Solar Energy Materials & Solar Cells 132 (2015) 570–577

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Enhancing performance of inverted polymer solar cells using two-growth ZnO nanorods

Yu-Che Ho [a], Ping-Yi Ho [a], Hsin-Che Lee [a], Sheng-Kai Chang [a], Yun-Ru Hong [a], Ching-Fuh Lin [a,b,c,*]

[a] Graduate Institute of Photonics and Optoelectronics, National Taiwan University, No. 1, Section 4, Roosevelt Road, Taipei 10617, Taiwan, ROC
[b] Graduate Institute of Electronics Engineering, National Taiwan University, No. 1, Sec 4, Roosevelt Road, Taipei 10617, Taiwan, ROC
[c] Department of Electrical Engineering, National Taiwan University, No. 1, Section 4, Roosevelt Road, Taipei 10617, Taiwan

ARTICLE INFO

Article history:
Received 28 April 2014
Received in revised form
7 October 2014
Accepted 8 October 2014
Available online 29 October 2014

Keywords:
Organic solar cell
Inverted structure
Two-growth ZnO nanorods
Solution process
PBDTTT-C-T/PC71BM
PTB7/PC71BM

ABSTRACT

In ordinary polymer solar cells, the short exciton diffusion length causes increasing probability of electron–hole recombination as the active layer thickness exceeds the diffusion length. Hence, the diffusion sets a thickness limitation of the active layer. ZnO nanorods have been used to provide an advantage of electronic path, making it possible to increase the effective thickness of the active layer. However general hydrothermal treatment has a limitation of the ZnO nanorod length because the nanorods accelerate their growth speed horizontally after growing over a period of time, leading to the reduction of space to be filled with the organic light absorber. Thus, in this work, two-growth ZnO nanorods are employed to overcome the above limitation. The first growth process is for defining nanorod density, while the second process is to increase the length without much expansion of the rod size. This allows for elastically tuning the morphology between the active layer and the ZnO electron transport layer to achieve deeper and superior infiltration of organic light absorber. Consequently, this improves the performance of the device. The power conversion efficiencies of devices in PBDTTT-C-T/$PC_{71}BM$ and PTB7/$PC_{71}BM$ are then enhanced from 5.40% to 7.80% and 7.24% to 8.01%, respectively.

1. Introduction

Over the last two decades, polymer solar cells have served as one of the central issues of renewable energy studies due to their potential of flexible applications, low-cost manufacturing and solution-processing possibility [1–3]. Within the development of polymer solar cells that seek for stability and lifetime, an inverted structure with reverse electron flow has shown its significance recently [4–14]. In conventional structures, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PPS), a conductive polymer, which is frequently deposited as the hole transport layer (HTL), is found to cause corrosion to ITO. Additionally, as an air-sensitive metal, Al is used as the top electrode, which causes defects in device mechanisms and lifetimes [15,16]. Compared with the conventional structure of polymer solar cells, the inverted structure hence dramatically affects stability and lifetime of devices employing high-work function metal as the anode on the top of the devices and separating the PEDOT:PPS from the ITO [17].

Among inverted structural polymer solar cells, ZnO commonly serves as the electron transport layer [18]. Because of its wide bandgap and ability to match energy level with an organic solar device and its ability to be manufactured at a large scale in a solution process, there were many studies about the manufacture of plane ZnO layer in past reviews [19–21].

Even so, some limitations exist for the thickness of the active layer in polymer solar cells because of the diffusion length of the carriers. Thus, in the inverted structure polymer solar cells, we fabricate the ZnO nanorod structure with a low-cost hydrothermal growth process, substituting the ZnO film. Through embedding the ZnO nanorods into organic light absorbers to provide an advantageous electronic path, this structure allows a thicker organic active layer. Moreover, ZnO nanorod structure promotes valid area of the junction between ZnO and organic light absorbers. Hence, the efficiency of electron-collection, transportation, and suppression of the leakage current would be improved [22–27].

In the past research and development of the hydrothermal growth for zinc oxide nanostructures, there are indications that the hydrothermal zinc oxide nanostructures can form into not only

* Corresponding author at: Institute of Photonics and Optoelectronics, National Taiwan University, Taipei 10617 Taiwan, ROC.
Tel.: +886 2 33663540; fax: +886 2 23642603.
E-mail address: lincf@ntu.edu.tw (C.-F. Lin).

http://dx.doi.org/10.1016/j.solmat.2014.10.013
0927-0248/

rods but also other types of morphology by regulating the growth-environment conditions [28–33] or adopting additive and changing pH in nanostructures growth process [34–37]. However, ZnO nanostructures are rarely combined with low-bandgap polymer solar cells into devices with an explicit result; hence we employ the ZnO nanorod structure into our research. By controlling different growth periods and growth concentrations, we adjust the morphology of columnar structure and the spacing between rods and rods density in order to provide a good infiltration of organic light absorbers [38,39]. Moreover, the research shows that the contact morphology between ZnO nanorod structure and the organic light absorbers plays a key role in increasing the efficiency of solar cells.

However, in reality, while we hope to elevate device efficiency by applying longer lengths of ZnO nanorods [40,41], general hydrothermal treatment has a limitation of the ZnO nanorod length because the nanorods accelerate their growth horizontally after growing over a period of time, leading to the reduction of space to be filled with the organic light absorbers. This causes the device performance to not enhance but, rather, reduce [42].

