Polymer solar cells based on a PEDOT:PSS layer spin-coated under the action of an electric field*

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In the process of fabrication of polymer photovoltaic (PV) devices, poly (3, 4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) thin film, acting as an anode buffer layer, is spin-coated under the action of an electric field. The PV devices with a PEDOT:PSS layer spin-coated under the action of a static electric field exhibit improved short-circuit current density (J_{sc}) and power conversion efficiency (PCE). The investigation of morphology shows that the appropriate intensity of the electric field can increase the roughness of the surface of the PEDOT:PSS layer, which results in improved contact between the anode and hole transport layer and thus enhances the J_{sc} of the devices. Chemical analysis is also provided by x-ray photoelectron spectroscopy (XPS) spectra.

Keywords: polymer solar cell, photovoltaic, spin-coating under electric field
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1. Introduction

Poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) is one of the most commonly used anode buffer layers for both organic light-emitting diodes (OLEDs)[1−3] and organic photovoltaic (PV) devices.[4−6] The popularity is due to its many advantageous properties such as high work function, high stability in its p-doped form, high conductivity, good film-forming properties and good transparency.[7−9]

PEDOT:PSS is a blend of oxidatively doped, cationic, conducting polythiophene derivative PEDOT and PSS polyanion.[9] The molecular structures of PEDOT and PSS are shown in Fig.1. When the PEDOT:PSS dispersion is coated onto a substrate, a thin polymer film is formed with a vertical phase segregate,[9−11] consisting of PEDOT:PSS grains surrounded by a shell formed by excess PSS.[8−10] It is noted that the core-shell structure of the PEDOT:PSS grains is likely to limit the conductivity as there is a charge blocking layer of insulating PSS at the grain boundaries.[10] Several approaches to the modification of PEDOT:PSS films have been reported, including mixing with organic solvents,[8,10,12−15] treating with mild oxygen plasma[1,2] and ultraviolet-ozone,[16] and using a light sputtering method.[17] These approaches can effectively enhance the conductivity of the PEDOT:PSS layer.

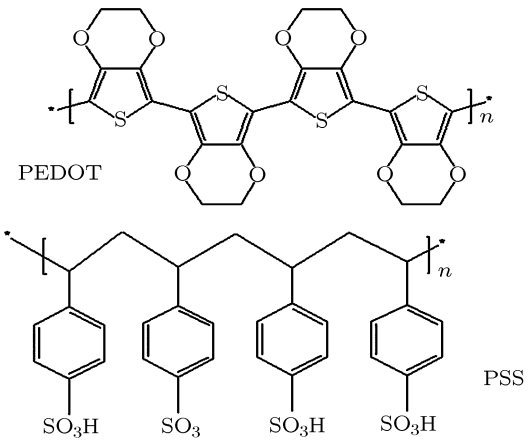


Fig. 1. The chemical structures of PEDOT and PSS.

In the present work, the technique of spin-casting PEDOT:PSS under the action of a vertical elec-

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tric field is developed and used to fabricate polymer PV devices based on poly(3-hexylthiophene): [6, 6]-phenyl C_{61}-butyric acid methyl ester (P3HT:PCBM) composites. The resulting devices exhibit improved photovoltaic properties.

2. Experiment

In our experiment, a common structure of ITO/PEDOT:PSS/P3HT:PCBM/Al is used. Here the PEDOT:PSS layer was fabricated by spin-coating under the action of a vertical electric field applied to the indium–tin oxide (ITO) substrate. Figure 2 shows cross-sectional views of the experimental setup for the application of the electric field during the spin-coating of PEDOT:PSS. The distance from the anode to ITO glass substrate was about 0.5 cm. The process of PEDOT:PSS formation could be divided into 3 steps. The first step is to place ITO glass substrates on the spin-coating platform and drop the PEDOT:PSS solution on the ITO substrates; the second step is to apply an electric field to the substrate for 1 min, where the direction of the electric field is perpendicular to the substrate surface; the third step is to spin-cast the sample to obtain a PEDOT:PSS film under the electric field. All the samples were dried at 80 °C for 5 min, and then annealed at 150 °C for 30 min in ambient condition. A blend of P3HT and PCBM was used as an active layer. P3HT and PCBM were dissolved into chlorobenzene in a weight ratio of 1:1, and the concentration of P3HT was 15 mg/ml. The solution was dropped on the top of the substrates with PEDOT:PSS, forming an active layer with a thickness of around 100 nm. Finally, a 3×3 mm^2 Al cathode was deposited through a shadow mask on top of the active layer by thermal evaporation in a vacuum lower than 1.333×10^{-3} Pa.

