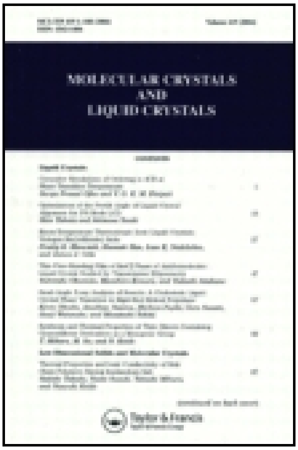

Molecular Crystals and Liquid Crystals

Effects of Anode Buffer Layers on the Performance of P3HT/C_{70}-PCBM Photovoltaic Devices

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Effects of Anode Buffer Layers on the Performance of P3HT/C_{70}-PCBM Photovoltaic Devices

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In this paper, we fabricated and compared the photovoltaic properties of two different kinds of PEDOT:PSS buffer layer systems. The first was with the PEDOT:PSS buffer layers of different PEDOT to PSS ratios, 1 to 2.5 for Baytron P and 1 to 6 for Baytron PVP AI4083, respectively. The second system included the buffer layers with the same PEDOT to PSS ratio, but with the changed conductivities by doping with 2, 4, 6, 8, and 10 wt% of glycerol. The power conversion efficiency was governed by the series resistance of the device and the resistivity of the applied PEDOT:PSS films, while the parallel resistance and the diode rectification characteristics are affected by the ratio of PEDOT to PSS on buffer layer.

Keywords: buffer layer; doping; organic solar cell; PEDOT; polymer photovoltaic device

INTRODUCTION

The polymer photovoltaic devices have attracted much attention due to their possible low production cost and easy manufacturing by solution process [1,2]. Recently, the power conversion efficiency (PCE) of photovoltaic devices over 5% has been realized [3–5]. In addition, through the optimization of the donor/acceptor energy levels, the efficiency up to 10% is expected form recent simulation results [6]. For an ideal photovoltaic device, a high parallel resistance (Rp) and a low series resistance (Rs) are required [7,8]. The Rp usually reflects

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the degree of leakage current through the device, which relates to the overall quality of the films, meanwhile, the Rs is attributed to the ohmic loss in the whole device, which includes the resistance of the active layer, metal-organic contacts, the electrodes, and the parasitic probe resistance [8,9].

To facilitate hole injection, an extra interfacial layer, poly(3,4-ethylenediozythiophene)/poly(styrenesulfonate) (PEDOT:PSS), is usually applied to modify the surface of ITO. On the other hand, an improper PEDOT:PSS layer will reduce the short-circuit current and fill factor (FF) owing to the increased Rs [10]. The conductivity of the doped PEDOT:PSS increased over two orders of magnitude after doping with polyalcohols, and a few groups reported that hole extraction from polymer photovoltaic devices could be improved by doping polyalcohols into the PEDOT:PSS [4,11,12]. Also it is well known that the conductivity of PEDOT:PSS was also changed by PEDOT to PSS ratio, but only few attempts so far have been made to study the relation among the PEDOT to PSS ratio of PEDOT:PSS, the conductivity of buffer layer, and the device performance in polymer photovoltaic devices [12,13].

In this work, to understand the effects of the PEDOT to PSS ratio and the conductivity of buffer layer on the P3HT/C_{70}-PCBM photovoltaic devices, two different PEDOT:PSS buffer layer systems were introduced. The first was with PEDOT:PSS buffer layers of different PEDOT to PSS ratios, Baytron® P (**PEDOT P**) for 1:2.5 ratio and Baytron® PVP AI4083 (**PEDOT AI4083**) for 1:6 ratio, respectively. The second was with the same PEDOT to PSS ratio buffer layers, but with different conductivities by doping with 2, 4, 6, 8, and 10 wt% of glycerol to **PEDOT AI4083** to get **PEDOT G2**%, **G4**%, **G6**%, **G8**%, and **G10**%.

EXPERIMENTAL

All solvents used in this study were of HPLC grade. Poly(3-hexylthiophene) (P3HT) was purchased from Reike Metal Ltd. [6,6]-Phenyl C_{71}-butyric acid methyl ester (C_{70}-PCBM) was purchased from Nano-C. Two different PEDOT:PSS (Baytron® P and Baytron® PVP AI4083) in aqueous solution were purchased from H. C. Starck. The resistivities of PEDOT:PSS films were measured at room temperature with a Cascade Microtech four-point probe, a Keithley 197 voltage meter, and a Keithley 224 programmable current source.

