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# Inverted polymer solar cells including ZnO electron transport layer fabricated by facile spray pyrolysis

Yong-Jin Noh[b], Seok-In Na[b,*], Seok-Soon Kim[a,**]

[a] Department of Nano and Chemical Engineering, Kunsan National University, Kunsan, Jeollabuk-do 753-701, Republic of Korea
[b] Professional Graduate School of Flexible and Printable Electronics and Polymer Materials Fusion Research Center, Chonbuk National University, 664-14, Deokjin-dong, Deokjin-gu, Jeonju-si, Jeollabuk-do 561-756, Republic of Korea

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ABSTRACT

Efficient inverted polymer solar cells (PSCs) were fabricated with ZnO electron transport layers (ETLs) prepared by spray pyrolysis, which is a simple and cost efficient method producing a thin oxide layer by direct spray of precursor on hot substrate. To investigate the effect of substrate temperature on the structural and optical properties as well as performance of PSCs, ZnO ETLs were fabricated by spray pyrolysis on hot substrate controlled at 150, 250, and 350 °C, respectively. The PSC with ZnO prepared by spray pyrolysis at 150 °C exhibited poor power conversion efficiency (PCE) of 0.94% due to the mismatched energy level and microscopic roughness of ZnO ETL. On the other hand, enhanced efficiency of 2.99% and 3.22% was obtained by using ZnO prepared by spray pyrolysis at 250 and 350 °C, respectively. Enhancement of efficiency at higher temperature is attributed to better matching of ZnO coated ITO work-function with the lowest unoccupied molecular orbital (LUMO) energy level of PCBM and the formation of smooth and homogeneous polycrystalline ZnO, resulting in improved interfacial property and electron transport. In the durability test, inverted ZnO solar cell was retained above 80% during 9 days in an ambient atmosphere without any encapsulation, while conventional solar cells showed dramatic decrease of efficiency.

## 1. Introduction

Recently, interests in polymer solar cells (PSCs) have been dramatically increased due to their advantages of light weight, cost-efficient solution processability, and superior mechanical flexibility. Among various solution processable systems, bulk-heterojunction (BHJ) solar cells based on interpenetrating networks of conjugated polymer and [6,6]-phenyl $C_{61}$ butyric acid methyl ester (PCBM) have shown dramatic increase of efficiency up to ~8% as a result of optimization of active layer morphology and device architecture, interface control, and development of novel electron acceptor and donor [1–5]. In spite of relatively high efficiency of conventional BHJ solar cells composed of indium tin oxide (ITO)/hole transporting layer (HTL)/conjugated polymer:PCBM/metal electrodes, their poor reliability over time should be absolutely improved for the practical use of PSCs as an alternative to the fossil fuels. It is well known that the most typically used poly(3,4-ethylene dioxy thiophene):poly(styrene sulfonic acid) (PEDOT:PSS) HTL, inserted to modify the interface between active layer and ITO for the improvement of charge transport and collection, induces significant degradation of the cell performance with time. PEDOT:PSS has several problems such as hygroscopic properties and inhomogeneous electrical properties, in particular, strong acidic nature of PEDOT:PSS that corrodes the ITO hole collecting contact leads to poor long-term stability of conventional PSCs [6,7]. In addition, low work-function metal cathodes such as Al and Ca/Al result in device instability due to the diffusion of oxygen into the photoactive layer and easy oxidation of Al surface leading to the formation of insulator $Al_2O_3$ [8,9].

To enhance stability of PSCs, studies on the p-type like transition metal oxide and 2-dimensional carbon materials such as graphene and graphene oxide, replacing PEDOT:PSS hole selective layer in the conventional structure, have been reported by several groups [10–13].