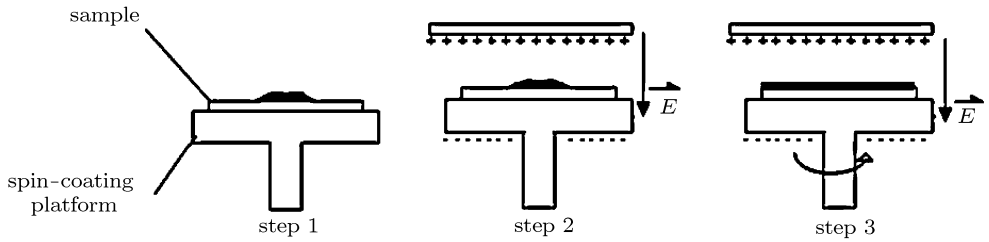


Fig. 2. The cross-sectional views of the experimental setup for the application of the electric field during the spin-coating of PEDOT:PSS.

All devices were illuminated through ITO electrodes. A forward bias was defined as positive voltage applied to the ITO electrode. Photocurrent–voltage curves were recorded by a Keithley 2410 Source Measure Unit under illumination. A xenon lamp with an illumination intensity of 55 mW/cm^2 was used as an illumination source. The atomic force microscopy (AFM) spectrum was measured by Digital Instruments Nanoscope IIIa. The x-ray photoelectron spectroscopy (XPS) spectrum was performed by a MKII spectrometer.

3. Results and discussion

Figure 3 shows the photocurrent–voltage (I–V) curves of the devices with PEDOT:PSS films fabricated under different intensities of electric fields. The devices with PEDOT:PSS fabricated under electric

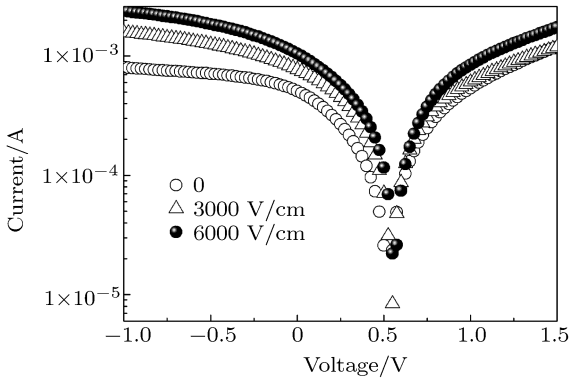


Fig. 3. Photocurrent-voltage (I–V) characteristics of the ITO/PEDOT:PSS/P3HT:PCBM/Al devices with PEDOT:PSS films fabricated under different intensities of electric fields.

field exhibit an improved short-circuit current density (J_{sc}). When the film was spin-coated under an electric field of 6×10^3 V/cm is used, the device shows that the open-circuit voltage (V_{oc}) is 0.5625 V, the J_{sc} is 11.7 mA/cm^2, the fill factor (FF) is 0.245, and the power conversion efficiency (PCE) is 2.93% under an illumination intensity of 55 mW/cm^2 (as summarised in Table 1). Both the J_{sc} and the PCE (η) are enhanced by a factor of 2 compared with those of the reference device which contains a PEDOT:PSS layer spin-coated under no action of electric field.

