2. Existence of nanoripples on ZnO results in a higher contact area between ZnO and active layer, leading to an enhanced photovoltaic performance.

1. Introduction

Use of solar light as energy source has been regarded as one of the environmental-friendly ways of producing energy. Among various energy devices using light, organic solar cell (OSC) has been attracting particular attention for the last decades due to its cost-effectiveness and potential application in flexible devices [1–5]. One of disadvantages of OSCs is its short life-time, which is due to the fast (photo)-degradation of various interfaces existing in OSCs [6–8]. In order to increase stability of OSC, an inverted structure of OSC (IOSC) has been developed: in a regular device structure, electron–hole pairs are created in polymer active layers, holes and electrons are injected into transparent conducting oxide and counter-electrode (e.g. Al), respectively. In contrast, in IOSC, electrons are injected into the transparent conducting oxide, i.e. the electrode alignment is reversed [9–20].

Various methods have been used for improving power conversion efficiency of OSCs. Different polymers were used as light-harvesting layer for enhancing power conversion efficiency of OSCs [21,22]. Carrier mobility has been increased by doping highly-conducting nanostructures such as carbon nanotubes and metal nanoparticles in active and buffer layers existing in OSCs [23,24]. Methods for increasing light absorption and more efficiently separating electron–hole pairs have also been developed using various intermediate layers and modifiers [25–29].

Among various nanomaterials used as electrodes and buffer layers in OSCs, nanorods and wires with a high conductivity and increased contact area between electrodes and active layers have attracted much attention [5,30–37]. Synthesis of nanowires can be achieved using electrochemical or hydrothermal methods [34–39]. In the present work, a simpler strategy for the formation of ZnO nanoripple structure, whose dimension is comparable to that of nanowires, is presented. Surface structures comparable to the nanowire-incorporated thin films can spontaneously form by properly heating spin-coated ZnO films. For spin-coating of ZnO, various mixtures of ZnO nanoparticles and zinc acetate solution were used. It is demonstrated that by adjusting the amount of ZnO naonaprticles added in zinc acetate solution nanoripple size can be controlled for the best device performance of IOSC consisting of these ZnO thin films on transparent conducting oxide as hole-blocking and electron-colleting layer.

2. Experimental

The IOSCs studied in the present work consisted of a stack of 150 nm thick-indium tin oxide film on glass/ZnO/active layer/Ag as shown in Fig. 1. For the preparation of diverse ZnO thin films, ZnO sol–gel solutions with various amounts of ZnO nanoparticles were spin-coated and heated differently (Fig. 2). The mean thickness of ZnO film was about 70 nm, and the detailed structure of each ZnO

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* Corresponding authors. Tel.: +82 55 280 3545; fax: +82 55 280 3570.
E-mail addresses: ydkim91@skku.edu (Y.D. Kim), lgh1636@kims.re.kr (K.H. Lee).

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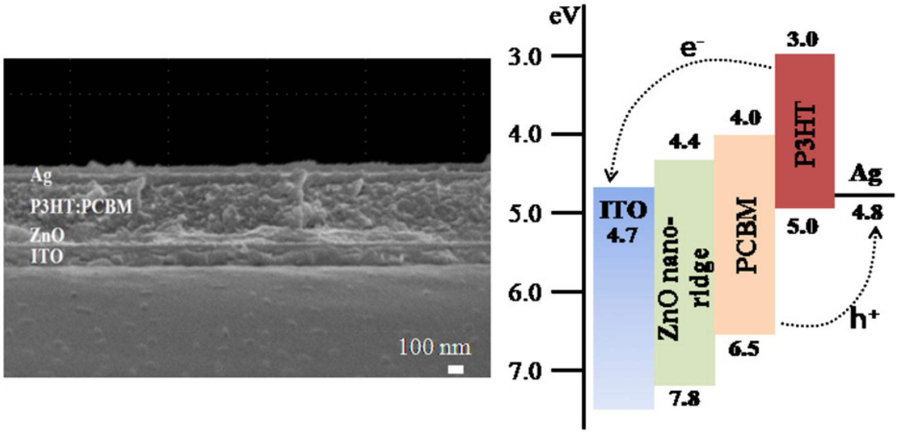

Fig. 1. *Left:* Scanning electron microscopy (SEM) images of and IOSC device fabricated in the present work. *Right*: The band diagram of IOSCs consisting of active layer (P3HT), hole-blocking and electron accepting layers (P3HT and ZnO) and both electrodes (indium tin oxide and Ag) are displayed [41,42].

