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## Rational design of metallic nanowire-based plasmonic architectures for efficient inverted polymer solar cells

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#### Abstract

Plasmonics can improve the performance of polymer solar cells (PSCs) by localizing and concentrating light, and the location of the plasmonic metallic nanostructure in devices plays an important role in how to design high-performance plasmonic solar cells. Here, by varying the location of silver nanowires (Ag NWs) within the device architecture (at the interface between indium–tin–oxide and cathode buffer layer, cathode buffer layer and active layer, active layer and anode buffer layer, respectively), a systematic study on plasmonic effect on the properties of photovoltaic material was presented. The density of photogenerated excitons, the electron delocalization and the effective conjugation length of the photovoltaic material in our pre-designed plasmonic structures were increased, and the enhancements of plasmonic effects were effective in a broad spectral range. When the pre-designed plasmonic structures were incorporated into the inverted PSCs, short circuit current density ( $J_{sc}$ ) for all the interface of indium–tin–oxide and cathode buffer layer. The power conversion efficiency of the optimized plasmonic inverted device reached 4.05% under AM1.5 illumination (100 mW/cm<sup>2</sup>), which was due to the enhancement of  $J_{sc}$  without reducing the open-circuit voltage and FF of the plasmonic inverted PSCs by introducing Ag NWs. © 2015 Elsevier Ltd. All rights reserved.

Keywords: Inverted polymer solar cell; Plasmonic; Silver nanowire

### 1. Introduction

Polymer solar cells (PSCs) offer great potential for the development of low-cost, lightweight, flexible and large area electronic devices (Kim et al., 2007; Ma et al., 2015). The effective absorption of solar spectrum and the collection of the photogenerated carriers with minimal losses to

http://dx.doi.org/10.1016/j.solener.2015.08.016 0038-092X/© 2015 Elsevier Ltd. All rights reserved. recombination will enable the improvement of the power conversion efficiency (PCE) of PSCs (Atwater and Polman, 2010; Kim et al., 2011). One feasible approach for enhancing the absorption efficiency is to increase the thickness of active layer (Yang et al., 2011). Nevertheless, due to the low carrier mobility of organic materials, the thicker films for the active layer inevitably cause higher charge recombination rate, thereby decreasing the charge collection efficiency (Tvingstedt et al., 2007). To overcome the above contradictory issue, one good solution is to build desirable plasmonic filed at the interface between metal and

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active layer, which can not only reduce the physical thickness of the active layer, but also keep the optical thickness constant.

So far, tremendous studies have been directed toward the incorporation of plasmonic structures such as noble metal nanoparticles into the photovoltaic devices with an aim to enhance the device performance by the plasmonenhanced absorption. It is known that the plasmonic enhancement of photovoltaic devices depends on the geometries (In et al., 2015), dimensions (Liu et al., 2014) or intrinsic metallic properties (Cui et al., 2015) of the metallic nanoparticles. Another important approach, particularly, is the influence of the location of the plasmonic metallic nanostructure in the devices. In general, understanding of the effects of the location of the plasmonic nanostructures on the devices performance is crucial for the plasmonic device fabrication. For example, the previous studies proposed to design different device architectures such as back nanograting (Li et al., 2012a), plasmonic backscattering (Cheng et al., 2012), by the incorporation of metallic nanoparticles into the active layer (Wang et al., 2012), at the front or rear electrode (Leem et al., 2015) or even dual plasmonic nanostructures (Li et al., 2012b) to improve the device performance. However, most of previous studies focused on the effect of single or dual plasmonic structures on the performance of PSCs. The effects of the location of metallic plasmonic nanoparticles in device architectures on the performance of PSCs and the underlying mechanisms are lack of systematic study. Accordingly, a systematic study of the location of plasmonic metallic nanoparticles in the device might gain insight into the plasmonic effects in PSCs.

