

Postproduction Annealing Effect on Solar Cells Based on Polymer and Zinc Oxide Nanorod Composites

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ABSTRACT

In this work, we study the effect of postproduction annealing on the polymer-ZnO-nanorod solar cells. The morphological, crystalline, optical and electrical properties of devices are investigated. The experimental results show that the postproduction annealing treatment worsens the performance of solar cells. The device without postproduction annealing has a power conversion efficiency (PCE) of 1.06% under Air Mass 1.5, 100-mW/cm² illumination. After postproduction annealing at 150 °C for 3 minutes, PCE decreased from 1.06 to 0.31%. The reduction of PCE results from the poor infiltration of the photoactive layer and the broken electron transport path in ZnO nanorod. Therefore, postproduction annealing treatment is not effective in the BHJ polymer-ZnO-nanorod solar cells.

Keywords: ZnO nanorod, bulk-heterojunction (BHJ), polymer solar cells, post-annealing, photovoltaics

1 INTRODUCTION

Organic photovoltaic (OPV) devices based on blends of poly(3-hexylthiophene) (P3HT) and methanofullerene [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) have attracted much attention because of their properties of low production cost and flexible, large-area fabrication.[1, 2] Recently, the postproduction annealing treatment had been reported in the literatures due to the improvement of the performance of the OPV devices.[3, 4] Thermal annealing at temperature approaching the glass transition temperature of the polymer leads to the formation of nanodomains within the P3HT:PCBM blend layer and then the modification of charge transport pathways, allowing for improved charge mobility.[5] Moreover, the postproduction annealing under the existence of metal cap induced increase both in the interfacial area between the P3HT:PCBM blend layer and metal electrode and in the crystallization of P3HT, resulting in the reduction of series resistance and the enhanced photocurrent in the solar cells.[6] Consequently,

postproduction annealing treatment is usually an important process for polymer solar cells.

The solar cells based on polymer and ZnO nanorod composites can improve charge carrier collection and transport because the nanostructures could offer the direct and ordered path for photogenerated electrons to the electrode. The low mobility of the charges inside the photoactive matrix is one of the factors limiting the efficiency of the OPV devices. The optimal thickness of the active layer is determined by a tradeoff relationship between absorption of light and charge carrier transport in the active layer. The “thickness dilemma” could be solved by using a nanostructured oxide such as ZnO nanorod vertically aligned to the substrate.[7, 8] ZnO nanorod may allow for the use of thicker active layers leading to increased efficiencies. On the other hand, ZnO nanorod arrays can grow perpendicularly to the substrate at low temperature (<100 °C) using a hydrothermal method.[9] As a result, the solar cells based on polymer and ZnO nanorod composites ZnO can be fabricated by all-solution processing. ZnO nanorod is well suited to the application for polymer solar cells.

However, there is always a common infiltration problem for the hybrid polymer solar cells using the nanostructures. The problem can be observed from the cross sectional scanning electron microscopy images of these devices; [7, 8, 10] thus, the infiltration of the polymer into the ZnO nanorod arrays is of particular importance for optimizing the performance of these BHJ solar cells with small rod-to-rod spacing. Because of the lack of optimized device structure and processing, results on these polymer BHJ solar cells based on ZnO nanorod arrays have yet to demonstrate increased performance over blend solar cells. Therefore, there is room for improvement on polymer-ZnO-nanorod solar cells.

Nevertheless, the research on postproduction annealing treatment of polymer-ZnO-nanorod solar cells has not been reported. In this work, we study the effect of postproduction annealing on the polymer-ZnO-nanorod solar cells. The morphological, crystalline, optical and electrical properties of devices were investigated. We report

the postproduction annealing effect on the infiltration of P3HT:PCBM blend and the deformation of ZnO nanorods. The chemical structures of the investigated materials and a schematic view of the device geometry (ITO/ZnO nanorod array/P3HT:PCBM blend/PEDOT:PSS/Pt) are shown in Figure 1.

