ZnO-morphology-dependent effects on the photovoltaic performance for inverted polymer solar cells

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A B S T R A C T

We report on the effects of zinc oxide (ZnO) morphology on the photovoltaic performance of inverted polymer solar cells (PSCs). Three different ZnO layers, fabricated from a sol-gel, nanoparticles (NPs), or nanorods (NRs), were employed as electron-collecting interlayers (ECIs) to compare their electrical, morphological, and optical properties in poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl] (PTB7): [6,6]-phenyl-C\textsubscript{70}butyric acid methyl ester (PC\textsubscript{70}BM)-based inverted PSCs. The work functions of all the ZnO layers were lower than or similar to the electron affinity of the acceptor, PC\textsubscript{70}BM, allowing the ZnO-coated indium tin oxide (ITO) substrates to act as efficient electron-collecting electrodes. The ZnO NRs induced not only stronger scattering effects but also more efficient electron collection than those of the devices with ZnO sol-gel or NP ECIs, resulting in enhanced external quantum efficiency and, consequently, the highest power conversion efficiency (8.38 ± 0.09\%) under illumination (AM 1.5G, 100 mW/cm\textsuperscript{2}). The optical effects of the ZnO NRs were confirmed by a finite-difference time-domain simulation.

1. Introduction

As an alternative renewable energy source, polymer solar cells (PSCs) have shown great potential because of their simple and cost-effective processing methods, their ability to control the optical and electrical properties of organic materials, and their excellent mechanical properties for flexible applications [1–3]. In recent years, many studies have focused on improving PSC photovoltaic performance, e.g., by synthesizing novel materials and designing new device geometries, and power conversion efficiencies (PCEs) of up to 11.7\% have been reported [4].

Among the new device architectures, the advent of the inverted geometry has engendered significant advances in device stability [5–8]. In the conventional device geometry, electron-collecting electrodes (ECEs) with low work functions (WFs) are exposed to air. However, the ECEs are often incorporated with reactive metals such as Ca and Al, which are vulnerable to oxidation in air [9], leading to limited device environmental stability. In contrast, for devices with the inverted geometry, these unstable electrodes have been removed from air-contacting interfaces [10,11], and instead, they employ a transparent low-WF ECE, commonly composed of a transparent conductor modified with low-WF electron-collecting interlayers (ECIs), which are fabricated at the bottom of the inverted-geometry device. In this context, ECE materials should fulfill several requirements to maximize device performance: low optical absorption to allow photons to pass through and sufficiently high conductivity and low WF to minimize losses in the power density and open circuit potential, respectively.

Zinc oxide (ZnO) is considered a promising candidate for both ECIs and electron acceptor materials in photoactive layers due to its relatively low WF, high electron mobility, high optical transmittance in the visible range, and long-term environmental stability [12–14]. Many studies have characterized inverted PSCs containing ZnO used as the ECI, and various fabrication methods have been reported to produce the ZnO layers, including atomic layer deposition (ALD), sputtering, and solution-based approaches using nanoparticles (NPs) and sol-gels [15,16]. However, only few studies have been conducted on characterizing the morphology-dependent optical effects of ZnO ECIs on the photovoltaic performance [17,18]. Instead, most studies related to ZnO ECIs have focused on enhancing their intrinsic properties, such as energy levels, conductivity, transmittance, etc. [19,20]. Recent works...
have suggested that adopting metal-based nanostructures for transparent electrodes could induce light scattering and trapping effects, leading to enhanced light absorption in a photoactive layer and consequently an improved PCE [21,22]. These effects include a longer optical path length and diffuse transmission due to light scattering, as well as enhanced light trapping induced either by near-field excitation of localized surface plasmons in metal nanoparticles or excitation of surface plasmon polaritons by the periodical structure [23–25]. However, ZnO-morphology-dependent light scattering and trapping effects on inverted PSC performance have not been comprehensively studied. This study examines ZnO-morphology-dependent optical effects on the photovoltaic performance of PSCs based on poly(3,4-ethylenedioxythiophene):poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS)/[6,6]-phenyl-C61-butyric acid methyl ester (PC61BM)/ZnO layers. Various ZnO layer types: sol–gel-processed ZnO, ZnO NPs, ZnO NRs, and ZnO nanorods (NRs), were employed as the ECI on top of a glass/indium tin oxide (ITO) substrate to investigate the ZnO layer’s optical effects. The morphological and optical properties of the ZnO layers were studied using an atomic force microscope (AFM) and an ultraviolet-visible (UV–vis) spectrometer. In addition, the ZnO-morphology-dependent optical density in the photoactive layer was simulated using the finite-difference time-domain (FDTD) method.

2. Experimental section

To study the dependence of the photovoltaic performance on ZnO morphology, PSCs were assembled with ECIs fabricated from three different ZnO samples: ZnO sol–gel, ZnO NPs, and ZnO NRs, employing blends of the donor polymer, PTB7, with the acceptor, PC70BM, as the photoactive layer.

2.1. ZnO preparation and characterisation

Various ZnO layers were formed on top of glass/ITO substrates.

(1) A ZnO sol–gel solution was prepared by mixing 1.24g zinc acetate dihydrate (Zn(CH3COO)2·2H2O) and 0.5g ethanolamine into 2-methoxyethanol (10g), which were all obtained from Sigma-Aldrich (St. Louis, MO, USA). The solution was spin-coated onto the substrate at 4000 rpm for 60 s, followed by annealing at 200 °C for 30 min.

