Active Layer Spin Coating Speed Dependence of Inverted Organic Solar Cell Based on Eosin-Y-Coated ZnO Nanorod Arrays

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Abstract. The active layer spin coating speed dependence of the performance of inverted organic solar cells (OSCs) based on Eosin-Y-coated ZnO nanorods has been investigated. An active layer consisted of poly(2-methoxy-5-(2’-ethyl)-hexyloxy-p-phenylenevinylene) (MEH-PPV) as donor and phenyl-c61-butyric acid methyl ester (PCBM) as acceptor was employed, whereas ZnO nanorods were utilized as electron transporting layer. The active layer was deposited on top of Eosin-Y-coated ZnO nanorods with various spin coating speeds (1000-4000 rpm). Inverted OSCs with a structure of FTO/Eosin-Y-coated ZnO nanorods/MEH-PPV:PCBM /Ag were characterized through the current density-voltage (J-V) measurement under illumination intensity of 100 mW/cm². Based on the investigation, the short circuit current density (Jsc) and the power conversion efficiency (PCE) enhanced significantly, whereas fill factor slightly increased with spin coating speed. The two-diode equivalent model was found to fit the experimental J-V curves very well. The optimum PCE of 1.18 ± 0.07 % was achieved at the highest spin coating speed of 4000 rpm, as a result of the decrement of diffusion current density (Jdiff), recombination current density (Jrec), and ideality factor, thus further confirms the strong built-in electric field in thinner photoactive layer.

1. Introduction
Organic solar cells (OSCs) based on conjugated polymers and fullerene derivatives have the potential to offer low-cost processing using roll-to-roll printing techniques to fabricate large-area photovoltaic devices on flexible and light-weight substrates [1, 2]. Recently, inverted OSCs based on ZnO nanorod arrays (NRAs) have attracted a lot of attention due to the environmental stability and ease of processing [3]. Vertically aligned ZnO NRAs known as good electron transporting layer can be grown at low temperature by hydrothermal method, thus promising for low-cost fabrication process of inverted OSCs device.

Previously, the effects of MEH-PPV:PCBM blend active layer thickness in conventional bulk heterojunction solar cells structure of ITO/PEDOT:PSS/MEH-PPV:PCBM/Al have been investigated by controlling the solution concentration and spin coating speeds [4]. It has been found that open circuit voltage (Voc) remains almost unchanged with spin coating speed, whereas short circuit current density (Jsc) gradually increases due to stronger built-in electric field which results in shorter
pathways for photogenerated electron and holes to transport to the corresponding electrodes. However, when spin coating speed is higher than 5000 rpm (thinner film), both $V_{oc}$ and $J_{sc}$ reduce.

Chou et al. (2009) reported that the performance of inverted OSCs with structure of ITO/ZnO NRAs/P3HT:PCBM/Ag) can be improved by varying spin coating rate in order to lengthen the solidification time of polymer and thickness of active layer. It was noted that the decrease of spin coating rate results in thickened active layer and thus enhanced light harvesting. Although the probability of exciton recombination is relatively high in a thicker (~400 nm) active layer, these limitation can be overcome by effective infiltration of polymer into the ZnO NRAs which further promotes better charge separation [5]. Recently, the correlation between experimental current density-voltage ($J-V$) plots and theoretically $J-V$ plots based on single and two-diode model approach for conventional OSCs with structure of ITO/PEDOT/MEH-PPV:PCBM/LiF/Al have been well studied [6]. It was found that two-diode model fits well to the experimental $J-V$ curve compared with single diode model under illumination intensity of 100 mW cm$^{-2}$.

The aim of this study is to investigate the effect of active layer spin coating speed on the photovoltaic performance of inverted OSCs. The diode characteristics of inverted OSCs were investigated by extracting several important parameters from experimental current density-voltage ($J-V$) curve using two-diode equivalent model. The inverted device structure of fluorine doped tin oxide (FTO)/Eosin-Y-coated ZnO NRAs/MEH-PPV:PCBM/Ag were used[7]. Herein, a thin organic Eosin-Y dye layer was spin coated onto ZnO NRAs to improve the wettability of ZnO and enhance charge transfer efficiency at polymer/ZnO NRAs interface. Based on the results, it was found that the enhancement of $J_{sc}$ with spin coating speed is due to the decrement of recombination current density ($J_{rec}$) and ideality factor. The spin coating speed of 4000 rpm leads to optimum device performance with power conversion efficiency (PCE) of 1.18 ± 0.07 %.