The inverted structure was chosen as it is suggested to be an ideal structure of PSCs since it is more resistant against degradation as compared with the traditional PSCs (Lim et al., 2012). The silver nanowires (Ag NWs) were chosen for the plasmonic metallic nanostructure, because they can enhance light harvesting efficiency by the localized surface plasmon resonance (LSPR), plasmonic waveguide effects and electric antenna characteristics (Dong et al., 2014), which are ideal plasmonic metallic nanostructures. Here, three kinds of plasmonic structures, the metallic nanoparticles introduced at the interfaces between indium-tin-oxide (ITO) and cathode buffer layer, cathode buffer layer and active layer, active layer and anode buffer layer, respectively, were designed to investigate the effect of different location of metallic nanoparticles on performance of plasmonic inverted PSCs. The choice of these three plasmonic structures was based on the effective improvement of the performance of single structure plasmonic solar cells in the previous reports (Notarianni et al., 2014; Zhang et al., 2014b; Yang et al., 2014). Moreover, steady state photoluminescence (PL) can be used to measure the excitons generation rate (Wu et al., 2011), the effective conjugation length and the electron delocalization (Barugkin et al., 2015), and distinguish the band-to-band transitions from parasitic absorption (Spano et al., 2009). Time-resolve

photoluminescence (TRPL) can be used to measure the coupling efficiency between excitons and plasmons (Geng et al., 2008). Therefore, the steady state PL and TRPL were supposed to study the effects of the designed plasmonic structures on the conjugation length, the density of photogenerated excitons and electron delocalization, the coupling of excitons and plasmons of the photovoltaic materials. Additionally, the pre-designed plasmonic structures were used in the inverted PSCs, and the relevant performances of the inverted PSCs were studied. It was found that by locating Ag NWs at the interface of ITO and cathode buffer layer, the optimized plasmonic inverted PSC showed the best performance with the PCE up to 4.05% under AM1.5 illumination (100 mW/cm<sup>2</sup>).

#### 2. Experimental

#### 2.1. Device fabrication

Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>61</sub>butyric acid methyl ester (PCBM) (Luminescence Technology Corp., Taiwan) were used as supplied. Ag NWs were synthesized using the soft solution processing (Sun et al., 2002). ZnO nanoparticles were synthesized according to previously reported method (Beek et al., 2005). The inverted PSCs devices used P3HT as the electron donor and PCBM as the acceptor, Ag NWs as the metallic plasmonic nanostructure. The structure of reference sample is: quartz/ZnO/photovoltaic material (denoted herein as the "reference sample"), and the plasmonic samples designed to have the following three structures: quartz/ Ag NWs/ZnO/photovoltaic material (denoted herein as the "sample A"); quartz/ZnO/Ag NWs/photovoltaic material (denoted herein as the "sample B"); guartz/ZnO/photovoltaic material/Ag NWs (denoted herein as the "sample C"). The reference inverted PSCs were fabricated to have the following simple structures: ITO/ZnO/P3HT: PCBM/MoO<sub>3</sub>/Al (denoted herein as the "reference device"), and the plasmonic inverted PSCs have three structures: ITO/Ag NWs/ZnO/P3HT:PCBM/MoO<sub>3</sub>/Al (denoted herein as the "Device A"); ITO/ZnO/Ag NWs/ P3HT:PCBM/MoO<sub>3</sub>/Al (denoted herein as the "Device B"); ITO/ZnO/P3HT:PCBM/Ag NWs/MoO<sub>3</sub>/Al (denoted herein as the "Device C"). Quartzs or ITO-coated glasses were cleaned ultrasonically with detergent, distilled water, ethanol, acetone, and isopropyl alcohol (IPA) sequentially. Then, the substrates were dried and treated with oxygen plasma for 10 min prior to use. A 20-30 nm layer (measured by Veeco Dektak 6M Stylus Profiler) of ZnO was deposited by spin-coating onto the pre-treated glass (2500 rpm for 60 s). The ZnO layer was annealed on a hot plate at 200 °C for 15 min. The blend solution of P3HT:PCBM at a 1:1 weight ratio was prepared in chlorobenzene forming a final concentration of 20 mg/mL. The solution was spin-coated and the thickness was maintained at 80 nm. The plasmonic samples were spin-coated with Ag NWs (0.2 mg/mL in IPA) and dried at 80 °C for 5 min. We

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