Thus, in this work, we focus on the method that can not only make a longer structure of the ZnO nanorods but also avoid the problem of shrinking space between the nanorods. We employ two-growth ZnO nanorods in order to overcome the above limitation. The first growth process is performed in order to define the nanorod density, while the second process is meant to increase the nanorod length without much expansion of the rod size. This allows for elastically tuning the morphology between the active layer and the ZnO electron transport layer in order to achieve deeper and superior infiltration of organic light absorbers. Consequently, the two-growth ZnO nanorods improve the power conversion efficiency (PCE), open-circuit voltage (VOC), and fill-factor (FF) of the device. Also, we apply different systems of the organic active layer on this ZnO NRs platform to come up with a universal method for enhancing the device performance. Lastly, the power-conversion efficiencies of devices in PBDTTT-C-T/$PC_{71}BM$ and PTB7/$PC_{71}BM$ are enhanced from 5.40% to 7.80% and 7.24% to 8.01%, respectively.

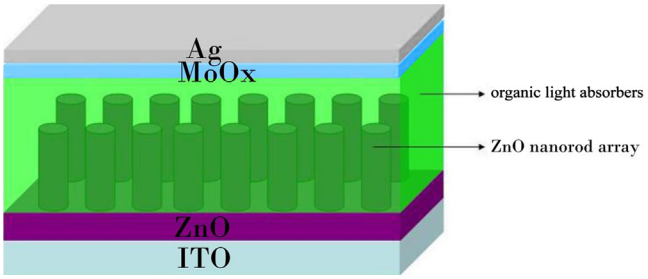

Fig. 1. Schematic diagram of the device structure with ZnO nanorod array.

2. Experimental section

The fabrication procedure of the polymer solar cells with the embedded ZnO nanorods is based largely on a solution process. The architecture is shown in Fig. 1. In this study, the organic light absorbers are sandwiched between MoO_x and ZnO. Air-stable material ITO and silver are employed as the electrodes. Furthermore, ZnO is formed into ZnO nanorod structure for the infiltration of the organic light absorbers.

The fabrication steps are as follows. Firstly, the ZnO sol–gel solution (0.45 M) was spin-coated on the well-cleaned ITO substrates (250 nm,15 Ω/sq) and dried on a hot plate at 200 °C to form a ZnO seed layer and film. The sol–gel solution was prepared by mixing zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$) and monoethanolamine ($CH_2(OH)CH_2(NH_2)$) in 2-methoxyethanol ($CH_3O(CH_2)_2OH$), as a ZnO seed layer. Subsequently, after annealing in nitrogen for 1 h at 200 °C, the hexagonal column formations of

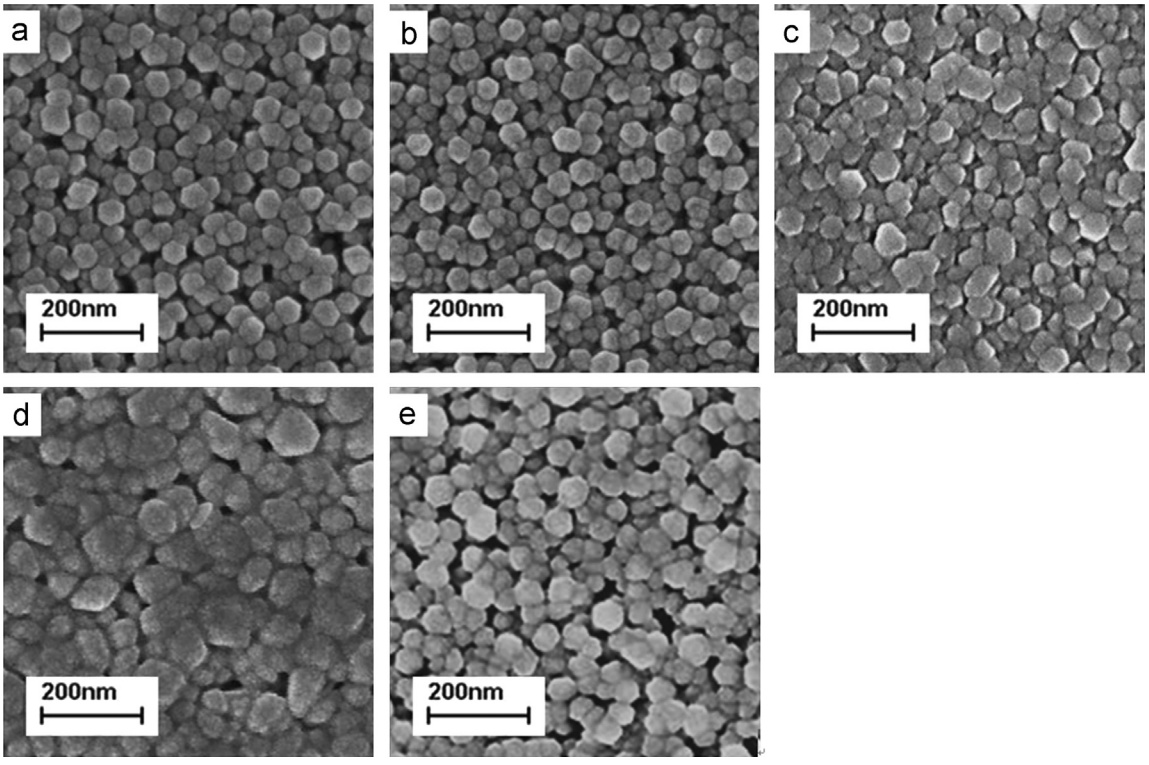

Fig. 2. Top-view SEM images of ZnO nanorods and spacing morphology of one-growth for (a) 60, (b) 75, (c) 90, (d) 105 min, and (e) the two-growth for 1st: 65 min and 2nd: 60 min.