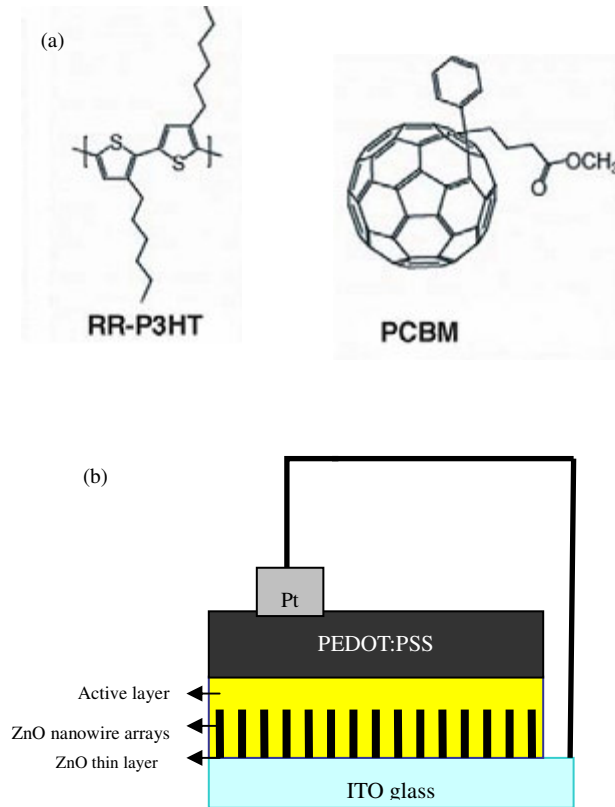


Figure 1: (a) The chemical structures of the constituent materials in the active layer and, (b) schematic of a device structure of polymer-ZnO-nanorod solar cells fabricated in this study.

2 RESULTS AND DISCUSSION

In this study, we present an inverted bulk-heterojunction solar cells using ZnO nanorod arrays between ITO and active layer and platinum as a hole-collecting electrode.

2.1 Sample Preparation

All devices were prepared on indium tin oxide (ITO) coated glass substrates with a sheet resistance of $7 \Omega/\text{sq}$. A ZnO seed layer was deposited from a 0.5 mol solution of zinc acetate dihydrate (Merck) in 2-methoxyethanol (Merck) by spin coating at 3000 rpm and then dried at 100°C for 1 h as described previously.[9] ZnO nanorod arrays were subsequently grown from the ZnO seed-coated substrates placed face down in an aqueous solution of 50 mM zinc nitrate (Sigma Aldrich) and 50 mM

hexamethylenetetramine (Sigma Aldrich) at 90°C for 4 h using a hydrothermal method.[9, 11]

The active layer was fabricated by spin coating a solution of 1.5wt% of P3HT and PCBM (1:1 by weight) in dichlorobenzene (DCB) solution on top of the ZnO nanorod arrays at 1000 rpm for 40 s. The blend layer was subsequently dried under N_2 atmosphere at 155°C for 10 min. Next, poly(3,4-ethylenedioxythiophene): polystyrene sulfonic acid (PEDOT:PSS) (Baytron P) as a hole transporting layer was deposited on the blend layer by spin coating at 8000 rpm for 60 s, and then dried in an oven at 80°C for 10 min. A platinum (Pt) top electrode was deposited to complete the device under high vacuum ($\sim 1 \times 10^{-6}$ torr) using an e-beam evaporation. Finally, to make comparison between the devices with and without postproduction annealing, a postproduction annealing treatment was achieved by heating the device on a hotplate at 150°C for 3 min.

2.2 DEVICE PERFORMANCE

Figure 2 shows the J–V curves of the devices with and without postproduction annealing treatment. The device without postproduction annealing treatment (red squares) exhibited an open circuit voltage (V_{oc}) of 0.43 V, a short circuit current density (J_{sc}) of $8.0 \text{ mA}/\text{cm}^2$, a calculated fill-factor (FF) of 0.31, and a power conversion efficiency (PCE) of 1.06 %. However, after postproduction annealing at 150°C for 3 minutes, V_{oc} decreased from 0.43 to 0.21 V, J_{sc} from 8.0 to $0.52 \text{ mA}/\text{cm}^2$, FF from 31 to 19.2%, and PCE from 1.06 to 0.31% (Fig 2.). Electrical measurements were taken in air. Current density–voltage (J–V) curves were measured with a Keithley 2400 source meter, under illumination at $100 \text{ mW}/\text{cm}^2$ from a 150 W Oriel solar simulator with AM 1.5G filter.

