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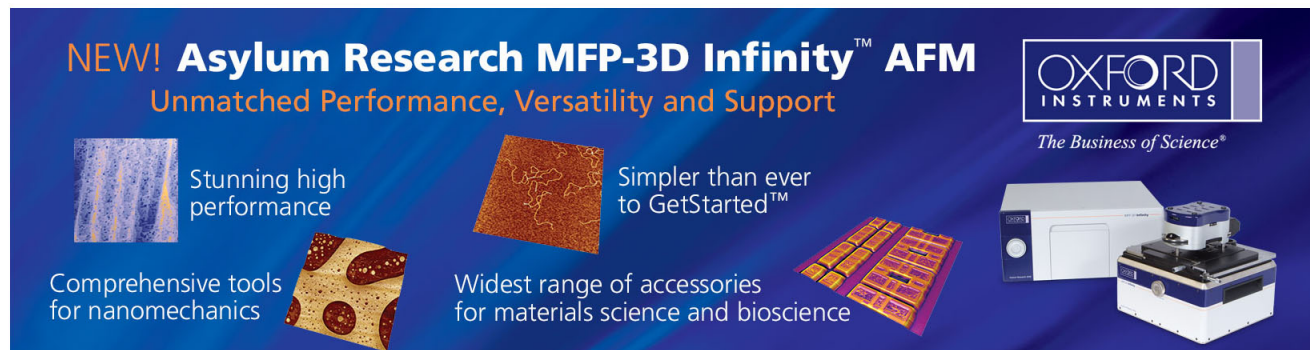
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Modified buffer layers for polymer photovoltaic devices

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The influence of anode buffer layers on the performance of polymer photovoltaic devices based on blends of poly(3-hexylthiophene) and [6,6]-phenyl-C-61-butyric acid methyl ester has been investigated. The buffer layers consist of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) doped with different concentrations of mannitol. Improved power conversion efficiency, up to 5.2%, has been observed by reducing the resistance of PEDOT:PSS after doping. One extrapolation method has been developed to exclude the resistance from the connection of the electrodes from the total device resistance. The results confirm that the device improvement is due to the reduction of series resistance of the PEDOT:PSS after the mannitol doping. © 2007 American Institute of Physics. [DOI: 10.1063/1.2437703]

Organic photovoltaic devices (PVs) have attracted considerable attention due to their potential for flexible, lightweight, and low-cost applications of solar energy conversion. Recently, the power conversion efficiency (PCE) of photovoltaic cells around 5% has been realized.^{1,2} In addition, through the optimization of the donor/acceptor energy levels, the efficiency up to 10% is expected from recent simulation results.³ In practice, a high shunt (parallel) resistance (R_{sh}) and a low series resistance (R_s) are required simultaneously for an ideal photovoltaic device.^{4,5} The R_{sh} usually reflects the degree of leakage current through the device, which relates to the overall quality of the films. Meanwhile, the R_s 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.^{5,6} Typically R_s decreases with the thickness of the active layer but increases when the operation temperature or the intensity of incident light becomes higher.⁷ Furthermore, it has been reported that the bulk resistance of the indium tin oxide (ITO) of the devices with an area larger than 0.01 cm² dominates the series resistance of organic PVs based on small molecules.⁶

To facilitate hole injection, higher work function materials are preferred as the anode of PVs. Thus, an extra interfacial layer, poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS), which has higher work function (5.2 eV),⁸ is usually applied to modify the surface of ITO (4.7 eV).⁹ On the other hand, Aernouts *et al.* indicated that an improper PEDOT:PSS layer will reduce the short-circuit current (I_{sc}) and fill factor (FF) owing to the increased series resistance.¹⁰ In addition, Zhang *et al.* reported that hole extraction from polymer PVs could be improved by doping polyalcohols into the PEDOT:PSS.^{11,12} Although it is well known that the conductivity of the doped

PEDOT:PSS increased over two orders of magnitude after doping with polyalcohols,¹² only few attempts so far have been made to study the significance of the bulk resistance of PEDOT:PSS in polymer PVs.

