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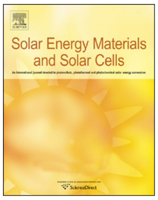

Efficiency improvement of organic solar cells with imprint of nanostructures by capillary force lithography

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ABSTRACT

Organic solar cells imprinted with nanostructures, by the capillary force lithography process using soft molding, on either the active layer or the electron transport layer (ZnO) of an inverted organic solar cell are made. With proper control of the wetness of the ZnO or the active layer, either of them can be readily driven by the capillary force into the cavities formed by the nanostructures on the soft mold during the imprint. The nanostructures demonstrated here can be either regular gratings or arrays of nanorods. Due to light scattering and intrusion of the nanostructures into the active layer, both light absorption and carrier transport can be significantly improved, which can effectively increase both the fill factor and the power conversion efficiency (PCE). For solar cells having nanostructures imprinted on the electron transport layer of ZnO, the PCE can increase from 2.39 to 2.65% for gratings or 3% for arrays of nanorods, respectively, and the fill factor can increase from 0.5 to 0.57 for arrays of nanorods. For solar cells having nanostructures of gratings imprinted on the active layer, the fill factor increases from 0.5 to 0.6, the current density increases from 9.02 mA/cm^2 to 9.73 mA/cm^2, and the PCE increases from 2.4 to 3.05%. The use of capillary force to imprint nanostructures eliminates the use of costly imprint equipments and possible damage of the active layer by contacting with air.

1. Introduction

Recently, more research attention has been paid to the development of polymer solar cells due to its rapid efficiency improvement, the cost effective energy harvesting, ease of processing, and compatibility with flexible substrates. The power conversion efficiency (PCE) of polymer solar cells has reached as high as 10% [1–4]. However, higher PEC of polymer solar cells has been reported by using different polymer materials [3,4]. Many effective approaches have been carried out to improve the performance of solar cells through the synthesis of new narrow bandgap materials for better photon harvesting, optimization of phase segregation in the bulk heterojunction (BHJ) layers, interfacial modification for better charge carrier collection, and design of novel configuration cells [5–10]. However, in the past, problem and improvement of light trapping have received relatively little attention. Only a few work is reported to improve light trapping through the use of microlenses or functional microprism on the glass to reduce light scattering [11,12]. The periodic nanostructured designs for organic photovoltaics where a photonic crystal is formed between blended P3HT:PCBM and nanocrystalline zinc oxide is adopted to enhance light trapping for photovoltaic improvement [13]. In addition, few works [14,15] present the use of the nanoimprint technique to make nanostructures on the active layer to enhance the light trapping to improve solar cell performance. However, the use of nanoimprint technique requires moving out the test sample from glove box to the outside environment for an imprint process and leads to serious damage of the polymeric active layer by immediate contact with both oxygen and water moisture. One possible solution is to move the imprint machine inside the glove box. However, this may significantly increase the capital cost. The current work demonstrates that imprint of an organic solar cell can be made by a soft lithography process using capillary force so that the imprint can be readily made inside a glove box without the use of expansive imprint equipments. The imprint of nanostructures can be made on either the active layer of the blended P3HT with PCBM or the electron transfer layer made by a spin coated ZnO that is synthesized from a sol–gel process if proper wetness of the imprinted materials can be controlled. The organic solar cells made are an inverted structure with glass ITO/ZnO/P3HT+PCBM/PEDOT:PSS/Ag, as shown either in Fig. 1a with nanostructures imprinted on the ZnO layer or Fig. 1b with nanostructures imprinted on the active layer.

The soft mold is made of PDMS material that has a very low surface energy. The use of PDMS mold can avoid serious problem of adhesion during the imprint. In addition, the PDMS mold can be readily made by coating the liquid-like PDMS materials on an organic or inorganic mold with nanosturctures. Nanostructures on the PDMS mold can be readily formed by peeling off the rubber-like

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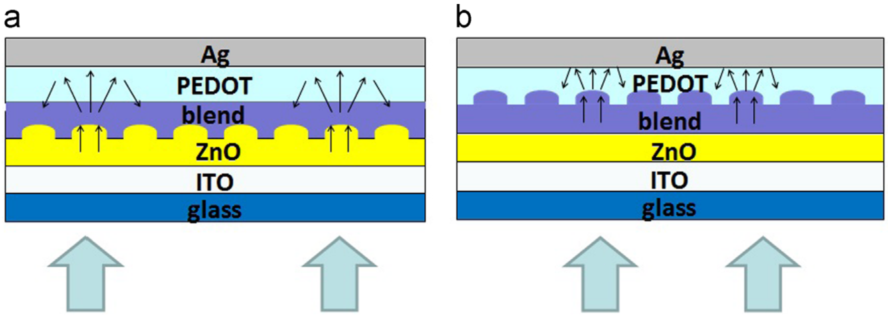

Fig. 1. Schematic diagram of the inverted solar cells with nanostructure imprinted on (a) the electron transfer layer of ZnO or (b) the active layer.

PDMS materials. The nanostructures selected for the imprint are either regular gratings or arrays of nanorods. The PDMS mold with regular nanostructures and smooth surface can be used to imprint the ZnO or the active layer by capillary force lithography. More detailed discussions on the problems of nanoimprint on either the ZnO or the active layer are presented. Both the optical and electronic characteristics of the imprinted solar cells will be measured and presented.