(2) ZnO NPs were synthesised by solution precipitation. Tetramethylammonium hydroxide (TMAH, Sigma-Aldrich, St. Louis, MO, USA) (5 mM) was dissolved in 10 ml ethanol (Daegu Chemical Co, Korea) and slowly mixed with a solution of 30 ml dimethyl sulfoxide (DMSO, Sigma-Aldrich, St. Louis, MO, USA) and 3mM zinc acetate dihydrate for 1 h under an argon atmosphere. The ZnO NPs were washed with acetone and dispersed in ethanol, and the solution was spin-coated onto the substrate at 5000 rpm for 50 s, followed by annealing at 150 °C for 30 min.

(3) ZnO NRs were grown by the hydrothermal method. ZnO seeds were prepared by mixing 50 mg zinc acetate dihydrate (Sigma-Aldrich, St. Louis, MO, USA) with 10 ml n-propanol (C3H8O, Sigma-Aldrich, St. Louis, MO, USA). The ZnO seeds were spin-coated onto the glass/ITO substrate at 3000 rpm for 30 s and annealed at 110 °C for 2 min. The spin coating and annealing processes were repeated 4 times. After the fifth coating, the substrates were annealed at 310 °C for 60 min to evaporate any remaining solvent and improve the adhesion between the ZnO seeds and substrate. An aqueous solution was prepared by mixing 25 mM zinc nitrate hexahydrate (Zn(NO3)2·6H2O, Daegu Chemical Co., Korea) and 25 mM hexamethylenetramine (HMT; C6H12N4, Sigma-Aldrich, St. Louis, MO, USA) in 300ml deionized (DI) water then stirred for 1 h 75 °C. To grow ZnO NRs with lengths of tens of nanometers, the ZnO-seed-coated substrates were immersed in the aqueous solution for either 10, 20, or 30 min. Finally, the prepared substrates were removed from the solution, cleaned with DI water, and dried with nitrogen gas.

The various ZnO layers’ surfaces were characterized using a field emission scanning electron microscope (FESEM) (Philips, Netherlands) and an AFM (Dimension 3100 Multimode AFM, Veeco, USA) under atmospheric conditions. The optical scattering spectrum of the ZnO layers was measured using a UV–vis–NIR spectrometer ( Cary 5000, Varian Technology) to investigate the optical properties. The WFs were measured by a Kelvin probe (Besocke Delta Phi, Julich, Germany) in ambient air, averaging 10 measurements and using a highly oriented pyrolytic graphite (HOPG) sample (WF = 4.6 eV) as the reference.

2.2. Device fabrication and characterisation

A solution of pure PTB7 and PC70BM was created using a mixture of chlorobenzene and 1,8-diiodooctane (both from Aldrich, St. Louis, MO, USA), (97:3, v/v) as the solvent. The final solution had a weight ratio of 1:1.5 (PTB7:PC70BM) and a total PTB7:PC70BM concentration of 25 mg ml−1. The PTB7:PC70BM solution was stirred overnight in a nitrogen-filled glove box. Pre-patterned ITO-coated glass with a sheet resistivity of 15 Ω sq−1 (AMG Inc., Korea) was cleaned in an ultrasonic bath of detergent water, rinsed with DI water, and then cleaned in sequential ultrasonic baths of DI water, acetone, and 2-propanol. The substrates were dried with nitrogen after each bath.

An approximately 90 nm layer of PTB7:PC70BM (measured by spectroscopic ellipsometry) was deposited on top of the ZnO-coated glass/ITO substrates by spin coating at 1000 rpm for 40 s. The samples were loaded into a vacuum thermal evaporation system, and a 10 nm layer of MoOx (estimated from the crystal thickness monitor) was deposited through a shadow mask at 0.1–0.15 nm s−1 with a base pressure of ~1×10−7 Torr. Without breaking the vacuum, a 100 nm Ag layer was deposited through the previously used shadow mask at 0.1–0.2 nm s−1 with a base pressure of ~1×10−7 Torr.

The current density-voltage characteristics (J–V) under illumination were measured using a solar simulator (ORIEL Corporation, USA) under air mass (AM) 1.5 global (G) conditions with 100 mW cm−2 light intensity (calibrated using the standard silicon solar cell). The external quantum efficiency (EQE) was measured by an incident photon-to-current efficiency (IPCE) measurement system (Oriel IQE 200 system, USA). The active area of the device was accurately determined to be approximately 0.09 cm2 for each individual device using an optical microscope.

2.3. Finite-difference time-domain simulation

Optical density distributions for the different ZnO layers were simulated using Lumerical Solutions software (Vancouver, Canada). The simulation domain condition was periodic boundary conditions for the x- and y-axes and the perfectly matched layer (PML) condition for the z-axis. The mesh size was 1 nm throughout to produce a finely scaled design. We considered z and x to be the incident light and polarization directions, respectively. Absorption and scattering were estimated by the frequency-domain field and power monitor.

3. Results and discussion

Fig. 1(a)–(c) show AFM images of the three ZnO layer topologies. All ZnO layers were estimated using ellipsometry to be approximately 20 nm thick. The root mean squared (RMS) surface roughness, derived from the AFM height profiles, area = 0.25 µm2, were 12.1 nm, 2.5 nm, and 1.6 nm for the sol–gel, NP, and NR layers, respectively. The ZnO sol–gel layers were more wrinkled and had a rougher surface than the NP and NR layers. Smoother surfaces are expected to form better photoactive layers and to aid the electron selectivity of this interface [26].
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