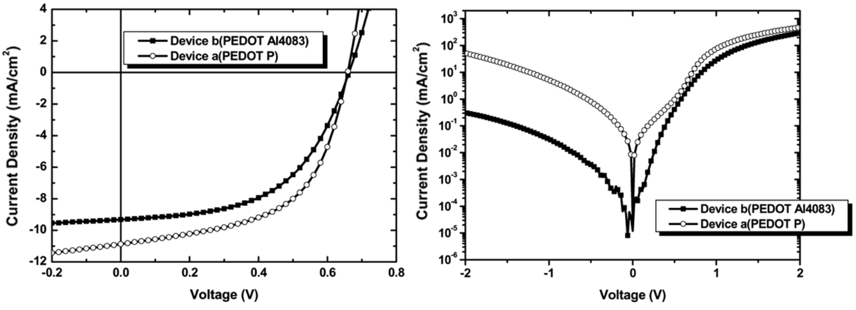
Photovoltaic Device Fabrication

Composite solution with P3HT and C_{70}-PCBM in 1:1 wt ratio was prepared using 1,2-dichlorobenzene solvent with the concentration of

1.5 wt%. The polymer photovoltaic devices were fabricated with a typical sandwich structure of ITO/PEDOT:PSS/P3HT:C_{70}-PCBM/Al. The ITO coated glass substrates were cleaned through a routine cleaning procedure, including sonication in detergent followed by distilled water, acetone, and 2-propanol. **PEDOT G2**%, **G4**%, **G6**%, **G8**%, and **G10**% were prepared by adding 2, 4, 6, 8, and 10 wt% of glycerol to Baytron® PVP AI4083 and then all PEDOT:PSS aqueous solution were stirred at ambient condition for 24 hours before using. A 45 nm thick layer of PEDOT:PSS was spin coated on a cleaned ITO substrate after exposing the ITO surface to ozone for 10 minutes. The PEDOT:PSS layer is baked on a hot plate at 120°C for 20 minutes under argon atmosphere. Active layer was spin coated from the pre-dissolved composite solution after filtering through 0.45 μm PP syringe filters. The thickness of the active layer was maintained at 100 nm. The device structure was completed by depositing 150 nm Al cathode as top electrode onto the polymer active layer under 3×10^{-6} torr vacuum in thermal evaporator. Current density-voltage (J-V) characteristics of all polymer photovoltaic cells were measured under the illumination of simulated solar light with 100 mW/cm^2 (AM 1.5 G) by Oriel 1000 W solar simulator. Electric data were recorded using a Keithley 236 source-measure unit and all characterizations were carried out in an ambient environment. The illumination intensity used was calibrated by a standard Si photodiode detector from Bunkoukeiki Co., Ltd. Thickness of the thin film was measured using KLA Tencor Alpha-step 500 surface profilometer with an accuracy of ±1 nm.

RESULTS AND DISCUSSION

Firstly, we fabricated and compared two devices of different buffer layers having different PEDOT to PSS ratios, **PEDOT P** (**device a**) and **PEDOT AI4083** (**device b**). The PCE of **device a** is better than that of **device b**, with the values of 4.00% and 3.31%, respectively. The higher PCE of **device a** is attributed to the high Jsc value, though both devices have the same open circuit voltage (Voc) of 0.66 V, as shown in Figure 1(a). The higher Jsc value of **device a** is caused by 2 order lower resistivity of **PEDOT P** compared to **PEDOT AI4083**, which is measured form the four-point probe of each PEDOT:PSS thin film, and each resistivity is 6.29 Ω cm and 445 Ω cm, respectively, as shown in Table 1. The Rs and the Rp in Table 1 were derived from the slope of the J-V characteristic curve under dark conditions close to +2 and 0 V [14]. The Rs of **device a** is also lower than that of **device b**, with the values of 2.2 Ω cm^2 and 2.8 Ω cm^2, respectively. But for the case of Rp, **device b** has 2 order higher value of



(a) (b)

FIGURE 1 J-V characteristic curves of the P3HT:C$_{70}$-PCBM devices with buffer layers of **PEDOT P** and **PEDOT AI4083** under at 100 mA/cm^2 light illumination (AM 1.5) (a) and in the dark (b).