2. Experiments

2.1. Fabrication of solar cells

Before fabrication of the inverted solar cells, sol–gel solution of ZnO was prepared first which will be used as an electron transfer layer of the solar cell. The sol–gel ZnO was prepared by mixing 2-methoxyethanol with zinc acetate dehydrate at a ratio of 160 g versus 1 L. and stabilized with ethanolamine for one day for complete reaction. All the chemicals used for formation of sol–gel ZnO are bought from Uni-Onward Corp. XRD measurements are performed to check and ensure the correct crystalline structure of the spin coated ZnO layer after baking at 300 °C for 30 min. After cleaning and patterning the ITO for the electrodes, sol–gel solution of ZnO synthesized was spin coated on the ITO glass (Uni-Onward Corp.) and baked at 300 °C for 30 min to form a thin layer of 60 nm in thickness. However, the baking duration can be varied to maintain suitable wetness of the ZnO layer in order for imprinting nanostructures by the capillary force lithography process using soft mold in contact with the ZnO layer. More detailed nanoimprinting processes are discussed in the next section. After imprint, the active layer made by blending poly (3-hexylthiophene) (P3HT, Uni-Onward Corp.) and [6,6]-phenyl-C60-butyric acid methyl ester (PCBM, Uni-Onward Corp.) was then spun coated on the top of ZnO. After settling in nitrogen glove box for 60 min, the active layer was baked at 110 °C for 10 min. If imprint of nanostructures on the active layer is required, to maintain suitable wetness in the active layer in order to imprint by capillary force lithography process the settling and baking of the active layer is made after the imprint. After baking of the active layer, a thin layer of PEDOT:PSS poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (Clevios PVP. AI4083) used as hole transfer layer was spin coated and baked at 150 °C. Then, a thin layer of Ag is vaporized on the PEDOT:PSS and acts as anode to complete fabrication of the inverted solar cells. The completed solar cells are annealed at 150 °C for 30 min. to enhance both the crystalline structure of the active layer and the contact of the PEDOT:PSS with the electrode. It can be expected that the nanostructures on either the ZnO or the active layer of the solar cell can scatter the incident light, as shown in Fig. 1a or b, that light can travel through the active layer in a much longer distance. Therefore, more light can be trapped and absorbed by the active layer which can increase generation of electron–hole pairs and increase the short circuit current of the solar cells. In addition, the nanostructures on the active layer may provide better charge carrier transport and collection which can significantly increase the cell performance. The nanostructures on either the ZnO or the active layer are observed by SEM 7001. The *I–V* and other characteristics of the solar cells are measured, under a sun light simulator (Oriel 91160A 300 W) illuminated at AM 1.5G, with a Keithley 2400 Source Meter.

2.2. Fabrication of PDMS mold with nanostructures and nanoimprint

The attempt to use the soft imprint technique with soft mold to make nanostructures on either the ZnO or the active layer is attributed to fact that the soft mold is usually made of polymer, which is inherently a low surface energy material and that may possibly avoid the problem of adhesion during the imprint. Both the PDMS and the polyurethane acrylate (PUA) material which are frequently used as a soft mold in the area of soft imprint or soft lithography are adopted. The PDMS material can be readily made into a mold by coating the liquid-like material on a hard mold. After solidified, the PDMS layer can be readily peeled off from the hard mold. The inverse structure on the hard mold can be transferred onto the PDMS layer which can be used as a soft mold to transfer the nanostructures to either the ZnO or the active layer.

The types of hard molds used to make the PDMS soft molds are either the nanostructured gratings in a DVD disc or the arrays of nanorods made on a silicon substrate. The regular nanostructures or gratings are made by first peeling off the upper plate of a DVD disc. Then the DVD disc with gratings is cleaned in alcohol to remove the irregular, recorded signals, and washed in isopropanol with sonication for 10 min. The size of gratings has a depth of 150 nm, line width of 400 nm and gap of 350 nm. The nanostructures made on the silicon substrate are first transferred onto the PUA mold which is then used to transfer the nanostructures onto the PDMS mold. The arrays of nanostructures on the silicon substrate should be made into arrays of nanoholes which are made by E-beam lithography process. The nanostructures transferred onto the PUA become nanorods where the diameter and the height of the nanorods are 300 nm, 100 nm, respectively. The gap between neighboring nanorods is 700 nm. The nanostructures transferred onto the PDMS materials become nanoholes which transferred finally onto the ZnO or active layer become nanorods.

The liquid-like material of PDMS is prepared by blending the primary agent with the hardener (Sylgard 184) at a ratio of 10:1, and is then coated on either the DVD or the PUA mold with nanostructures. The nanostructures on the DVD disc or the PUA mold can be conveniently transferred onto the PDMS surface, as shown in the SEM images of the PDMS mold in Fig. 2a and b, by coating the PDMS on the surface of the hard mold under vacuum condition for 1 h to avoid possible air bubbles trapped in the nanostructures. The PDMS mold is then solidified by heating up to 80 °C for 2 h.