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Investigation of buffer layer modified by doping glycerol for polymer photovoltaic devices

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1. Introduction

Organic photovoltaic devices (OPVs) have attracted considerable attention due to their potential for flexible, lightweight, and low-cost application of solar energy conversion. Bulk heterojunction organic photovoltaic devices (OPVs) have recently been intensively investigated with a view to increasing their efficiency.[1-4] One of the most studied system is regioregular-poly(3-heylthiophene-2,5-diyl) (P3HT) blended with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM). The power conversion efficiency observed from P3HT : PCBM solar cells reaches 3%-5% in different institutions.[5-8] Another studied system is surface treatment of electrode including oxidation, the addition of a self-assembled layer, [9,10] or poly(3,4-ethylene dioxythiophene) (PEDOT): poly(styrene-sulfonate) (PSS) layer insertion[11] that can lower or raise the work functions of cathodes and anodes, or enhance the cohesion, and thus lower the interfacial series resistance(R_s). In practice, a low series resistance (R_s) is required simultaneously for an ideal photovoltaic device. The R_s is attributed to the Ohmic loss in the whole device, which includes the resistance of the active layer, metal-organic contacts. Nevertheless, an improper PEDOT:PSS layer will reduce the short-circuit current (I_{sc}) and fill factor (FF) owing to the increased series resistance.[12] Although it is well known that the conductivity of PEDOT:PSS increased over two orders of magnitude after doping with polyalcohols,[13] 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, aiming for improvement of the conductivity and hence the performance of OPVs, we modified PEDOT : PSS buffer layer by doping glycerol. Although the similar study that doping sorbitol in PEDOT:PSS has been reported,[13] we reported more sufficient and detail issues to demonstrate the improvement of PEDOT:PSS film quality and performance of OPVs. We discussed the interface between PEDOT:PSS film and P3HT:PCBM active layer by using atomic force microscopy (AFM) measurement.

2. Experiments

The inset of Fig. 1 schematically depicts the device configuration and the molecule structures we used in this work. The entire structure is described as glass /indium-tin-oxide (ITO) /PEDOT:PSS (+glycerol) /P3HT:PCBM /aluminum (Al). For modification of PEDOT:PSS film, glycerol was doped into PEDOT:PSS solution (Bayerton P VP A1 4083) and then stirred for at least 24 h. To fabricate devices, the PEDOT:PSS was first spin-coated onto the ultraviolet ozone treated ITO/glass (RITEK Corp., $15\Omega/\Box$) at 4000 rpm for 60 s and then

baked at 150°C for 30 min. Regioregular P3HT (98.5% electric grad, Rieke Metals, Inc.) was blended with PCBM (Nano-C, Inc.) and then dissolved in 1,2-o-dichlorobenzene to yield a P3HT:PCBM (1:1 in weight ratio) solution. The blend solution was stirred for at least 24 h at 40 °C. The P3HT:PCBM active layer was obtained by so-called solvent annealing procedure as described in Ref. 14. After spin-coating P3HT:PCBM solution onto PEDOT:PSS layer at 600 rpm for 60 s, the samples were then transferred to the Petri glass dishes that had been filled with a saturated vapour of 1,2-o-dichlorobenzene and maintained wet for 2 h. Calcium (Ca) (60nm) and Aluminium (Al) (150 nm) were thermally deposited onto the surface of the P3HT:PSS film inside a vacuum chamber (1x10⁻⁶ Torr) as the device cathode. All the procedure are implemented inside a nitrogen-filled glove box except for coating the PEDOT: PSS layer. The active area of the device is 1 mm². Current-voltage (J-V) characteristics of the completed devices were measured using a keithley 2400 sourcemeter under 90 mW/cm² white light illumination (Oriel 96500 150 W solar simulator equipped with an AM 1.5 G filter) through the ITO/glass side. The surface morphology of the films is studied by AFM (Digital Instrument Nanoscope IIIa).



Fig. 1.Device structure and molecule structures we used in this work

3. Results and discussion

Figure 2 shows the *J*-V characteristics curves of the polymer photovoltaic devices with different-concentration modified buffer layer. The most optimum concentration was 30 mg/ml. The short-circuit current density (J_{sc}) of the reference device was 8.43 mA/cm² and the open-circuit voltage (V_{oc}) was 0.6 V; the fill factor (*FF*) was 0.67. According to formula $\eta_e = (I_{sc}V_{oc}FF)/P_{in}$, the value of power conversion efficiency (PCE) (η) calculated from the obtained data was equal to 3.37 %.[15] Compared with the device made from neat PEDOT:PSS, incorporation of glycerol into PEDOT:PSS buffer layer led to improvement of PCE. The most optimum concentration was 30 mg/ml; the PCE and J_{sc} were 4.27 % and 10.46 mA/cm², respectively, on this concentration. However, the variation of *FF* was not conspicuous while doping glycerol into

PEDOT:PSS with different concentration.



One may wonder why the performance increased conspicuously while PEDOT:PSS buffer layer was modified by glycerol. First of all, we conferred the effect of the conductivity of glycerol-PEDOT:PSS film on the device performance. Fig. 3 shows the conductivity of the devices with different glycerol-concentration modification. From this figure, it was found that the conductivity of PEDOT:PSS film increases with the increase of the concentration of glycerol doped into PEDOT:PSS. However, with the increase of the concentration, we also found that the morphologies of PEDOT:PSS films have become rough. The rougher morphologies would influence the growth quality of P3HT:PCBM active layer and the leakage current of the devices.



Figure 3 Conductivity of the PEDOT:PSS film modified with different concentration of glycerol and roughness of the opposite concentration PEDOT:PSS surface.

Fig. 4 presents the J-V characteristics curves of the devices with different glycerol-concentration modification under the dark. At the negative bias and the linear regime of forward, as shown in Fig. 3, where the current is limited by shunt (parallel) resistance (R_{sh}) due to the leakage current, the current gradually increased with doping concentration. The increasing current with doping concentration further supports that the excess glycerol caused that the device leakage.[16] This is reason why the electric performance was not relatively improved with the increase of the concentration.



Fig. 5 shows the electric hysteresis curves of the devices with different glycerol-concentration modification. After measuring the black curve from -2 to 2 V, the red curve was measured from 2 to -2V continuously. The red and black curves will be over-lapped together on the ideal device. If these curves were not over-lapped together, it presented that there were many defects in the device which can catch the carriers transmit through the device. The

caught carriers would form the space charges that hinder the transmission of the carriers generated in P3HT:PCBM active layer. From this figure, we can find that glycerol can improve the defects of PEDOT:PSS film.



Electric hysteresis characteristics of the devices without doping glycerol. Inset is hysteresis characteristics of the devices with doping glycerol.

4. Conclusion

The modification of the PEDOT:PSS film by doping glycerol indeed enhances the conductivity of the film, and then improves the performance of OPVs. The best power conversion efficiency value we obtained was 4.27% after modifying PEDOT:PSS film. Nevertheless, with the increase of concentration, the quality of the PEDOT:PSS morphologies became rougher. The effect would influence the device leakage current. This is reason why the electric performance was not relatively improved with the increase of the concentration. We also found that the defects of PEDOT:PSS film were improved by doping glycerol into PEDOT:PSS. For fabricating high power-conversionefficiency polymer photovoltaic devices, this is an excellent method that doping polyalcohols into PEDOT:PSS to improve the conductivity of the film. At the same time, glycerol will be a good candidate for polymer photovoltaic device.

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