2. Methodology
The thin ZnO seed layer was made by the sol-gel spin coating process. The sol-gel precursor solution consisting of 0.2 M equimolar of zinc acetate dehydrate and diethanolamine (DEA) in ethanol, was spin coated on top of pre-cleaned FTO substrate. The sample was immediately annealed at 300 °C for 1 h in air. The ZnO NRAs with length of about ~250 nm were hydrothermally grown at 90 °C using oven for 45 min in equimolar solution of 40 mM zinc nitrate hexahydrate and hexamethylenetetramine (HMT). The ZnO NRAs-coated substrate was rinsed with deionized water and dried to remove residual organic material. A thin layer of 0.3 mM Eosin-Y organic dye was spin coated on top of ZnO NRAs. The MEH-PPV and PCBM(1:3 by weight) dissolved in chloroform were spin coated onto Eosin-Y-coated ZnO NRAs with different spin coating speed from 1000 to 4000 rpm in air. Finally, without further annealing the samples, silver electrodes (180 nm) were sputtered with a low deposition rate of 2.20 nm s$^{-1}$ by introducing oxygen at flow rate of 5 cc/min. The effective active area of devices was defined as 0.07 cm$^2$ using mask.

The absorption spectra of blend films consisted of organic active layer and Eosin-Y-coated ZnO NRAs were investigated using a Dynamica Halo DB-20 UV-Vis spectrometer. The $J-V$ characteristics of the devices were measured with Keithley 237 SMU under illumination at 100 mW/cm$^2$ from a solar simulator with AM 1.5G filter. The incident photon to current conversion efficiency (IPCE) was measured using Newport IPCE system at a chopping frequency of 10 Hz. All device preparation, fabrication and measurements were conducted under ambient atmosphere (without encapsulation).

3. Results and discussion
Figure 1 shows the optical absorption spectra of MEH-PPV:PCBM deposited on Eosin-Y-coated ZnO NRAs at different spin coating speeds. Absorption of MEH-PPV:PCBM at visible range of 400-580 nm decreased significantly as the spin coating speed increased from 1000 to 4000 rpm. Similar phenomena has been observed on the thickness of the active layer on top of the ZnO NRAs layer which reduced from ~375 nm to ~150 nm (measured by surface profilometer) with increasing spin coating speed.
Figure 1. (a) Optical absorption spectra and (b) Active layer thickness of MEH-PPV:PCBM deposited on Eosin-Y-coated ZnO NRAs at different spin coating speeds.

Four devices for each parameter have been fabricated and were characterized under 100 mW cm\(^{-2}\) illumination. Figure 2a shows the \(J-V\) characteristics of MEH-PPV:PCBM devices with different spin coating speeds. The series resistance \((R_s)\) and shunt resistance \((R_{sh})\) were derived from the inverse slope of \(J-V\) curve at \(V_{oc}\) and \(J_{sc}\), respectively, as shown in Table 1. The \(J_{sc}\) improved significantly from 3.42 ± 0.24 to 5.61 ± 0.08 mA cm\(^{-2}\) with increasing spin coating speed. In contrast, the \(V_{oc}\) decreased slightly from 0.63 to 0.59 V with spin coating speed. This can be attributed to the increase of leakage current from ZnO NRAs to Ag electrode as suggested by the decrement of shunt resistance \((R_{sh})\) at higher spin coating speed.

Figure 2. (a) Current density-voltage \((J-V)\) characteristics (b) ideality factor \((n)\), \(J_{diff}\) and \(J_{rec}\) of inverted OSCs device with different spin coating speeds under the illumination of simulated AM 1.5 G sunlight at 100 mW cm\(^{-2}\).

