Effect of electrode geometry on photovoltaic performance of polymer solar cells

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Abstract

This paper investigates the impact of electrode geometry on the performance of polymer solar cells (PSCs). The negative electrodes with equal area (0.09 cm\(^2\)) but different shape (round, oval, square and triangular) are evaluated with respect to short-circuit current density, open-circuit voltage, fill factor and power conversion efficiency of PSCs. The results show that the device with round electrodes gives the best photovoltaic performance; in contrast, the device with triangular electrodes reveals the worst properties. A maximum of almost a 19% increase in power conversion efficiency with a round electrode is obtained in the devices compared with that of the triangular electrode. To conclude, the electrode boundary curvature has a significant impact on the performance of PSCs. The larger curvature, i.e. sharper electrodes edges, perhaps has a negative effect on exciton separation and carrier transport in photoelectric conversion processes.

Keywords: polymer solar cell, P3HT:PCBM, electrode geometry, electric field distribution, electrode curvature

(Some figures may appear in colour only in the online journal)

1. Introduction

Development of new energy sources is gaining importance and has become an issue of common concern. Because solar energy is environmentally-friendly energy, its utilization is being investigated intensively by many researchers and is supported by many governments. The effective use of solar energy has become a very active research field, especially in the field of solar cells. Polymer solar cells (PSCs) represent one of the most popular research topics because of their numerous advantages such as being lightweight, ecofriendly, mechanically flexible and yielding low-cost production of electronic devices. The performance of PSCs significantly improved in the 1990s itself because of the introduction of bulk heterojunction structures. Recent advances indicate that the power conversion efficiency (PCE) of PSCs has been greatly advanced to reach a level of 9% [1–3].

The most representative research on bulk heterojunction PSCs is based on poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM) with the corresponding PCE up to 5% . Many researchers have been using different production processes and device structures to improve PCE, such as spin coating, dripping, inkjet printing and vacuum deposition. So far, some effective achievements have been obtained. These developments are reflected in the active layer, buffer layer, electrode materials, production process and changes in the cell structure [4–7], among others. In addition to the conventional structure of solar cells, researchers have also introduced inverted and tandem structures to further improve the PCE with promising results [8, 9].
Electrode materials and processes are the main factors in cell fabrication. In recent years, research in these areas has become of widespread concern [10–12]. However, there are only a few studies on the influence of electrode geometry on cell performance [13, 14]. The authors discussed the crossbar-type electrode geometry and island-type electrode geometry of PSCs. They concluded that the performance of the island-type is better than that of the crossbar-type because the electrode edge plays an obvious effect on determining the efficiency of PSCs. A series of works on optimizing the electrode geometry of dye-sensitized solar cells have also been reported [15–17]; they discussed the effect of mesoporous TiO2 electrode geometry on photovoltaic parameters of dye-sensitized solar cells (DSSCs). Generally, for PSCs, a rectangle is the common shape of PSC electrodes. In an organic photoelectric conversion process, the separated excitons, i.e. the earlier generated charge carriers will gather on the electrode to build an electric field (BEF). For the coming carriers, exciton generation and separation, as well as carrier distribution and transmission, will be affected by the earlier BEF. Therefore, the electrode geometry and boundary which can determine the BEF are the key factors for determining the distribution of excitons and carriers and hence the influence on the performance of PSCs.

In this work, four kinds of shapes of PSCs- round, oval, square and triangle patterned are fabricated by the evaporation of negative electrodes with the same area (0.09 cm²) and are evaluated. By analysing the physical mechanism by which the electrode geometry affects the electric-field distribution in the cells, a novel influencing factor of the electrode on the performance of PSCs is discussed. We hope this work might provide some useful reference for further realizing the physical mechanism of the carrier transport process inside the active layer of PSCs.

