

Enhanced Stability of Organic Photovoltaics by Additional ZnO Layers on Rippled ZnO Electron-collecting Layer using Atomic Layer Deposition

Kwang-Dae Kim, Dong Chan Lim,^{†,*} Myung-Geun Jeong, Hyun Ook Seo, Bo Yeol Seo,[†] Joo Yul Lee,[†] Youngsup Song,[†] Shinuk Cho,[‡] Jae-Hong Lim,[†] and Young Dok Kim^{*}

Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea. *E-mail: ydkim91@skku.edu

[†]Surface Technology Division, Korea Institute of Materials Science, Changwon 641-010, Korea. *E-mail: dclim@kims.re.kr

[‡]Department of Physics and EHSRC, University of Ulsan, Ulsan 680-749, Korea

Received October 17, 2013, Accepted November 1, 2013

We fabricated organic photovoltaic (OPV) based on ZnO ripple structure on indium tin oxide as electron-collecting layers and PTB7-F20 as donor polymer. In addition, atomic layer deposition (ALD) was used for preparing additional ZnO layers on rippled ZnO. Addition of 2 nm-thick ALD-ZnO resulted in enhanced initial OPV performance and stability. Based on photoluminescence results, we suggest that ALD-ZnO layers reduced number of surface defect sites on ZnO, which can act as electron-hole recombination center of OPV, and increased resistance of ZnO towards surface defect formation.

Key Words : Organic photovoltaic, ZnO, Surface defect, Stability, Atomic layer deposition

Introduction

For the last decade, organic photovoltaics (OPVs) have drawn much attention due to their easy fabrication and potential for application in flexible devices.¹⁻⁷ Recently, power conversion efficiency (PCE) of OPV rapidly increased up to 12%.⁸ For enhancing performances of OPVs diverse approaches have been used; low band-gap polymers with high light harvesting efficiency have been developed by many research groups.^{9, 10} Various buffer layers (*e.g.*, TiO₂, and ZnO as electron-collecting layers and NiO, and MoO₃ as hole-collecting layers) were used in order to more efficiently separate electrons and holes created in active layers by absorption of light.¹¹⁻¹⁵ Nano-structuring of surfaces of buffer layers increased contact area between active polymer and buffer layers, increasing efficiency for electron-hole separation.^{16,17}

We have recently shown that ZnO ripple structures can be easily prepared using solution process combined with well-controlled heat treatment process.¹⁸ Rippled surface of ZnO was found to be more efficient for separating electrons from active layers (a mixture of Poly(3-hexylthiophene); P3HT and [6,6]-phenyl-C₆₁-butyric acid methyl ester; PC₆₁BM), resulting in a higher photovoltaic performance comparing to that with flat ZnO surfaces as electron-collecting layer. Moreover, additional TiO₂ or ZnO was deposited using atomic layer deposition (ALD) on rippled ZnO surfaces, and we found that the photovoltaic performance can further be improved by optimizing thickness of additional TiO₂ or ZnO layers deposited by ALD.^{19,20} In addition, the photovoltaic cell using additional ultrathin ALD-TiO₂ layer showed significantly stable PCE for nearly 100 days.

In the present work, we fabricated OPV with 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'*]

phenediyl]] (PTB7) F20 as donor polymer and ZnO ripple-structure on transparent conducting oxide as electron-collecting layer, which showed a significantly higher initial performance of the photovoltaic comparing to that based on P3HT.⁷ We show that additional ALD-ZnO layers with a thickness of 2 nm not only increased PCE of the photovoltaic, but also stability of the device performance significantly. Physical origin of the enhancement in initial performance and stability of the photovoltaic devices based on PTB7-F20 and ZnO-ripple structure by additional ALD-ZnO layers are discussed. Note that the surface treatment of electron-collecting layer using ALD technique can lead to positive effect for not only device performance, but also its stability, and ALD technique is applicable to any kind of polymer. We suggest that the interface treatment using ALD technique is suitable and effective method for various application on optoelectronic device such photovoltaic cell.

Experimental

OPVs studied in the present work consisted of a stack of indium tin oxide (ITO)-coated glass/ZnO nano-ripple film with or without ALD-ZnO layer/bulk heterojunction of donor and acceptor polymer as active layer/poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate)(PEDOT: PSS)/Ag top-electrode (Figs. 1 and 2). The ITO-coated glass substrates (4 Ω/sq., 2.5 × 2.5 cm²) used as the transparent electrode were cleaned with distilled water, ultrasonicated in acetone, and boiled in isopropyl alcohol (IPA) and then dried in an oven at 100 °C. For the preparation of ZnO nano-ripple film, ZnO sol-gel solution of 0.75 M was spin-coated on the ITO-coated glass pretreated by UV ozone for 30 min. The solution was prepared by dissolving zinc acetate [Zn(CH₃COO)₂ · 2H₂O] in 2-methoxyethanol solvent containing ethanolamine as a stabilizer. After coating, this glass was heated to