Table 1. Photovoltaic performances under illumination intensity of 55 mW/cm^2 for ITO/PEDOT:PSS/P3HT:PCBM/Al devices with PEDOT:PSS films fabricated under different intensities of electric fields (0, 3×10^3 and 6×10^3 V/cm).

E/(V/cm)	J_{sc}/(mA/cm^2)	V_{oc}/V	FF	η/%
0	5.66	0.538	0.245	1.35
3×10^3	8.75	0.55	0.268	2.30
6×10^3	11.7	0.563	0.245	2.93

As mentioned in the introduction, PEDOT:PSS is a blend of an oxidatively doped, cationic, conducting polythiophene derivative PEDOT and a PSS polyanion. It should be noted that PSS has a net negative charge while PEDOT has a net positive charge.[10] During the PEDOT:PSS fabrication, a perpendicular electric field applied to the substrate allows PSS to move to the top of the solution drop, and the PEDOT chains to move to the bottom. Therefore, the PEDOT and PSS particles redistribute in the solution drop under the action of electric field, creating a gradient of PSS concentration in the solution drop. When the platform of the spin-coater begins to rotate under the action of electric field, part of the PSS particles will be swung away with the solvent due to the centrifugal effect, leading to a surface enriched in PEDOT.

As is well known, both PEDOT and PSS contain sulfur atoms. The S(2p) level shows large differences in binding energy depending on the S location, which is suitable for the composition analysis of the sample. A low binding energy peak (∼164 eV) corresponds to PEDOT and a high binding energy peak (∼168 eV) comes from PSS.[8,18] The S(2p) core level spectra of PEDOT:PSS fabricated under no action of electric field and under the action of a 6×10^3 V/cm electric field are depicted in Figs. 4(a) and 4(b) respectively. The spectra reveal the information about S(2p) from the surface (less than 3 nm) of the PEDOT:PSS thin film. In our experiment, the content of PEDOT sulfur in the thin films is lower than that required by the measurement accuracy of the spectrometer, only the S(2p) core level features originating from PSS sulfur are obtained via XPS spectra. From the spectra in Fig. 4, the area is about 1157.2 (arb. units) for PEDOT:PSS formed under no action of electric field, and 896.7 (arb. units) for that formed under the action of a 6×10^3 V/cm electric field. It can be concluded that the content of PSS is reduced under the action of electric field during spin-coating. In other words, the ratio of PEDOT to PSS in the surface of the thin film spin-coated under electric field is increased.

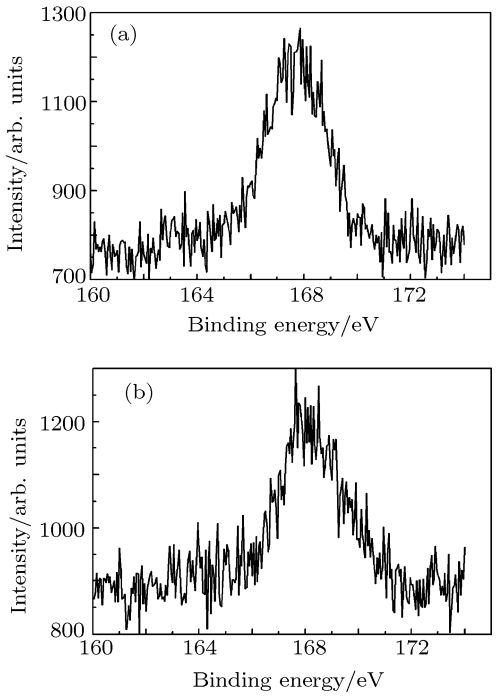


Fig. 4. S(2p) core level spectra of PEDOT:PSS fabricated under no action of electric field (a) and under the action of a 6×10^3 V/cm electric field (b).