2. Experiment

2.1. Experimental materials

Regioregular active materials P3HT and PCBM were purchased from Luminescence Technology Corp. and Solenne BV. As an aqueous dispersion Poly(3,4-ethy-lenedioxythiophene): poly(4-styrenesulfonate) (PEDOT: PSS) was purchased from Bayer AG (CLEVIOS™ P VP Al 4083). All the chemicals were used as received without further purification. The indium tin oxide (ITO) substrate with a sheet resistance of average 15 Ω/square and transmission of 85% was purchased from Kaivo.

2.2. Device fabrication and measurement

In the experiment, the ITO substrate was cut into 1.8 × 1.8 cm chips. Four kinds of cells were produced on one substrate so as to ensure the devices of different geometry having the same preparation conditions. In order to eliminate the disturbance caused from uncertainties, the simplest cell structure, Glass/ITO/PEDOT:PSS/P3HT: PCBM/LiF/Al, was employed in the experiment. The schematic structure of the PSC device is shown in figure 1(a).

Because the etching process of the ITO anode easily results in a concave and convex defect of the electrode edge, firstly the active and buffer layer are straightly spin coated onto the ITO substrate. Then, the cathode is evaporated on the active layer using a mask with equal area but different shape (round, oval, square and triangular). In addition to the electrode being evaporated in vacuum, the other production processes, including the current voltage (J-V) measurement, were manufactured in an atmosphere environment.

The specific processes and condition parameters adopted in this work are listed as follows.

Substrate cleaning: aqueous detergent/deionized water/acetone/alcohol/deionized water (10 min for each process, at 30 °C, in an ultrasonic basin). The cleaned substrates were dried in air.

Preparation of the active layer solution: P3HT 10 mg, PCBM 9 mg, 1, 2-dichlorobenzene 1 mL are mixed and stirred at 60 °C for 24 h.

Film preparation and thickness measurement: spin coater (Laurell WS-400), step profiler (Veeco Dektak 150). PEDOT: PSS spin coating (thickness: ∼ 50 nm): 1500 rpm 15 s/3000 rpm 30 s/110 °C annealed for 10 min (in air). Spin coating of the active layer (thickness: ∼ 180 nm): 500 rpm 15 s/700 rpm 30 s/110 °C annealed for 10 min (in air).

Evaporation electrode: thermal evaporation deposition (Maikenuo UNILAB-2000), vacuum 5 × 10⁻⁴ Pa. LiF evaporation (thickness: ∼ 0.8 nm)/99.99% Lithium Fluoride. The rate of evaporation of LiF is 0.01 nm s⁻¹. Al electrode evaporation (thickness: ∼ 100 nm): 0.09 cm² pattern mask (Four kinds of shapes)/99.995% Aluminum. The rate of evaporation of Al is 0.09 nm s⁻¹.

Figure 1. Schematic structure of the (a) PSC device, (b) accumulation of charge near the cell corner and (c) accumulation of charge around the sharp corners.
Solar simulator: 1000 W Xenon lamp, AM 1.5 G, 100 mW cm\(^{-2}\) (Abet Technologies Cop.).

J-V measurement: four wire method, Keithley 2400 source meter.

In the measuring process of the J-V curve, another mask which is curved according to the four electrode pattern was attached on the front of the cell. It can insure illumination to shine on the effect region of the cell, i.e. the evaporated aluminum electrode region. The anode lead was linked from the edge of the ITO substrate; the cathode led from the center of the Al island electrode using a section of copper wire and silver sol.

3. Results and discussion

3.1. Description of the electric field

Because the purpose of our present work is to study the influence of the electrode shape on cell performance, it is necessary to first discuss the geometric distribution of the electric field between the electrodes of PSCs. According to the charge distribution in bulk heterojunctions, we can qualitatively analyze the potential and electric-field distribution. The schematic of the accumulation of charge near the cell corner and around the sharp corners are shown in figures 1(b) and (c). Near the cell corner (figure 1(b)), the electric field distribution is relatively uniform and the carrier motion is ideal. While around the sharp corners (figure 1(c)), the electric field distribution is nonuniform and asymmetrical, which will influence the generation, separation and transportation of the newly formed excitons in the active layer.