Researches on the inverted device architecture having reversed charge-collecting nature at the electrodes also have been a hot issue for the development of highly efficient and stable PSCs resulting from the replacement of PEDOT:PSS and low work-function metal electrodes [14]. General inverted configuration includes an ETL inducing effective electron collecting at the ITO and a HTL leading to efficient hole collection at the top metal

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[*] Corresponding author.
[**] Corresponding author. Tel.: +82 634694772.
*E-mail addresses:* nsi12@jgnu.ac.kr (S.-I. Na), sskim@kunsan.ac.kr (S.-S. Kim).

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electrodes such as high work-function Ag and Au. For the successful demonstration of highly efficient inverted PCSs, introduction of optimized buffer layers between electrodes and active layer is one of the most important points. ZnO, $TiO_2$, Ca, $Cs_2CO_3$, and water-soluble polymers have been utilized as promising ETLs on ITO and for efficient hole collecting at metal electrode, PEDOT:PSS and metal oxide such as $MoO_3$ and $V_2O_5$ have been used as HTLs on active layer [15–21]. The ETLs on ITO must be highly transparent to permit transmission of incident lights, and must show superior selective carrier transporting properties. Moreover, considering current status that solution processed PSCs have received an increasing attention as candidates for a low cost printable photovoltaic application, fabrication of very thin charge transport layer by simple and fast printing technique, instead of vacuum process or conventional spin coating, is highly desirable for the realization of low-cost and all printed or roll-to-roll processed PSCs [22].

Here, we report efficient and stable inverted BHJ solar cells based on Poly (3-hexylthiophene) (P3HT):PCBM blends hybridized with ZnO ETL produced by spray pyrolysis which is a relatively simple and atmospheric pressure method for the deposition of thin metal oxide with low cost and high speed. Furthermore, this technique is very compatible with roll-to-roll based typical manufacturing lines and effective to realize large area devices. Characterization of ZnO thin films produced by spray pyrolysis and its application to catalyst or thin film transistors have been reported, and there are few reports on the application of pyrolized ZnO thin films to solar cells [23–30]. Gledhill et al. applied pyrolized ZnO thin film as window layer in $Cu(In,Ga)(S,Se)_2$ solar cells and Zhu et al. reported on the quantum dot-sensitized solar cells using pyrolized ZnO film of hierarchical structure assembled by micrometer-sized aggregates of nanosized crystallites [28,29]. Peiró et al. reported on the application of pyrolized ZnO as seed layer for the growth of ZnO columnar structure for use in polymer/metal oxide solar cells [30]. Because conditions of spray pyrolysis such as precursor constituent and concentration, substrate temperature, and flow can strongly affect the structural, electrical, and optical properties of ZnO, in this study, properties of ZnO prepared at various temperatures were characterized and their effects on the performance of inverted PSCs were investigated. To our knowledge, this is the first report on the application of pyrolized ZnO thin films as ETLs to PSCs describing the effect of substrate temperatures during spray pyrolysis of ZnO.

## 2. Experimental

As transparent electrodes in PSCs, ITO-coated glass substrates (16Ω/□) were cleaned with a special detergent followed by ultrasonication in deionized water, acetone, and isopropyl alcohol and then kept in an 100 °C oven for several hours to remove residual solvents. Fabrication of inverted PCSs starts with deposition of ZnO layers on cleaned ITO by spin-on based sol–gel and spray pyrolysis. To fabricate reference cell, ZnO was fabricated by spin-on based sol–gel process using a 0.75 M zinc acetate solution in 96% 2-methoxy ethanol and 4% ethanolamine followed by heat-treatment at 150 °C for 10 min in air as published elsewhere [16]. ZnO sol–gel solution was further diluted with 2-methoxy ethanol as a volume ratio of 1:6 for the use as a coating solution in spray pyrolysis.