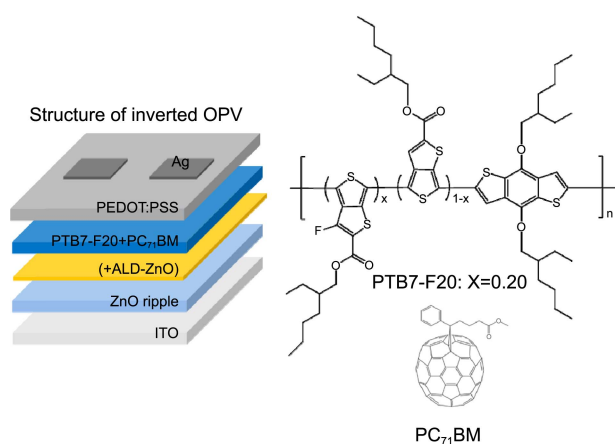


Figure 1. Schematic diagram of the structure of OPVs fabricated in the present work together with structures of the polymers used as donor (PTB7-F20) and acceptor (PC₇₁BM) in the bulk heterojunction are displayed.

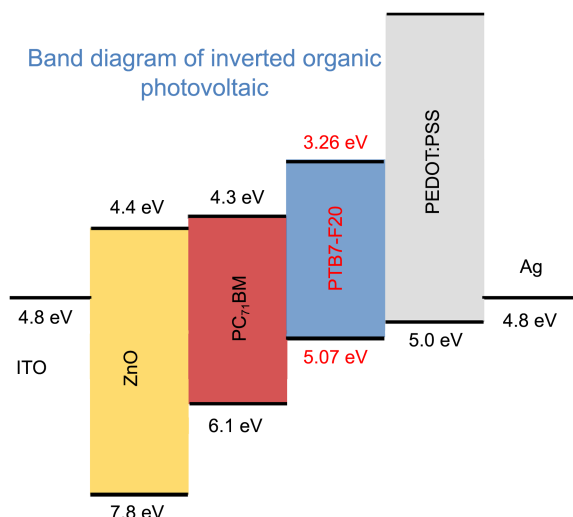


Figure 2. Band diagram of the OPV fabricated in the present work is shown.⁷

350 °C with a constant heating rate of 22 °C/min in a furnace. The details of synthesis and effects of ZnO nano-ripple film on performance of OPVs have been reported elsewhere.¹⁸

The ZnO film surface was further modified by using an ALD system (LUCIDA M100, NCD). Diethyl zinc [DEZ, Zn(C₂H₅)₂] and water (H₂O) vapor were used as the zinc precursor and reactant, respectively. The temperature of the DEZ source was maintained at 10 °C using a cooling circulator. The canister containing the water source was at room temperature. During deposition, Ar gas was supplied to the reaction chamber continuously at a flow rate of 100 sccm. The thickness per cycle of ZnO ALD was 1.39 Å/cycle. In order to grow ZnO thin layers of 2 nm, ALD cycle of 14 was used.

For preparation of active layer, a mixture of PTB7-F20:PC₇₁BM (8:12 mg) was dissolved in 1 mL of chlorobenzene with 3% in volume of 1,8-diiodooctane (Aldrich) under stirring overnight at 60 °C. Then, this solution was spin-

coated on ZnO nano-ripple films under Ar condition at room temperature (1000 rpm/40 sec).

The PEDOT:PSS (Clevios P VP AI 4083, Heraeus) used as hole injection layer was diluted in IPA. A mixture of PEDOT:PSS/IPA (volume ratio of 1:10) was spin-coated onto the active layer under Ar condition at room temperature (5000 rpm/60 sec). It is worth emphasizing that no post-annealing of PEDOT:PSS layers was used.

The Ag metal (100 nm) as a top electrode was thermally evaporated onto the PEDOT:PSS layer under a vacuum condition with a base pressure of 3×10^{-6} Torr condition. The active surface area of the device with metal mask was 0.38 cm².

The current density-voltage (*J-V*) curves of the OPV devices were taken using a PEC-L11 model 13 (Pecell Technologies Inc.) under AM 1.5 simulated illumination with an intensity of 100 mW/cm². The intensity of sun light illumination was calibrated using a standard Si photodiode detector with a KG-5 filter. The atomic force microscopy (AFM) was operated in contact mode with a rate of 0.3 Hz to produce topographic images of the sample surface using the Pt-coated cantilever tips from Nanosensors, Switzerland (spring constant of 3 N/m and resonance frequency of 75 kHz). Photoluminescence (PL) spectra were obtained using a HORIBA JOBIN YVON, LabRam HR800. Samples were pumped with He-Cd laser of wavelength of 325 nm.