It is generally known that the charge distribution of a charged body correlates with the curvature of the pattern. In bulk heterojunction PSCs, early generated carriers reach the electrode to form an initial electric field that will influence the subsequent exciton separation and carrier transport. A larger curvature, i.e. sharper electrode edges, can gather more carriers to form a strong electrode field. Therefore, the electric-field distribution of the cells will be nonuniform and asymmetrical because of the different geometric shapes (round, oval, square and triangular). Figure 2 depicts the schematics of the electric-field distributions corresponding to the different electrode patterns used in this study.

3.2. Performance analysis of PSCs

In order to more accurately explore the influence of the electrode shape, a shadow mask corresponding to the shape of each cathode was firmly attached on the front of PSCs to ensure that the anode and cathode receive the same illumination during the measurements. Figure 3 shows the J-V characteristics of the devices with different electrode geometries under white light illumination. From figure 3, the short-circuit current density (\(J_{SC}\)) of the cell equipped with a round electrode (R cell) is the largest one and is approximately 14% more than that of the triangular electrode (T cell). Meanwhile, the cell with an oval electrode (O cell) also possesses a larger current density compared with the T cell and square cell (S cell) whose electrode
edges are angular. Therefore, one can conclude that the curvature of the electrode is one of the determinants of $J_{sc}$ in PSCs. On the other hand, regarding the open-circuit voltage ($V_{oc}$), few differences, which are caused by the curvature of the electrode, can be found among the four kinds of shapes of PSCs.

$J_{sc}$ and $V_{oc}$ of the cells can be obtained from the J-V curves of our measurement. The fill factor (FF) and PCE of the devices are calculated based on equations (1) and (2).

According to the general theory of organic semiconductors, the FF of the cell is defined as the maximum power and it is expressed as

$$\text{FF} = \frac{P_{\text{max}}}{I_{sc}V_{oc}} = \frac{I_{\text{max}}V_{\text{max}}}{I_{sc}V_{oc}},$$  \hspace{1cm} (1)

Where $V_{\text{max}}$ and $I_{\text{max}}$ are voltage and current at the maximum power point, respectively.

The PCE of PSCs is defined as the ratio of the device’s maximum output power ($P_{\text{max}}$) and the irradiation power ($P_{\text{in}} = 100\text{ mW cm}^{-2}$). That is,

$$\eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{\text{FF} \times V_{oc} \times I_{sc}}{P_{\text{in}}}. \hspace{1cm} (2)$$

The resulting parameters are summarized in table 1. It is obvious that the FF and PCE are strongly influenced by electrode geometry, similar to the short-circuit current. For comparison, the relationships between $J_{sc}$, $V_{oc}$, FF, PCE and electrode geometry are summarized in figure 4. The experimental results show that the geometry of the electrodes has an apparent impact on the cell performance.

Table 1. Photovoltaic performance characteristics of PSCs with different electrode geometries.

| Device | $V_{oc}$(V) | $J_{sc}$(mA cm$^{-2}$) | FF  | $P_{\text{max}}$(%) | $P_{\text{mean}}$(%) | $R_{\text{s}}$(Ω cm$^{-2}$) | $R_{\text{sh}}$(Ω cm$^{-2}$) |
|--------|-------------|-------------------------|-----|---------------------|-----------------------|-----------------------------|-----------------------------|
| R cell | 0.57        | 6.93                    | 0.59| 2.34                | 2.07                  | 17.0                        | 376.8                       |
| O cell | 0.60        | 6.18                    | 0.57| 2.14                | 1.93                  | 19.4                        | 383.9                       |
| S cell | 0.58        | 6.03                    | 0.56| 1.99                | 1.87                  | 20.0                        | 391.8                       |
| T cell | 0.59        | 6.00                    | 0.52| 1.89                | 1.68                  | 24.4                        | 321.1                       |

Figure 4. The relationship between the different electrode geometries of PSCs and device performance: (a) current density, (b) open-circuit voltage, (c) FF and (d) PCE.

$$R\  cell > O\ cell > S\ cell > T\ cell.$$  \hspace{1cm} (3)