In this work, mannitol (Aldrich), a structure isomer of sorbitol, was doped into two kinds of PEDOT:PSS, Baytron® P [PEDOT-PSS(P)] and Baytron® PVP CH8000 [PEDOT-PSS(P)], with different resistivities (1 and $1 \times 10^5 \Omega \text{ cm}$), to evaluate the effect of the resistance of the doped PEDOT:PSS on the efficiency of the polymer PV. To fabricate the devices, PEDOT:PSS was firstly spin coated on the ultraviolet ozone treated ITO. After annealing the PEDOT:PSS film at 140 °C for 1 h, the active layer poly(3-hexylthiophene) P3HT (Rieke Met. Inc.) and [6,6]-phenyl-C-61-butyric acid methyl ester PCBM (Nano-C) (1:1 in weight ratio) were then spin coated from 1,2-dichlorobenzene to form a $205 \pm 10 \text{ nm}$ thin film. The prepared organic film was then treated following the so-called solvent annealing procedures as described in Ref. 2. Finally, Ca and Al electrodes were deposited via thermal evaporation at the cathode. The active area of the device is 0.12 cm². The resistivity of PEDOT:PSS was measured by four-point probe station (Napson, RT-80). The current-density–voltage (J - V) curves were measured by a Keithley 2400 source-measure unit. The photocurrent was obtained under illumination from a Thermal Oriel solar simulator (AM1.5G). The illumination intensity used was calibrated by a standard Si photodiode detector with KG-5 filter (Hamamatsu, Inc.). The calibration method based on IEC-69094-1 spectrum followed the procedures described in Ref. 13.

Figure 1(a) shows the J - V characteristics of the devices under illumination (100 mW/cm²), with different doping concentrations of mannitol in the PEDOT-PSS(EL). The device with pristine PEDOT:PSS(EL) shows poor performance with open-circuit voltage (V_{oc})=0.53 V, short-circuit current density (J_{sc})=1.17 mA/cm², and FF=26.8%. The calculated

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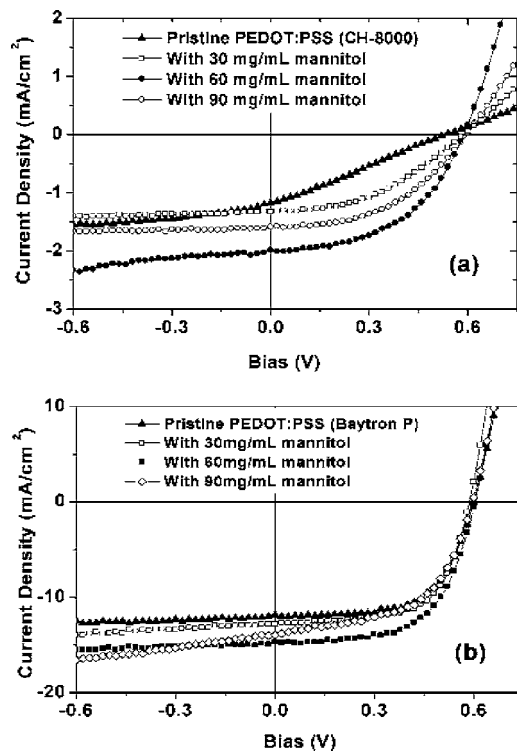


FIG. 1. Current/voltage characteristics of polymer PVs with different concentration of mannitol-doped anodes: without doping (\blacktriangle); with 30 mg/ml doping (\square); with 60 mg/ml doping (\bullet); and with 90 mg/ml doping (\circ) in (a) low conductivity, 10^{-5} S/cm, and (b) high conductivity, 1 S/cm, PEDOT:PSS. All device were measured under illumination of AM1.5 (100 mW/cm^2).

PCE is equal to 0.17%. On the other hand, after doping of mannitol (30 mg/ml), the J_{sc} and FF both increased and, thus, the PCE also increased to 0.34%. After further increasing the doping concentration to 60 mg/ml, the J_{sc} and FF reached 1.33 mA/cm^2 and 42.8%, respectively. However, the efficiencies slightly decreased after doping with 90 mg/ml mannitol. It is worthy to note that the FF is relatively low, 26.8%, for the device with pristine PEDOT:PSS(EL), implying a higher series resistance and a lower shunt resistance. After modification with mannitol, the FF was improved to nearly 50%,¹⁴ indicating that the series and/or the shunt resistance have been improved. The improvement of the device performance could be due to the reduction of the resistance of the PEDOT:PSS upon the doping of mannitol, leading to a decrease of the device R_s . In addition, it has also been suggested that the increase of series resistance will reduce the effective internal electric field in the active layer, which is essential for efficient charge collection to the electrodes from an organic photovoltaic model.¹⁵ Consequently, the device efficiency will be lower.¹⁵