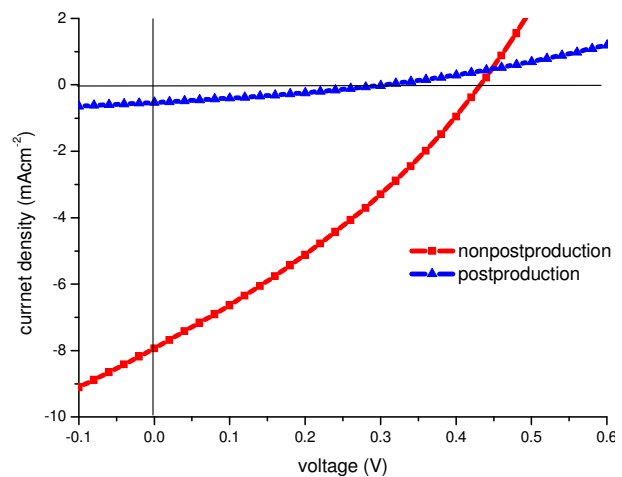


Figure 2: Current density versus voltage for device without postproduction annealing (red rectangles) and with postproduction annealing (blue triangles) under Air Mass 1.5, $100\text{-mW}/\text{cm}^2$ illumination.

2.3 Sample Characterization

The cross sectional morphologies of BHJ polymer-ZnO-nanorod solar cells were obtained by a field-emission scanning electron microscope (FESEM). Figure 3 shows the SEM images of the devices without postproduction annealing treatment. The polymer infiltrates well (Fig. 3), and ZnO nanorods align vertically to the substrate. Therefore, electrons could transport successfully to ZnO nanorods after the dissociation of excitons because of the large interface between PCBM and ZnO nanorods.

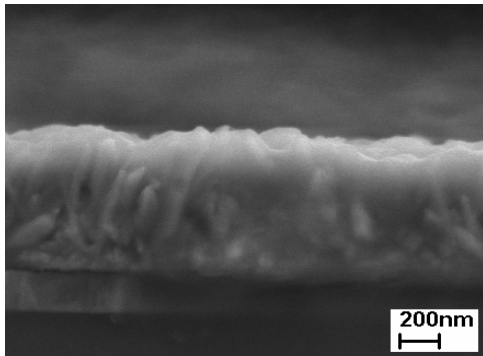


Figure 3: FESEM cross-sections of the P3HT:PCBM blend intercalated into the ZnO nanorods without postproduction annealing

To further investigate the devices without annealing, we study the XRD. A distinct diffraction pattern with characteristic narrow peaks was measured (Fig. 4). The XRD pattern of BHJ solar cells based on ZnO nanorod arrays without postproduction annealing treatment shows the peaks at $2\theta = 34.4^\circ$, where the (002) diffraction peak ($2\theta = 34.4^\circ$) is the preferential c-axis orientation in the ZnO nanorod arrays prepared by the hydrothermal method.

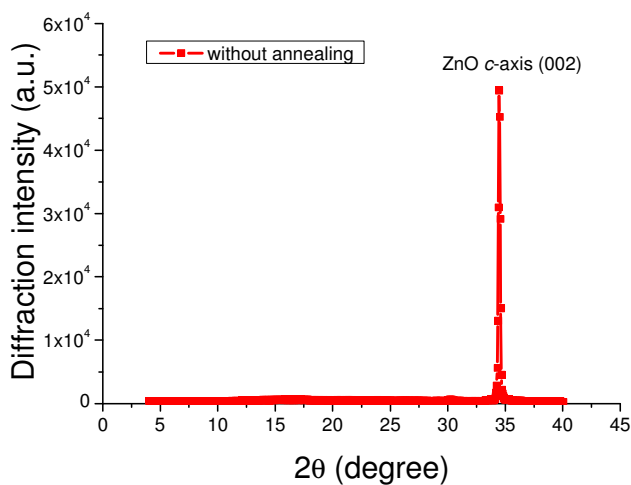


Figure 4: X-ray diffractogram of BHJ polymer-ZnO-nanorod solar cells without postproduction annealing.

Hence, the intensity of the (002) diffraction peak is the

strongest in the XRD pattern for the sample without postproduction annealing treatment.