290.9 Ω cm^2 than that of **device a** of 2.4 Ω cm^2, this means **device b** causes less charge carrier recombination. This trend of Rp was quite well related with the diode rectification characteristics of each device which measured at ±2 V of J-V characteristic curve in the dark. **Device b** showed 2 order higher diode rectification characteristics than that of **device a** with the values of 961 and 9.16, respectively.

Ideal device is required the low Rs and the high Rp [7,8]. To meet these criteria, small portions of glycerol were added to **PEDOT AI4083** to reduce the resistivity of buffer layer and the Rs of devices

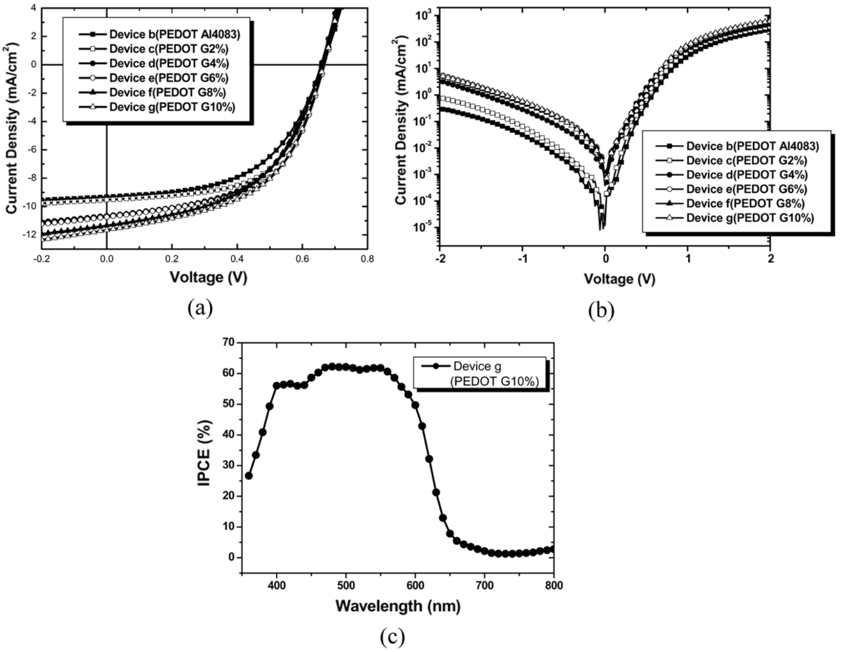
TABLE 1 Performance of P3HT:C$_{70}$-PCBM Devices Depend on Anode Buffer Layers Under a Simulated Photovoltaic Light with 100 mA/cm^2 Illumination (AM 1.5)

Device	Buffer layer (PEDOT)	Voc (V)	Jsc (mA/cm^2)	FF	PCE (%)	Rs^a (Ω cm^2)	Rp^a (10^3 Ω cm^2)	Diode characteristics^a	Resistivity^b (Ω cm)
a	P	0.66	10.87	0.56	4.00	2.2	2.4	9.16	6.29
b	AI4083	0.66	9.32	0.54	3.31	2.8	290.9	961	445.84
c	G2%	0.66	9.53	0.58	3.68	2.3	229.2	474	3.85
d	G4%	0.66	10.66	0.53	3.75	1.8	25.3	137	1.08
e	G6%	0.67	10.74	0.55	3.96	1.5	10.2	99	0.54
f	G8%	0.66	11.34	0.50	3.78	1.6	10.6	108	0.46
g	G10%	0.67	11.66	0.52	4.05	1.4	14.9	111	0.31

[a] Series resistance, parallel resistance, and diode rectification characteristics calculatied from the J-V curves in the dark.

[b] Measured from the thin film of each buffer layer with four-point probe.