Since the resistance of PEDOT:PSS has been proven to be one of the issues in polymer PVs, highly conducting PEDOT:PSS(P) doped with mannitol was used instead as the buffer layer for the PVs to further improve the performance [Fig. 1(b)]. With 60 mg/ml of mannitol added, the device exhibits pronounced improvement with $J_{sc}=14.7 \text{ mA/cm}^2$ and FF=60.1%, while V_{oc} remains nearly constant at 0.59 V. The corresponding PCE is 5.2%, which is among the highest values reported in organic solar cells. On the other hand, the efficiency decreased after doping with 90 mg/ml mannitol due to a relative low FF. The lower FF may come from the

TABLE I. Performance of ITO/PEDOT:PSS(P)/P3HT:PCBM/Ca/Al photovoltaic devices with different concentration of mannitol under illumination of AM1.5 (100 mW/cm^2).

Anode	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	R_s^a ($\Omega \text{ cm}^2$)	Resistivity ^b ($\Omega \text{ cm}$)
Pristine PEDOT:PSS	0.60	12.0	63.4	4.5	1.90	20.29
30 mg/ml mannitol in PEDOT:PSS	0.59	13.1	63.2	4.9	1.42	3.72
60 mg/ml mannitol in PEDOT:PSS	0.59	14.7	60.1	5.2	1.29	0.53
90 mg/ml mannitol in PEDOT:PSS	0.59	13.8	55.2	4.5	1.01	0.16

^aCalculated from the I - V curves in the dark.

^bMeasured from the four-point probe.

lower shunt resistance, which was induced by random leakage current in higher conductivity PEDOT:PSS layer. The excess mannitol would cause serious phase separation and more defects in the PEDOT:PSS, inducing leakage through the device. A summary of the device performance using PEDOT:PSS(P) is shown in Table I. In the table, it is found that the higher concentration of polyalcohol presented, the lower the resistivities of PEDOT:PSS became. Meanwhile, the R_s is decreased as predicted. Accordingly, the resistivity of PEDOT:PSS influences the entire device efficiency.

Previously, different PEDOT:PSS have been used as the buffer layers of the polymer PVs.¹² The active layer was polyfluorene copolymer blended with PCBM. In that cases, it was found that the short-circuit current increased with the high conductivity of the buffer layer, but the V_{oc} and the FF decreased. On the other hand, in our cases, the decreases of V_{oc} and FF were not apparent owing to the sufficiently high shunt resistance, thus improving the PCE overall. It is probably due to the fact that the concentration of the dopants is optimized, and the numbers of defects and leakage paths of the semiconducting layer (P3HT:PCBM) are much lower.

To further investigate the effect of the doping on the R_s and R_{sh} of the device, the J - V characteristics of these solar cells with different modified anodes were measured in the dark (Fig. 2). As shown in Fig. 2(a), at reverse (negative) bias and at the linear regime of forward bias, where the current is limited by R_{sh} due to the leakage current, the current gradually increased with the dopant concentration. The increasing current with doping concentration further supports that the excess mannitol causes the device leakage. On the

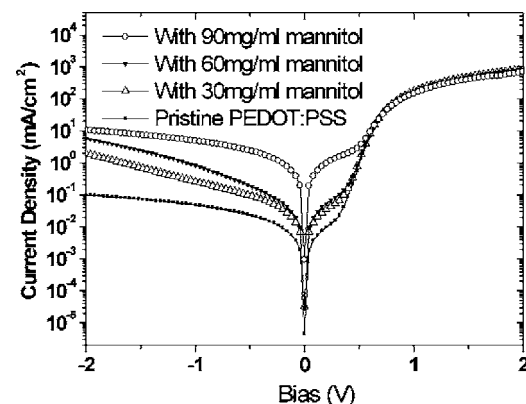


FIG. 2. Current/voltage characteristics with different concentrations of mannitol. All devices were measured in the dark.