2.4 POSTPRODUCTION ANNEALING EFFECT

Figure 5 shows the SEM images of the devices with postproduction annealing treatment. The infiltration of the polymer into the spacing of ZnO nanorods becomes poor, and ZnO nanorod arrays were deformed after postproduction annealing (Fig. 5). That is, after postproduction annealing treatment, the wetting of ZnO nanorod arrays by P3HT:PCBM blend (photoactive layer) is poor, resulting in void spaces between the ZnO nanorods. This causes the reduction of the interfacial area between ZnO nanorods and photoactive layer, and then interruption of the transport pathways of carriers. It is believed that the photocurrent is primarily limited by the photogeneration rate and by the quality of the interfaces.[12] The decrease in J_{sc} ($V=0$) of the post-annealed device implies a significant increase in the series resistance. Therefore, the poor quality of the interfaces accounts for the worse performance.

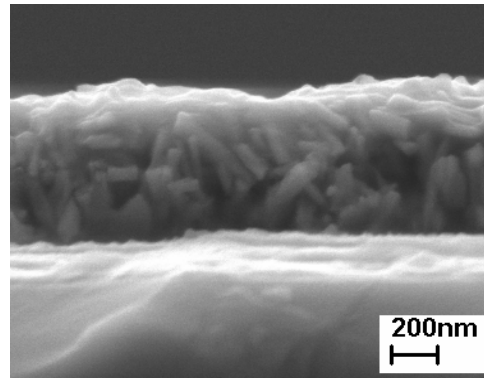


Figure 5: FESEM cross-sections of the P3HT:PCBM blend intercalated into the ZnO nanorods with postproduction annealing.

To further understand the reasons behind the increase in the series resistance, the XRD was studied (Fig. 6). However, when the sample is post-annealed, the intensity of (002) diffraction peak significantly decreases. This result implies that the ZnO nanorod arrays of post-annealed device are not aligned vertically and even broken. Moreover, there is a peak at $2\theta = 26.5^\circ$ in the XRD patterns. This peak indicates that post-annealed sample has special molecular structure of P3HT, in combination with the aggregation of P3HT in crystalline nanodomains. Therefore, it is reasonable to suggest that the postproduction annealing treatment support the formation of the nanocrystalline P3HT domains, and then the aggregation of P3HT may cause not only the void spaces between ZnO nanorods but also the deformation of ZnO nanorods. We also observe the phenomenon that ZnO nanorod arrays were deformed after

the postproduction annealing treatment from the SEM image (Fig. 5). It is possible that P3HT recrystallized in the photoactive layer during the post annealing, and some nanorods were broken due to the stress from the polymer shrinking or aggregating as the polymer cooling down to room temperature. As seen in the Figure 5, some nanorods were broken. The deformation of ZnO nanorods may make the carrier transport more difficult. Therefore, the electron transport path in ZnO nanorod was broken.

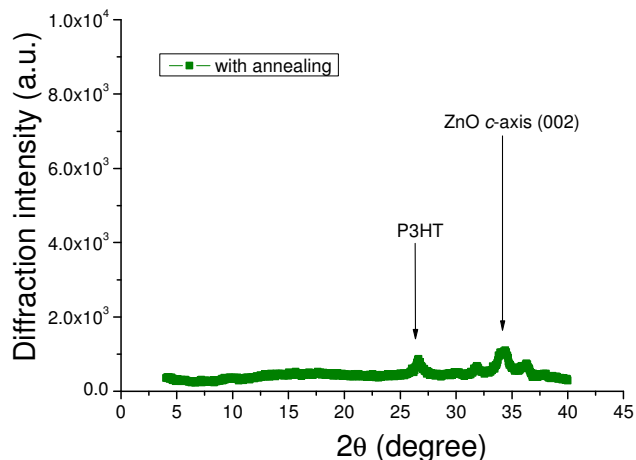


Figure 6: X-ray diffractogram of BHJ polymer-ZnO-nanorod solar cells with postproduction annealing.

4 CONCLUSION

We have studied the influence of postproduction annealing on the BHJ polymer-ZnO-nanorod solar cells. The postproduction annealing treatment leads to the worse performance of BHJ polymer-ZnO-nanorod solar cells due to the poor infiltration of the photoactive layer. Annealing photoactive layer results in the aggregation of the polymer. This aggregation causes the phenomenon that void spaces between nanorods are created, leading to the reduction of the interfacial area between the ZnO nanorods and photoactive layer, and ZnO nanorods are deformed on account of a pulling force. As a result, attempt to improve the performance of BHJ polymer-ZnO-nanorod solar cells through postproduction annealing treatment is not successful.

5 ACKNOWLEDGMENTS

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