Solar Energy Materials & Solar Cells 152 (2016) 34–41

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Plasmonic Ag nanowire network embedded in zinc oxide nanoparticles for inverted organic solar cells electrode

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ARTICLE INFO

Article history:
Received 18 January 2016
Received in revised form
7 March 2016
Accepted 20 March 2016
Available online 6 April 2016

Keywords:
Silver nanowire
Zinc oxide nanoparticle
Plasmonic
Organic solar cell
Oxide–Metal–Oxide
FDTD

ABSTRACT

Transparent Electrodes consisting of silver (Ag) nanowires (NWs) and zinc oxide (ZnO) nanoparticles (NPs) were fabricated by spin-coating. Thus, we demonstrated that by embedding AgNWs into the ZnO NPs, we fabricated a transparent multilayer electrode ZnO NPs/AgNWs/ZnO NPs (ZAZ) with a sheet resistance of 13 Ω/sq and an optical transparency of 88%. The optical properties of the ZAZ structure were investigated and calculated using a FDTD method. The modeling results showed a good agreement with the experimental results. Plasmonic behavior is highlighted. The ZAZ multilayer electrodes were experimentally optimized and were successfully integrated into an inverted organic solar cell based on P3HT:PCBM. A photovoltaic efficiency of 3.53% is obtained on the ITO-free organic solar cells (OSC) and is compared to traditional ITO-based devices with an efficiency of 3.16%. Numerical calculations of the intrinsic absorption of the active layer inside an organic solar cell integrating either ZAZ or ITO are performed. Moreover, we explored numerically, the plasmonic effect created by the AgNWs and how it can influence the absorption inside the active layer of solar cells, in order to take advantage of its electromagnetic field increases. We demonstrate that ZAZ electrodes are a promising alternative to conventional ITO films for high performance inverted OSCs due to better transmission and beneficial plasmonic effect.

1. Introduction

Transparent Electrodes (TEs) are a crucial component of a wide variety of devices due to their unique combination of optical and electrical properties (high transparency in the visible range and high electrical conductivity), such as touch panel screens, flat-panel displays, light-emitting diodes and solar cells. Nowadays, the TE frequently used is Indium Tin Oxide (ITO), or Fluorine-doped Tin Oxide, because they present many advantages such as high transmission (> 85% in the visible spectrum), low resistivity due to a low sheet resistance (approximately 10 Ω/sq)) [1] and a high work function [2]. However, they also have some disadvantages such as indium scarcity, aggressive techniques of deposits for organic materials, brittleness and the deposition of layer, which requires high temperature annealing [1,2]. This is incompatible with the recent interest of low-cost and flexible optoelectronic devices as long as they require the use of plastic substrates [2]. In order to avoid the use of these films, many alternative TEs have been explored during the last years. Among them, there are Carbon Nanotubes [3–5], graphene [6–8], highly conductive poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) [9] and metal nanowires or nanoparticles [10–12].

Silver nanowires (AgNWs) were considered as a potential alternative to replace ITO, due to their excellent optical and electrical characteristics [10,13,14]. However, the roughness of AgNWs is often reduced using planarization layers for example. A poor adhesion of the AgNWs on some substrates can also appear but can be controlled with appropriate processing, leading to suitable surface energy of the surface, which allows suitable morphology and fill-factor of the surface to be reached [10,13,14,15]. AgNWs is potentially used for future large-scale production such as roll to roll [16,17], spin-coating and spraying.

An additional promising transparent electrode proposed recently is the OMO structure (substrate/bottom Oxide/Metal/top Oxide). This idea of a multilayer which successfully reached its apogee according to the studies reported in many works. Several metals and oxides have been investigated for the realization of OMO multilayers, such as silver (Ag), copper (Cu) [18], tungsten trioxide (WO_3) [19], molybdenum trioxide (MoO_3) [20] and vanadium pentoxide (V_2O_5) [21]. Up to now, the oxide which has

Abbreviations: NW, nanowire; NP, nanoparticle; ZAZ, ZnO NPs/AgNWs/ZnO NPs; P3HT, poly(3-hexylthiophene); PCBM, 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C61; ITO, indium Tin Oxide; OSC, organic solar cell; TE, Transparent Electrode; OMO, substrate/bottom Oxide/Metal/top Oxide; FDTD, finite-difference time-domain

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http://dx.doi.org/10.1016/j.solmat.2016.03.021
0927-0248/

drawn significant attention is zinc oxide (ZnO) because of its low cost, and material abundance [25]. Vedraine et al. demonstrated that the use of ZnO as an oxide layer in the structure ZnO/Ag/ZnO (ZAZ), presents a transmission of 74% (every transmission in this article will be given at a wavelength of 550 nm) and sheet resistance of 7 Ω/sq, the electrode ZAZ was fabricated by Ion Beam Sputtering (IBS). The ZAZ electrode was also optically optimized using Finite-Difference Time Domain (FDTD) method [23].

A pioneering approach was reported on the structure OMO, where the metallic layer M is based on AgNWs in order to improve the transmission. Among these studies, the AgNWs embedded between two oxides of ITO (ITO/AgNWs/ITO), using a simple brush painting method, lead to a sheet resistance of 11.58 Ω/sq and a transmittance of 84.78% [24]. Another ITO-free electrode is to spin-coat the AgNWs between two sputtered ZnO, which showed a transmission of 91% at 550 nm and a sheet resistance of 8 Ω/sq [25]. Recently, AgNWs have been successfully embedded in ZnO using a roll to roll process leading to a transmission higher than 80% in the range of 550–900 nm. This electrode was integrated in an organic solar cells as well as in a tandem devices [16,17].