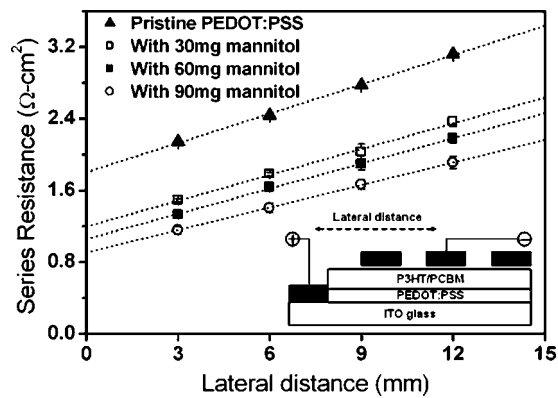


FIG. 3. Series resistance R_s as function of the lateral distance between the anode and the cathode in different doping concentrations; without doping (\blacktriangle), with 30 mg/ml doping (\square), with 60 mg/ml doping (\bullet), and with 90 mg/ml doping (\circ). Inset: the device structure and the definition of the lateral distance.

other hand, in the space charge limited current region (>1 V), the current slightly increased because of the lower series resistance upon doping.¹⁶

Technically, major contributions to the R_s include the bulk resistance ($R_{s,bulk}$) and the contact resistance ($R_{s,contact}$). The $R_{s,contact}$ originates from the interface between the electrodes and the active layer; the $R_{s,bulk}$ comes from the bulk resistance of organic layers (P3HT:PCBM blends and PEDOT:PSS) and electrodes (ITO and cathode metals). However, it has been reported that the ITO resistance contributes to the R_s seriously in the device with the area larger than 0.01 cm².⁶ Consequently, the resistance coming from the connection of the ITO anode should be considered as well for the large-area devices. In our cases, expect the P3HT:PCBM, the large area of ITO may also significantly contribute to the $R_{s,bulk}$. Furthermore, considering that the modified PEDOT:PSS is highly conductive, it is interesting to see if the modified “anode structure,” consisting of both ITO and modified PEDOT:PSS, could reduce the overall device resistance by reducing the surface resistance. To further understand how the doping of mannitol affects the resistance, the devices with different lateral distances between the anodes and the cathodes have been fabricated, as shown in the inset of Fig. 3. The lateral distance is defined as the separation between the centers of the anode and the cathode. From the Fig. 3, it can be seen that the total series resistance of the whole devices increases with the increasing lateral distance, suggesting that the surface/sheet resistance of ITO electrodes indeed contributed seriously to the total device resistance. Furthermore, Fig. 3 also reveals that the R_s decreased with increasing concentration of mannitol. The extrapolations of the fitting curves while the lateral distance equals to zero gives the net resistance $R_{s,net}$, excluding the resistances of the cathode and the anode in the lateral direction. Consequently, $R_{s,net}$ should be independent of the geometry design of the device, since the resistance from the connections has been removed. The calculated $R_{s,net}$ is 1.841 Ω cm² for pristine PEDOT:PSS. In contrast, with the higher doping concentration into PEDOT:PSS(P), $R_{s,net}$ falls to 1.197 , 1.024 , and 0.873 Ω cm² while doping 30, 60, and 90 mg/ml mannitol, respectively. On the other hand, the slopes in the four differ-

ent series of devices with different mannitol concentrations are almost identical, indicating the fact that the resistance in the lateral direction, which may be contributed from both ITO and PEDOT:PSS, is uniform. In other words, the value of lateral/sheet resistance only strongly depends on the ITO conducting area but depends weakly on the kinds of the PEDOT:PSS used, since the conductivity of ITO is much higher than that of PEDOT:PSS thin films. It suggests that the doping of PEDOT:PSS mainly affects significantly the series resistance only in the “vertical” direction (the inset of Fig. 3).

The other possible reason for the enhanced efficiency comes from the increase of the device area. However, in our devices, the pattern of PEDOT:PSS is identical to that of ITO. Consequently, the effective area remains the same even after the conductivity enhancement of PEDOT:PSS. In addition, the organic layers were further patterned by carefully scratching a trench between devices, which means that the surface conduction in this layer was no longer possible. However, similar device characteristics were still observed, indicating that the enhanced efficiency is not due to the increase of the area of the device.

In conclusion, the efficiency of polymer PVs has been improved by reducing the device series resistance by doping PEDOT:PSS with mannitol. From this study, it has been realized that the conductivity of PEDOT:PSS plays an important role in the polymer solar cells. Not only the bulk resistance of the active film (P3HT:PCBM) should be concerned, but the chosen of high-conducting PEDOT:PSS is also of importance to develop organic photovoltaic devices with high efficiency.

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