Table 1. Summary of photovoltaic parameters of devices at various spin coating speeds.

| Spin-coating speed \((x1000\ rpm)\) | \(J_{sc}\) \((mA cm^{-2})\) | \(V_{oc}\) \((V)\) | PCE \(\%\) | FF | \(R_s\) \((\Omega cm^{-2})\) | \(R_{sh}\) \((\Omega cm^{-2})\) | IPCE \(\%\) |
|---|---|---|---|---|---|---|---|
| 1 | 3.42±0.24 | 0.63±0.03 | 0.67±0.01 | 0.31±0.03 | 127±29 | 288±58 | 21 |
| 2 | 4.11±0.11 | 0.61±0.01 | 0.84±0.03 | 0.34±0.02 | 79±5 | 252±13 | 27 |
| 3 | 4.52±0.19 | 0.59±0.01 | 0.92±0.02 | 0.35±0.01 | 63±5 | 240±11 | 30 |
| 4 | 5.61±0.08 | 0.59±0.01 | 1.18±0.07 | 0.36±0.02 | 45±6 | 223±18 | 38 |
The increase of $J_{sc}$ with spin coating speed could be correlated with the active layer thickness. It is observed from Table 1 that series resistance ($R_s$) reduced dramatically by $\sim 65\%$ from $127 \pm 29$ to $45 \pm 6 \ \Omega \ cm^2$ with spinning speed. This indicates that the probability of photogenerated charge carriers, electron in particular, to transport from active layer to ZnO NRAs became higher with thinner active layer. The highest $J_{sc}$ achieved at spin coating speed of 4000 rpm leads to optimum PCE of $1.18 \pm 0.07 \%$. In order to further explain the dependence of photovoltaic performance on the active layer spin coating speed, the Eq. (1) based on two-diode equivalent model was used to fit the experimental $J$-$V$ curve under light illumination [6].

$$J = J_{ph} - \frac{V + JR_s}{R_{sh}} - J_{01}[e^{q(V + JR_s)/nKT} - 1] - J_{02}[e^{q(V + JR_s)/nkT} - 1]$$

(1)

Where $J$ is current density, $J_{ph}$ describes the saturation current density, which is related to the bulk recombination, diffusion and drift effect process [8] throughout the device and dominate at high forward bias voltage or denoted as diffusion current density, $J_{diff}$. The $J_{02}$ corresponds to charge carrier recombination via deep levels in the space-charge region of the junction and also known as recombination current density or $J_{rec}$[9], whereas ideality factor, $n$ indicates the diode quality, and $J_{ph}$ is the current generation upon light illumination. The two-diode equivalent model is an effective method to extract more detailed aspects in inverted OSCs where the parameters of the diode model can be related to the mechanisms of solar energy conversion [6].

It was found that the two-diode model fitted well to the experimental $J$-$V$ (symbol) curves as shown in Figure 2a, where the line and symbol in Figure 2a represents the fitting line and experimental $J$-$V$ curve, respectively. Figure 2b shows the extracted data parameters of ideality factor, $J_{diff}$ and $J_{rec}$ from fitted $J$-$V$ curve of Figure 2a. The $R_s$ and $R_{sh}$ from Table 1 were used as initial or estimated values to fit the experimental $J$-$V$ curves. From Figure 2b, $J_{diff}$ and $J_{rec}$ decreased significantly with respect to spin coating speed, where $J_{diff}$ was several order smaller than $J_{rec}$. Generally, lowering the spin coating speed will result in a higher photocurrent due to enhancement of light absorption with thick active layer. However, the series resistance and charge recombination rate also increase with increasing active layer thickness. Therefore, further increase in the active layer thickness above optimum value normally leads to lower device efficiency [10]. In this inverted OSCs, the lowest spin coating speed showed an increase of charge carrier recombination in the space charge region ($J_{rec}$) by two-order magnitude as shown in Figure 2b. It could be due to the increase of charge recombination of free charge carriers by space charge effect, low charge carrier mobilities and increased series resistance of device [11, 12]. On the other hand, the decrement of ideality factor with increase of spin coating speed is also consistent with the decrement of $J_{diff}$ and $J_{rec}$ and also the reduction of series resistance of the devices. These can be due to the reduction of trap-assisted recombination in the space charge region [13], where the photogenerated electron and holes turned out to be effectively separated and transport to the corresponding electrodes. This further confirms the existence of strong built-in electric field in thinner active layer which shortened the pathways for transporting the charge carriers, resulting in the increment of $J_{sc}$ and enhancement of device efficiencies. Based on the result, it is suggested that the decrement of $J_{diff}$, $J_{rec}$, and ideality factor (as shown in Figure 2b) with spin-coating speed, was mainly correlated to the photoactive layer thickness, since the growth of ZnO NRAs and other parameters remained the same for all devices.