Results and Discussion

Figure 3 shows AFM images of ZnO ripple structure before and after deposition of additional ALD-ZnO layers with a mean thickness of 2 nm. Before deposition of ALD-ZnO, ripple structure with a mean ripple width of ~200 nm can be identified. The root-mean square (RMS) roughness of the bare ripple surface was determined to be higher than 32 nm. After ALD-ZnO deposition, rippled surface structure can still be clearly identified, even though the surface roughness value was reduced with respect to that of the ZnO surface without ALD-ZnO.

Figure 4 and Table 1 compare performances of photovoltaic cells consisting of rippled ZnO surfaces with and without additional ALD-ZnO layers. Immediately after fabrication of these cells, the PCE values of both cells were determined to be higher than 7.5%. Particularly, the cell with

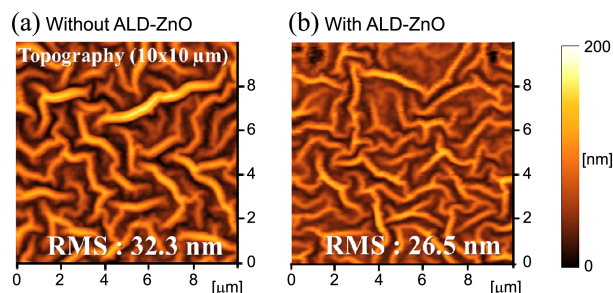


Figure 3. AFM images of ZnO ripples with and without ALD-ZnO (thickness of 2 nm) are shown.

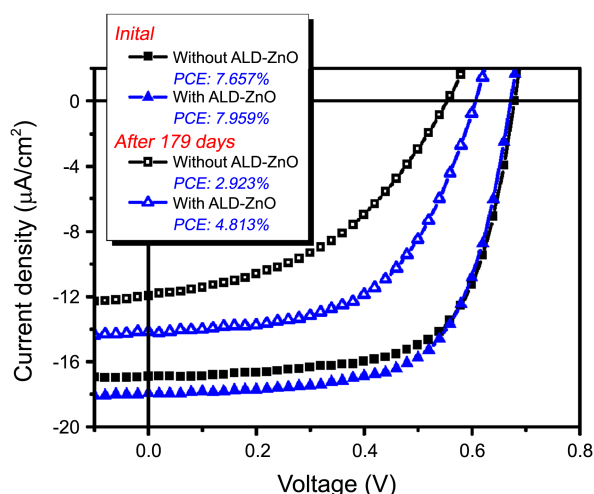


Figure 4. Photovoltaic performances of OPV with and without ALD-ZnO are compared. Measurements were performed just after cell fabrication and after 179 days for each cell.

Table 1. Power conversion efficiency (PCE), fill-factor (FF), open-circuit voltage (V_{oc}) and short-circuit current (J_{sc}) of OPVs with and without ALD-ZnO just after cell fabrication and after 179 days for each cell are summarized

Device description	Without ALD-ZnO		With ALD-ZnO	
	Initial	After 179 days	Initial	After 179 days
PCE (%)	7.657	2.923	7.959	4.813
FF	0.665	0.440	0.659	0.559
V_{oc} (V)	0.679	0.554	0.672	0.606
J_{sc} (mA/cm ²)	16.922	11.970	17.947	14.175

ALD-ZnO showed a PCE close to 8% which is higher than that of bare ZnO ripple structure. The cell with additional ALD-ZnO showed comparable open-circuit voltage (V_{oc}) and fill-factor (FF) to those of bare rippled ZnO surface; however, the short-circuit current (J_{sc}) of the cell with ALD-ZnO was slightly higher than that without ALD-ZnO. We have recently shown that the additional ALD-ZnO reduces number of surface defects on ZnO, which can act as electron-hole recombination center in OPV and reduce photocurrent.⁷

In order to shed light on the durability of these solar cells fabricated in the present work, the photovoltaic performances of these two cells were measured after 179 days. It should be noted that these photovoltaic cells were stored for 179 days without encapsulation under ambient conditions. For both samples, significant decreases in PCE with respect to values of respective fresh cells could be found. Though, it is notable that photovoltaic devices with ALD-ZnO showed a significantly higher performance comparing to that without ALD-ZnO 179 days after cell fabrication; for the cell with ALD-ZnO, the PCE was decreased from 8.0 to 4.8% by ~40%, whereas the PCE of the device without ALD-ZnO became 2.9% after 179 days, which is less than half of the initial PCE of the same cell (7.7%). As one can see in Table 1, V_{oc} s, J_{sc} s, and FFs of both cells were all reduced after 179 days;