The values of $J_{sc}$ decrease with increasing sharpness of the electrode contour. As discussed in figure 3, $J_{sc}$ will be smaller as the curvature of the electrode becomes larger, i.e. the angles of the electrode become sharper.
Generally, there are numerous complex influencing factors that determine the \( J_{sc} \) of PSCs, whose mechanism, however, has not been completely understood. \( J_{sc} \) is mainly determined by the quantum efficiency of the light absorption process, collection efficiency of the carriers at the electrode and internal electrical resistance [18]. Moreover, the thickness of the active layer, carrier mobility of the active layer-materials and, especially, the interfacial properties between the electrode and the active material can also affect the \( J_{sc} \).

In fact, the electrode geometry, where an uneven potential gradient can form an inhomogeneous BEF, might be another important factor that is reflected in the carrier mobility and carrier-collection efficiency. As mentioned above, the heterojunction causes a random carrier distribution within the active layer during the manufacturing process of a bulk heterojunction PSC. The early generated carriers reach the electrode to form the initial BEF that will influence the exciton separation and carrier transport in the photoelectric conversion processes. A larger curvature of the electrode, such as a square and triangular pattern, can lead to a larger accumulation of carriers that, in turn, forms a strong BEF field in the angular area. Therefore, a large force will be exerted on newly generated excitons and carriers will gather around the BEF. The excitons might be spatially confined and their separation rate will decrease because of the nonuniform electric field force. Meanwhile, this electric field force will lead to a transport imbalance between the holes and electrons and even increase the probability of the carrier recombination. On the other hand, the inside of the active layer is prone to accumulation of space charge, forming a space-charge layer that also easily leads to a carrier recombination while reducing the charge-collection efficiency.

As a result, the geometric shape of the electrodes can strongly affect the exciton separation, carrier transport, mobility of the carriers and carrier-collection efficiency. Hence, \( J_{sc} \) is lower in the case of \( S \) and \( T \) cells. This is the main physical mechanism by which the electrode geometry influences the performance of PSCs.

Figure 4(b) shows the relationship between \( V_{oc} \) and electrode geometry. Different cells acquire almost equal values of \( V_{oc} \), except in the case of the \( O \) cell. This indicates only a slight influence of the curvature of the electrode on \( V_{oc} \). \( V_{oc} \) mainly depends on the highest occupied molecular orbital (HOMO) of the donor material and the lowest unoccupied molecular orbital (LUMO) of the receptor material [19]. Therefore, its correlation with the electrode geometry is small.

Figure 4(c) illustrates the relationship between the FF and electrode geometry. These two factors exhibit a correlation similar to \( J_{sc} \). The FF of the \( R \) cell is the largest, whereas that of \( S \) cell is the smallest. With the increase in the sharpness of the electrode edges, the corresponding FF shows a decreasing trend. In the case of PSCs, FF is mainly affected by the transport properties of holes and electrons [20]. As already mentioned, the different electric-field distributions caused by the different electrode geometries determine the transport and mobility of the carriers.

Figure 4(d) summarises the measurement results of the PCEs for the cells with round, oval, square and triangular electrode shapes. Because the simplest cell structure is employed and electrode fabrication and J-V measurements are performed under an atmospheric environment, the absolute PCE values are lower than those reported in some references. Meanwhile, the Al cathode conduction system increases the potential of a large series resistance in the measuring process. Table 1 lists the data of the series resistance \( R_s \) and shunt resistance \( R_{sh} \), respectively. The PCE of PSCs is defined by the ratio of the device’s maximum output power to the incident irradiation power. Equation (2) shows that the PCE is proportional to the \( V_{oc}, J_{sc} \) and FF. As discussed previously, though the electrode geometry does not affect \( V_{oc} \), it significantly affects \( J_{sc} \) and FF. Therefore, \( R \) and \( O \) cells possess PCE values larger than \( T \) and \( S \) cells that have angular electrode profiles and thus display a smaller PCE. As a result, the electrode boundary curvature reveals a negative correlation with PSC performance.