Generally, the surface of PEDOT:PSS films is PSS-rich compared with the bulk,[8−10] and the ratio of PEDOT to PSS in the film surface strongly affects the electrical conductivity and sheet resistance of the thin film.[8,10,17] A larger PEDOT content offers higher electrical conductivity since PEDOT is the charge transporting species.[8,17] As analysed before, the PSS particles redistribute under the action of electric field, which might cause more PSS particles to sweep away with the solvent, due to the centrifugal effect, than those in the case of using the thin film spin-coated under no action of electric field. The increased ratio of PEDOT to PSS in the surface region of the thin film results in an increase of the volume fraction of the conductive regions, creating a better

connection between the conducting PEDOT:PSS particles/grains and hence a better pathway for charge transport.[8,11,17]

AFM images of the PEDOT:PSS films are shown in Fig. 5. The surface of the PEDOT:PSS layer spin-coated without the action of electric field applied is smooth with a root mean square (RMS) roughness of 0.86 nm. However, when spin-coated in the presence of electric field, the surface of the PEDOT:PSS layer becomes rougher, and the values of RMS roughness increase to 0.95 and 1.01 nm for the PEDOT:PSS thin films fabricated under the actions of 3×10^3 and 6×10^3 V/cm electric fields, respectively. The change in the morphology can improve the contact between the PEDOT:PSS layer and the hole transport layer, leading to the enhancement of J_{sc} of the PV devices.

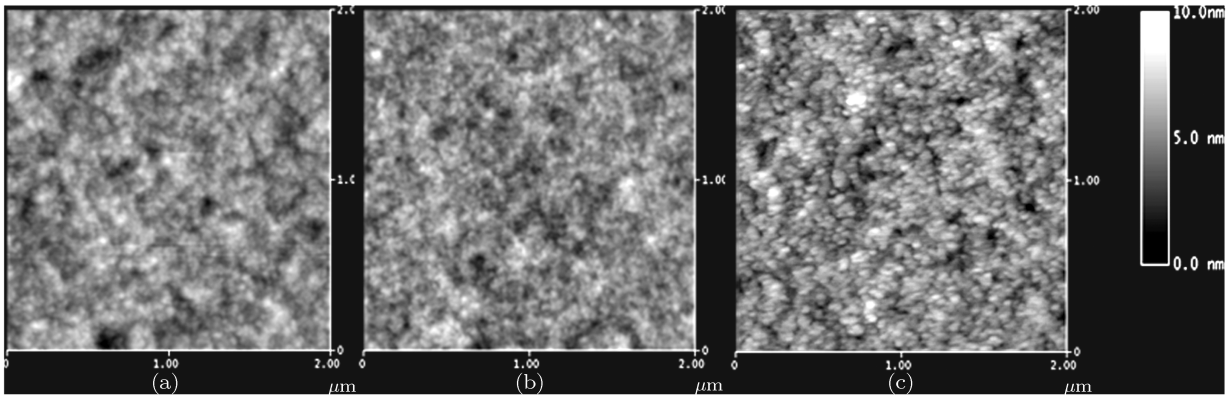


Fig. 5. AFM images of morphology of PEDOT: PSS layers fabricated under zero (a), 3×10^3 V/cm (b) and 6×10^3 V/cm (c) electric field.

4. Conclusion

The application of an electric field during the spin-coating of PEDOT:PSS thin films can change the distribution of PEDOT and PSS in the thin film, and lead to the increase of the ratio of PEDOT to PSS in the surface of the thin film, which then results in the improvement of the conductivity of the PEDOT:PSS thin film. Also, the surface of the thin film becomes rougher, which may improve the contact between the PEDOT:PSS layer and the hole transport layer. Both the increase of the conductivity of the PEDOT:PSS thin film and the improvement of the contact between the PEDOT:PSS layer and the hole transport layer lead to dramatically enhanced J_{sc} of the PV devices. The devices with PEDOT:PSS layer spin-coated under the action of a 6×10^3 V/cm electric field exhibit enhanced J_{sc} and η, which are 2.1 and 2.2 times those of the reference device, respectively. The results suggest that spin-coating PEDOT:PSS under an electric field can be a useful approach to the improvement of the properties of PV devices and OLEDs as well.

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