Furthermore, the IPCE of the devices was measured with different active layer spin coating speeds as shown in Figure 3, whereas the IPCE values at wavelength closed to the absorption peak of MEH-PPV (500 nm) are shown in Table 1. For active layer spin coated at 4000 rpm, the device exhibited highest IPCE of $\sim 38 \%$, which indicates better photocurrent generation efficiency compared to lower spin coating speed. The IPCE result is also consistent with the trend in $J_{sc}$ which increased with spin coating speed. Despite the increase of optical absorption (shown in Fig. 1a) with spin coating speed, the opposite trend was observed from IPCE spectra. The IPCE spectrum of the device with the lowest spin coating speed (1000 rpm) exhibited low photon conversion efficiency at wavelength (500 nm) corresponding to absorption peak of MEH-PPV. For thicker active layer deposited at low spin coating speed, where the majority of photons with wavelength close to 500 nm were mostly absorbed in the region close to transparent conducting oxide (FTO)/Eosin-Y-coated ZnONRAs. Meanwhile, photons
with wavelength away from 500 nm were more uniformly absorbed throughout the active layer. The distortion of IPCE spectrum of thick active layer suggests that photocurrent generation in the region close to Ag was more efficient than that in the region close to FTO at wavelength below 500 nm [14].

The air-stability of optimum inverted organic solar cells with structure of FTO/ZnONRAs/Eosin-Y/MEH-PPV:PCBM/Ag was measured at ambient air in room temperature over a week as shown in Fig. 4. Interestingly, after storing in air for 4 days, $J_{sc}$, $V_{oc}$, PCE, and FF increased significantly. It could be explained that oxidation of Ag electrode with time during exposure in air increased its effective work function to $-5.0$ eV [15] as shown in inset Figure 4. The decrease in series resistance from 45 to $34 \, \Omega \, \text{cm}^2$ provides evidence for the decrease of barrier for hole transport at the photoactive layer-silver electrode interface as a result of increase in the effective work function of Ag [16]. The optimized device exhibited maximum PCE of 1.47 % after 4 days.

Similar behavior has been observed from previous report by Olson et al. (2007), where the performance of the device (ITO/ZnO/ZnO fibers/P3HT/Ag) increased significantly after storing in air.
for 3 days. The increase of Ag work function was also proven by the increase of $V_{oc}$ by 0.2 V after 2 days and the $V_{oc}$ maintained up to 20 days. Therefore, by having air stable organic solar cells devices, the encapsulation process can be performed under ambient conditions, thus substantially reducing fabrication complexity and leading to cost-effective organic solar cells [15].

4. Conclusions
The effects of active layer spin coating speed on the performance of inverted OSCs based on Eosin-Y-coated ZnO NRAs have been investigated. It was found that the two-diode equivalent model fitted well to the experimental $J-V$ curves of inverted OSCs. The decrease of ideality factor is also consistent with the decrement of $J_{diff}$ and $J_{rec}$ and reduction of series resistance of the devices. These lead to the enhancement of $J_{sc}$ and device efficiencies and further confirm the existence of strong built-in electric field in thinner photoactive layer. The optimum PCE of $1.18 \pm 0.07 \%$ was achieved at spin coating speed of 4000 rpm and was found to increase significantly after storing in air for 4 days which is probably due to the better ohmic contact between the active layer and metal contacts.

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