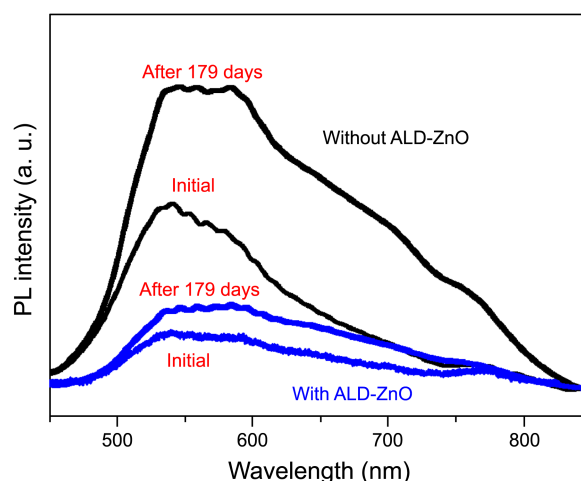


Figure 5. PL spectra of OPV with and without ALD-ZnO with are compared. Measurements were performed just after cell fabrication and after 179 days for each cell.

however, the decrease in photovoltaic performance of the cell without ALD-ZnO with time was generally much more pronounced than in the case with ALD-ZnO.

In order to shed light on the origin of the enhanced stability of the photovoltaic cell with ALD-ZnO, PL studies were carried out for photovoltaic cells with and without ALD-ZnO layers just after cell fabrication and after 179 days (Fig. 5). After measurement of initial PL spectrum each photovoltaic cell (with and without ALD-ZnO layer), these photovoltaic cells were stored for 179 days without encapsulation under ambient and dark conditions. Broad features could be found for each spectrum between 450–850 nm, which correspond to the states of surface defects of ZnO such as oxygen vacancies.^{21,22} It is well known that these surface defects of ZnO can act as recombination center of electron-hole pairs, and lead to the reduction in performance of photovoltaics consisting of ZnO as electron-collecting layers.^{21,22} Area of the broad PL features of each spectrum should be proportional to the number of defect sites of ZnO in each sample. From data taken from freshly prepared samples, one can notice that the PL peak intensity was significantly reduced by additional ALD-ZnO deposition (Figs. 5 and 6). Slightly higher performance of photovoltaic cell with ALD-ZnO just after cell fabrication could be related to the lowered defect density of ZnO upon ALD-ZnO deposition. After 179 days, surface defect density of ZnO increased for both cases with and without ALD-ZnO; however, PL peak area of the cell without ALD-ZnO (only ZnO ripple) became higher than double of the initial value of the same cell, whereas increase of the PL peak area of the cell with additional ALD-ZnO (ZnO ripple + ALD-ZnO layer) was relatively much less pronounced after 179 days (Figs. 5 and 6). These results qualitatively correlate with photovoltaic cell performance data shown in Figure 4 and Table 1; surface defects of ZnO ripple, which act as electron-hole recombination center in OPV, were decreased in concentration after deposition of 2 nm-thick ALD-ZnO layer. Moreover, the resistant towards surface defect formation on ZnO with time

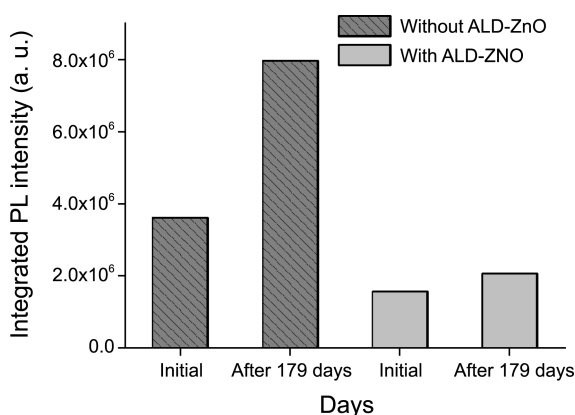


Figure 6. Defect densities on ZnO surfaces of OPV with and without ALD-ZnO are quantified just after cell fabrication and after 179 days for each cell. Defect density of each OPV was quantitatively determined by integral of the respective PL spectrum in Figure 5.

was also improved by deposition of ALD-ZnO layer.

Conclusion

In summary, OPVs were prepared based on ZnO-ripple structure as electron-collecting buffer layers. Additional ZnO layers with a thickness of 2 nm prepared using ALD not only increased initial photovoltaic performance but also enhanced stability of cell performance. It was found that ALD process decreased number of surface defects of ZnO and also increased resistance of ZnO surface towards surface defect formation, resulting in enhanced OPV performance and stability.

Acknowledgments. This research was supported by a grant from KIMS.

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