4. Conclusion

In conclusion, the influence factor of the electrode geometry on the photovoltaic performance of PSCs is discussed. Under identical electrode areas and manufacturing conditions, the electrode geometry shows a significant impact on the \( J_{sc}, FF \); however, it hardly affects the \( V_{oc} \). By analysing the formation process of the electric field in the electrode, we infer that angular electrodes form uneven electric fields that block the carrier transport and reduce carrier mobility, even in the case of excitons. We expect that this work on electrode geometry is useful for evaluating the performance of PSCs not only in laboratory studies but also in commercial applications.

Acknowledgments

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References

[1] He Z et al. 2012 Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure Nat. Photon. 6 593–7
[2] Dou L et al. 2012 Tandem polymer solar cells featuring a spectrally matched low-bandgap polymer Nat. Photon. 6 180–5
[3] Li M et al. 2014 Ferroelectric field effect of the bulk heterojunction in polymer solar cells Appl. Phys. Lett. 104 253905
[4] Guo X et al. 2010 Thiényl [3, 4-c] pyrrole-4, 6-dione-based donor-acceptor conjugated polymers for solar cells Macromolecules 44 269–77
[5] Bauer A et al. 2012 Zno: Al cathode for highly efficient, semitransparent 4% organic solar cells utilizing tiox and aluminum interlayers Appl. Phys. Lett. 100 073307
[6] Liang Z et al. 2012 Effects of the morphology of a zno buffer layer on the photovoltaic performance of inverted polymer solar cells Adv. Funct. Mater. 22 2194–201
[7] Schmidt-Hansberg B et al. 2012 Structure formation in low-bandgap polymer: fullerene solar cell blends in the course of solvent evaporation Macromolecules 45 7948–55
[8] You J et al 2012 Metal oxide nanoparticles as an electron-transport layer in high-performance and stable inverted polymer solar cells Adv. Mater. 24 5267–72

[9] Larsen-Olsen T T et al 2012 Roll-to-roll processed polymer tandem solar cells partially processed from water Sol. Energy Mater. Sol. Cells 97 43–9

[10] Li G, Zhu R and Yang Y 2012 Polym. Sol. Cells: Nat. Photon. 6 153–61

[11] Sista S et al 2010 High-efficiency polymer tandem solar cells with three-terminal structure Adv. Mater. 22 E77–80

[12] Cai W, Gong X and Cao Y 2010 Polymer solar cells: recent development and possible routes for improvement in the performance Sol. Energy Mater. Sol. Cells 94 114–27

[13] Kim M S et al 2008 Choice of electrode geometry for accurate measurement of organic photovoltaic cell performance Appl. Phys. Lett. 92 133901

[14] Cravino A, Schilinsky P and Brabec C J 2007 Characterization of organic solar cells: the importance of device layout Adv. Funct. Mater. 17 3906–10

[15] Lee W J, Ramasamy E and Lee D Y 2009 Effect of electrode geometry on the photovoltaic performance of dye-sensitized solar cells Sol. Energy Mater. Sol. Cells 93 1448–51

[16] Ito S et al 2006 Photovoltaic characterization of dye-sensitized solar cells: effect of device masking on conversion efficiency Prog. Photovoltaics: Res. Appl. 14 589–601

[17] Park J et al 2007 On the I-V measurement of dye-sensitized solar cell: effect of cell geometry on photovoltaic parameters Sol. Energy Mater. Sol. Cells 91 1749–54

[18] Nikitenko V, Von Seggern H and Bässler H 2007 Non-equilibrium transport of charge carriers in disordered organic materials J. Phys.: Condens. Matter 19 136210

[19] Rand B P, Burk D P and Forrest S R 2007 Offset energies at organic semiconductor heterojunctions and Their influence on the open-circuit voltage of thin-film solar cells Phys. Rev. B 75 115327

[20] Kroon R et al 2008 Small bandgap polymers for organic solar cells (polymer material development in the last 5 y) Polym. Rev. 48 531–82