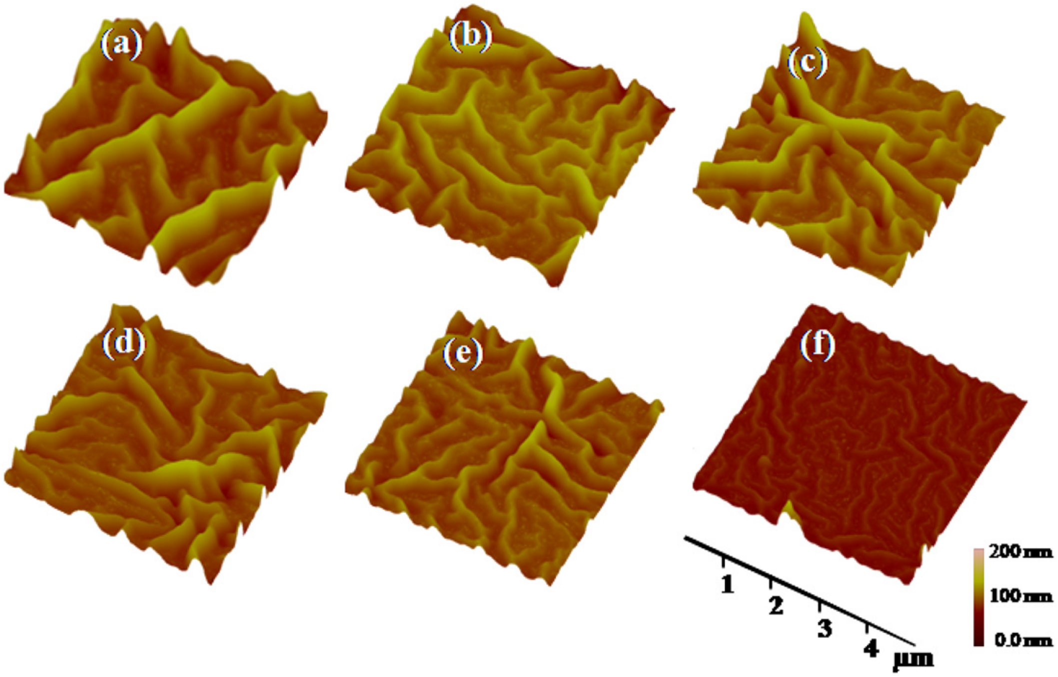

Fig. 2. AFM images of various ZnO film surfaces on indium tin oxide used as hole-blocking layers in IOSCs. (a) ZnO film was spin-coated using bare zinc acetate solution, and heated to 350 °C with a heating rate of 23 °C/min. (b–f) ZnO films were spin-coated using mixtures of ZnO nanoparticles and zinc acetate solutions. Then, the films were heated to 350 °C with a heating rate of 23 °C/min. From b to f, the amount of ZnO nanoparticles added was increased. Amount of ZnO nanoparticles added to 21 ml of zinc acetate solution was 0.25, 1, 3, 5 and 10 mg for b–f, respectively.

film is shown in Fig. 2. For the preparation of ZnO sol–gel solutions zinc acetate [$Zn(CH_3COO)_2.2H_2O$] was dissolved in 2-methoxyethanol solution containing ethanolamine as a stabilizer. Concentration of zinc acetate was 0.75 M. This solution was stirred at 60 °C for 30 min to yield a clear and homogeneous solution, which served as the coating solution. For the preparation of active layer, a mixture of regioregular poly (3-hexyl thiophene) (RR-P3HT) (30 mg/ml) and phenyl-C_{61}-butyric acid methyl ester (PCBM) (21 mg/ml) were dissolved in 1,2-dichlorobenzene under vigorous stirring overnight. Then, this solution was spin-coated on ZnO films deposited on indium tin oxide under atmospheric pressure at room temperature (600 rpm, 40 s). The thickness of active layer was 380 nm. Top electrode (Ag) was deposited by thermal evaporation method with a thickness of 100 nm under 5×10^{-6} torr condition. The active-area of the device with metal mask was 0.38 cm^2.

The structures of ZnO films on indium tin oxide were analyzed by atomic force microscopy (AFM, Vecco; MMAFM-2), and their optical properties were measured using UV/Vis transmittance spectrometer (Verian Cary 5000), respectively. Hall effects measurements were performed using ECOPIA NMS-3000 for determining carrier mobility. The current density–voltage (*J*–*V*) characteristics of the OSC devices were measured under AM 1.5 simulated illumination with an intensity of 100 mW/cm^2 (Pecell Technologies Inc., PEC-L11 model 13). The intensity of sunlight illumination was calibrated using a standard Si photodiode detector with a KG-5 filter. The *J*–*V* curves were recorded automatically with a Keithley SMU 2400 source meter by illuminating the OSCs.

3. Results and discussion

As shown in Fig. 1, the IOSCs fabricated and studied in the present work consisted of a stack of indium tin oxide-coated glass, ZnO thin films, RR-P3HT:PCBM layer and Ag electrode. As it