Spray pyrolysis on hot substrates fixed at varied temperatures was performed in ambient condition using $N_2$ gas with a flow rate of 40 cc/min. Here, the distance between spray and substrate was fixed at 10 cm and moving speed was optimized as 3 cm/s. Then, ZnO coated ITOs were transferred into a nitrogen filled glove box for the deposition of photoactive layer. P3HT and PCBM blends were spin-coated from a 1:0.5 wt ratio solution in chlobenzene (15 mg of P3HT/ml and 7.5 mg of PCBM/ml) at 2000 rpm and thermally annealed at 110 °C for 7 min to induce organization of P3HT. Subsequently, PEDOT:PSS HTLs were deposited by spin-coating on the active layers followed by heat treatment at 120 °C for 10 min in air. For successful formation of uniform PEDOT:PSS layer on hydrophobic active layer, PEDOT:PSS was mixed with n-butanol and isopropyl alcohol with a volume ratio of 1:2:2. Fabrication of devices was finished by thermal evaporation of 80 nm Ag top electrode in vacuum on the order of $10^{-6}$ Torr.

Cell performance was measured using a Keithley 2400 instrument under 1 sun (100 mW/$cm^2$) using a xenon light source and AM 1.5 global filter. A reference Si solar cell certified by the International System of Units (SI) (SRC-1000-TC-KG5-N, VLSI Standards, Inc) was used for accurate measurement. To study the stability of inverted device with ZnO ETL, change of cell performance was recorded as a function of exposed time in air using the same instrumental setup without any encapsulation process. Here, conventional normal device with a configuration of ITO/PEDOT:PSS/active layer/metal cathode was also fabricated to compare long-term stability. In case of normal structured PSC, low work function Ca/Al (20 nm/100 nm) was evaporated.

Structural properties of ZnO were characterized by X-ray diffraction (XRD, Bruker M18XCE) and field-emission scanning electron microscope (FE-SEM, Hitachi S-4800) measurements. The optical properties of ZnO ETLs were investigated via UV–vis spectrophotometer (Varian AU/DMS-100S) and the changes in the ITO work-functions by the use of ZnO ETLs were measured using Kelvin probe (KP 6500 Digital Kelvin probe, McAllister Technical Services. Co. Ltd).

## 3. Results and discussion

Although many research efforts have been devoted to the demonstration of fully printed PSCs, in contrast to relatively thick active layer of ~100–200 nm, it is difficult to print very thin interfacial charge transporting layer with a thickness of ~few nm or several tens of nm. As a promising process to fabricate ZnO thin films that serves as ETLs in inverted PSCs, we focused on the spray pyrolysis due to easy control of thickness as nano-scale under the optimized conditions [31]. Moreover, because spray pyrolysis allows the formation of crystalline thin films on large area under atmospheric conditions using cheap chemicals without vacuum system, it is attractive for applications to mass production and potentially all printed PSCs. To confirm the potential of ZnO produced by spray pyrolysis as ETLs, we fabricated PSCs containing ZnO ETLs via spray pyrolysis as shown in the schematics of device structure in Fig. 1(a). Here, to observe the effect of temperature on the structural and optical properties of ZnO as well as performance of PSCs, direct spray of zinc acetate precursor solution was performed on the hot substrates fixed at varied temperatures. For more precise control of thickness and morphology, ZnO layers were fabricated on ITO substrate using moving spray equipment shown in Fig. 1(b).

The role of substrate temperature on the morphology of ZnO ETLs was investigated through SEM surface images shown in Figs. 2 and 3. In the case of ZnO produced by widely used spin-on based sol–gel process, a homogenous ZnO layer was formed as shown in Fig. 2(a). In contrast to smooth sol–gel processed ZnO, ZnO fabricated by spray pyrolysis at 150, 250, and 350 °C showed different round features of droplets with different thicknesses and diameters due to multisprayed patterns such as superposition, merged, deposit ring known as coffee stain ring, and spherical solidification [32]. When the precursor solution was sprayed at 150 °C, larger droplets, resulting in microscopic rough surface, were formed because of enough time to spread after direct spray on the substrate. Smaller and thinner droplets were formed by increasing substrate temperature. In particular, ZnO sprayed at