In this work, we report on the interest and performance of AgNWs embedded into ZnO nanoparticle (NP) electrodes. To our knowledge, this is the first time such a multilayer electrode has been completely fabricated by spin-coating. We demonstrate that by an effective embedment of the AgNWs network between two ZnO NP layers, we could realize an indium-free ZnO NPs/AgNWs/ZnO NPs (ZAZ) electrode exhibiting a transmission and a sheet resistance higher than an ITO layer conventionally used into organic solar cells based on P3HT:PCBM. Using the FDTD method, we focus our numerical calculation on the study of optical properties of ZAZ electrode. An agreement between numerical and experimental results is shown which allows us to investigate the interest of this electrode. The use of a thin layer of ZnO makes it possible to take advantage of the plasmonic effect due to the AgNWs. We investigate the electric field increases inside an organic solar cell integrating the ZAZ electrode. Thanks to the good optical and electrical properties of the ZAZ electrode, the P3HT:PCBM bulk heterojunction (BHJ) organic solar cells (OSC) integrating ZAZ electrode as an anode, exhibited higher power conversion efficiency (PCE) than the reference OSC using a conventional ITO electrode.

2. Materials and methods

2.1. Experimental details on the elaboration and characterization of (ZAZ) electrodes

The ZnO NP (Genes'Ink, 5 nm-diameter) bottom layer (B-ZnO NPs) was spin-coated onto clean glass substrates (12×12 mm^2) using a speed of 6000 rpm for 50 s, followed by annealing at 130 °C for 10 min to remove the solvent. Then the AgNWs (Cambrios ClearOhm®) were deposited by spin-coating, using a speed of 2000 rpm during 50 s. After the annealing of AgNWs for 10 min at 100 °C in order to remove any trace of solvent, the ZnO NPs top layer (T-ZnO NPS) was directly coated onto the AgNWs/B-ZnO NPs/Glass using identical coating parameters of ZnO NPs bottom layer, where the structure of ZAZ electrode is shown in Fig. 1(a). Each thickness of ZnO NPs layers was successfully optimized experimentally in order to find a good compromise between a high transmission and a good conductivity. Thicknesses of each layer have been measured using a mechanical profilometer (DEKTAK XT). The electrical and optical properties of the optimized ZnO NPs/AgNWs/ZnO NPs (ZAZ) transparent electrode were examined using a four-point probe (experimental error of 1 Ω/sq)) and a UV/visible spectrometer (SAFAS 200 DES) (Fig. 1(b)). The surface morphology of the randomly distributed AgNWs and the ZAZ electrode was examined by a scanning electron microscopy (SEM) using (JSM-7400F de Jeol).

2.2. Solar cells manufacturing and characterizations

The organic active layer (P3HT:PCBM) was coated either on the ZAZ electrode or on a glass/ITO/ZnO NPs (40 nm experimentally optimized) substrate in the glove box under nitrogen atmosphere. A blended solution containing 60 mg poly(3-hexylthiophene) (P3HT, Rieke Metals) and 48 mg of 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C61(PCBM, American Dye Source) in 2 ml of 1,2-dichlorobenzene was prepared 24 h before being used. After spin-coating the P3HT:PCBM active layer at 1100 rpm for 30 s, a solvent-annealing treatment was performed by keeping the active film inside a covered glass jar for 120 min. Then, a layer of PEDOT:PSS (Clevios F010) was spin-coated at 5000 rpm for 50 s. To complete the device, 150 nm-thick silver (Ag) cathodes were deposited by thermal evaporation at a pressure of 2×10^{-6} Torr using a shadow mask of 0.18 cm^2. The photocurrent density–voltage (J–V) curves were measured in the glove box using a Keithley

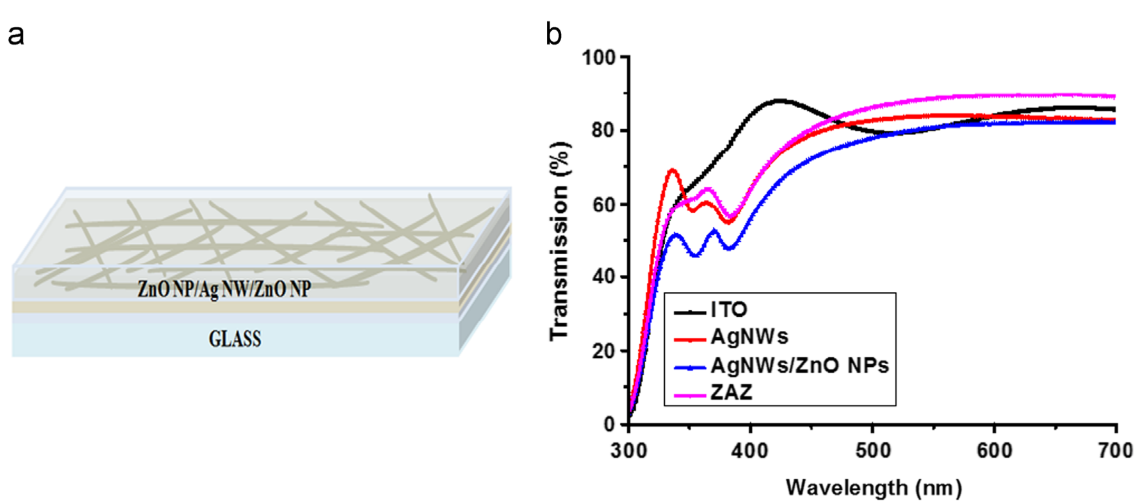

Fig. 1. (a) Structure of ZAZ electrode, (b) Measured transmission spectra of ZAZ, AgNWs, AgNWs/ZnO NPs and ITO electrodes.