by increasing the conductivity of PEDOT:PSS layer. **Device c**, **d**, **e**, **f**, and **g** were made with **PEDOT G2**%, **G4**%, **G6**%, **G8**%, and **G10**%, which were prepared by blending of **PEDOT AI4083** with 2, 4, 6, 8, and 10 wt% of glycerol, respectively. In the Table 1, it is found that the higher concentration of glycerol added, the lower the resistivities of PEDOT:PSS became as shown in Table 1. The current model for the structure of a PEDOT:PSS film is that it consists of polymer dispersion particles which have a PEDOT-PSS core surrounded by a PSS-rich shell. The core-shell nature of the polymer nanoparticles is likely to limit the conductivity as there will be a charge blocking layer, of insulating PSS, at the grain boundaries [13]. Glycerol act as a plasticizer, and the PEDOT-PSS core particles become swollen and aggregated each other to increases the interaction between PEDOT-PSS. The improved connectivity between conductive regions in the modified film renders much improved charge percolation pathways. By increasing portions of glycerol, FF turns to reduction over 4 wt% of glycerol, while Jsc improves gradually and Voc does not change any meaning value. Overall PCE increased until 6 wt% of glycerol concentrations after then it maintained at near 4.0% as shown in Table 1 and in Figure 2(a). The Rs is gradually reduced by adding glycerol till 4 wt% % of glycerol as expected, then maintains after that doping concentrations. In case of resistivity, it dropped rapidly till 4 wt% of glycerol, after then gradually decreased. The Rs and the resistivity of the devices over 4 wt% of glycerol (**device d-g**) are less than those of **device a** with **PEDOT P** as a buffer layer. The **device a** and **device c** have similar Rs's (2.2 $\Omega\,\text{cm}^2$ and 2.3 $\Omega\,\text{cm}^2$, respectively) and resistivities (6.29 Ω cm and 3.85 Ω cm, respectively), but **device c** has much higher Rp (229.2 $\Omega\,\text{cm}^2$) and diode rectification characteristics (474) than those of **device a** (2.4 $\Omega\,\text{cm}^2$ and 9.16, respectively). The low Rp and diode rectification characteristics of **device a** compared to **device c** is attributed to the low content of PSS in **PEDOT P** (PEDOT:PSS = 1:2.5) for **device a** than in **PEDOT AI4083** (PEDOT:PSS = 1:6) for **device c**. Excess PSS makes thicker insulating PSS layer at the surface of the PEDOT-PSS grains and this PSS layer prevents strong interaction between the heavily doped PEDOT film and the following layer (P3HT:C_{70}-PCBM film layer in this case) [14]. And Hwang *et al.* also found the work function was reduced by removing surface PSS layer on PEDOT:PSS film by sputtering [14]. Though the Rp and the diode rectification characteristics keep higher for the devices of glycerol doped buffer layers (**device c–g**) than **device a**, it is clear that the Rp and the diode rectification characteristics go down by increasing doping contents of glycerol. The added glycerol is disentangle PEDOT-PSS polymer grain and make better



(a) (b)

(c)

FIGURE 2 J-V characteristic curves of the P3HT:C_{70}-PCBM devices with buffer layers of **PEDOT AI4083** doped with different concentration of glycerol in under at 100 mA/cm^2 light illumination (AM 1.5) (a) and in the dark (b); and (c) for the incident photon-to-current conversion efficiency (IPCE) spectrum of **device g** with 10 wt% glycerol doped PEDOT.

mixing with outside non-PEDOT bounded PSS. This mixing and disentangle process reduced the relative PSS content on the surface of PEDOT:PSS film and that reduced surface PSS content decreased the work function of glycerol modified PEDOT:PSS film [13]. And this reduced work function increases the hole injection form active layer into PEDOT:PSS, but also reduces the electron blocking function, and reduces the Rp and the diode rectification characteristics. The reduced FF compensates the increased Jsc at the highly glycerol doped devices. The low FF may come from the lower Rp, which was induced by random leakage current in higher conductivity PEDOT:PSS layer. The excess glycerol would cause serious phase separation and more defects in the PEDOT:PSS, inducing leakage through the device [4]. When we made the device with 2 wt% doped Baytron P as a buffer layer, the resistivity dropped to 0.030 Ω cm, which was 200 times less than that of pristine Baytron P device. But this low resistivity causes the cross talk over the fabricated photovoltaic device and thus hinders the exact measurement of the active area, so we eliminate this experiment.

CONCLUSIONS

In this study, we studied the effect of the PEDOT:PSS ratio and the conductivity of buffer layers on the device performance of P3HT:C_{70}-PCBM photovoltaic cells. By increasing the glycerol doping to Baytron PVP AI4083, the short circuit current density (Jsc) was increase, while the fill factor turned to reduction by adding more than 4 wt% of glycerol. As a result the PCE was increased until 6 wt% of glycerol doping, after then it maintained at near 4.0%. Even though the series resistance and the resistivity of Baytron PVP AI4083 were enhanced to those of Baytron P through the doping of 2 wt% glycerol, the parallel resistance and the diode rectification characteristics were still keep 100 times higher values at doped Baytron PVP AI4083, which attributed to its higher PSS to PEDOT ratio.

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