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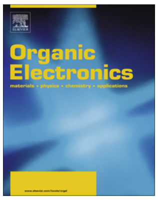

Cathodic multilayer transparent electrodes for ITO-free inverted organic solar cells

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ABSTRACT

We demonstrate cathodic multilayer transparent electrodes based on a ZnS/Ag/TiO_x (ZAT) structure for ITO-free inverted organic solar cells. A quality solution-based TiO_x layer is adopted as an inner dielectric layer to modify the effective work function of Ag, ensuring the ZAT electrode works as a cathode. The effect of the TiO_x layer is seen on the open-circuit voltage of a solar cell incorporating this layer, increasing to 900 mV from 600 mV in the case of a cell with a bare Ag layer for a bulk-heterojunction of poly[N-9″-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) and [6,6]-phenyl C_{70}-butyric acid methyl ester (PCBM70). The results of a joint theoretical and experimental study indicate that the photocurrent of a ZAT-based solar cell can be significantly enhanced by carefully balancing the optical-spacer and cavity-resonance effects, both of which are modulated by the thickness of the WO_3 layer used as a hole-collection layer at the top anode side. ZAT-based inverted solar cells with an optimized structure exhibit a power conversion efficiency as high as 5.1%, which is comparable to that of the ITO-based equivalent.

1. Introduction

Organic solar cells (OSCs) are emerging as a promising candidate for versatile, next-generation photovoltaic (PV) technology. Recent development of an OSC with power conversion efficiency approaching 10% [1,2] is regarded as a significant step towards its commercialization. In order for OSCs to compete with other emerging PV technologies, however, it is necessary to ensure that their device structure, material components, and fabrication process are compatible with low-cost manufacturing [3–6]. Differentiating features such as a high degree of flexibility should also be developed so that its advantages can be fully realized.

From the perspective of realizing low-cost OSCs, there has been strong interest in replacing indium tin oxide (ITO), a conventional electrode widely used in OSCs for decades, because indium is subject to price fluctuations due to limited supply and heavy demand. The poor flexibility of ITO electrodes has also been of concern in realizing highly flexible OSCs [7]. Among several alternative transparent electrodes suggested for OSCs [8–11], multilayer transparent electrodes (MTEs) based on dielectric–metal–dielectric (DMD) layers have recently garnered interest. Built on thin-film optics, the reflectance/transmittance of DMD-MTEs can be tuned in a wide range according to desired design specifications by varying the thickness of the participating dielectric layers. Unlike other emerging electrodes that often suffer from high resistivity, a sheet resistance (R_{sheet}) lower than 10 Ω/sq. is readily achieved in DMD-MTEs with transmittance (T) higher than 80% due to the high conductivity of the metal layers. In addition, DMD-MTEs were shown to have a mechanical flexibility that is far superior to ITO electrodes due to the ductile nature of thin metal layers [12]. Upon careful optical design considering the cavity resonance effect, performance

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comparable to that of conventional OSCs based on ITO has been demonstrated in OSCs with Ag-based MTEs such as $ZnS/Ag/WO_3$ [12], $MoO_3/Ag/MoO_3$ [13], or TeO_2/Ag/PEDOT:PSS [14]. Recently, we have shown that even devices with Cu-based MTEs of $ZnS/Cu/WO_3$ could also exhibit performance comparable to the conventional OSCs [15], demonstrating the potential importance of MTE-technology in realizing OSCs with a good cost-performance balance. Ag-based MTEs were also applied as a top electrode for a semi-transparent organic solar cell, which yielded efficiency close to that of an opaque cell [16].

Most of the MTEs reported to date, however, were anodes and thus were not applicable to inverted OSCs, which could potentially have significant advantages over those in a conventional structure [1,17]. In this work, we present a multilayer transparent electrode composed of $ZnS/Ag/TiO_x$ (ZAT) layers as an effective bottom cathode applicable to an inverted OSC. The basic properties of TiO_x layers deposited by solution processing on ZnS/Ag layers are examined, and the overall optical structure is optimized to maximize the short-circuit current density (J_{sc}) by carefully balancing the transmittance of the ZAT electrode, micro-cavity resonance, and constructive interference effect.

2. Experimental

Substrates were cleaned in an ultrasonic bath using soapy water, DI-water, acetone, and isopropanol in sequence and dried in a vacuum oven. The substrates were plasma-cleaned (PDC-32G, Harrick Plasma) before being loaded into a thermal evaporation chamber for deposition of ZnS (Alfa Aesar, 99.99%) and Ag (Alfa Aesar, 99.999%) layers. TiO_x was spin cast at 2500 rpm for 20 s either on a plasma-cleaned ITO glass or on the ZnS/Ag deposited glass and subsequently annealed on a hotplate at 80 °C for 10 min in ambient air. A blend of poly[N-9″-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) (1-material, Inc.) and [6,6]-phenyl C_{70}-butyric acid methyl ester (PCBM70) (Nano-C, Inc.) (35 mg/ml, 1:4 by weight, dissolved in dichlorobenzene) was spun-cast at 1100 rpm for 60 s in an N_2-filled glove box. The film was dried for an hour in the glove box and annealed on a hotplate at 80 °C for 10 min. The samples were then moved into the thermal evaporator for deposition of top anodes consisting of WO_3 (Alfa Aesar 99.99%) and Al layers. The final structure of each device was glass/y/PCDTBT:PCBM70/WO_3/Al with y being either $ZnS/Ag/TiO_x$ (ZAT) or ITO/TiO_x. The TiO_x solution was synthesized according to the method described in the previous work by Park et al. [18].

Current density–voltage (J–V) characteristics were measured with a source-measure unit (Keithley 238) under AM 1.5G illumination (1 Sun). The irradiance of the solar simulator (ABET technologies) was checked periodically using a calibrated Si photodiode. External quantum efficiency (EQE) spectra were measured using a monochromator coupled to a Xe arc lamp. An optical analysis was conducted with custom MATLAB™ codes based on the transfer-matrix formalism [19,20]. Optical constants of each layer were taken either from the literature [21] or measured using spectroscopic ellipsometry (Woollam, M2000D). The validity of the measured optical constants were carefully checked by comparing the actual transmittance with the calculated results (Fig. S1 in Supporting Information). Using these optical constants, the effect of each layer participating in the system was analyzed based on the transfer-matrix formalism in the framework of thin-film optics [12] (Fig. S2 for details).

The work functions of ZnS/Ag, and $ZnS/Ag/TiO_x$ were measured using UV photoelectron spectroscopy (UPS; AXIS Nova by Kratos Analytical) with a He I(21.2 eV) excitation source in an ultrahigh vacuum (1.0×10^{-9} Torr) in Jeonju Center of Korea Basic Science Institute (KBSI).

3. Results and discussion

3.1. Physical characteristics of cathodic MTEs with TiO_x

Fig. 1a shows the bright-field transmission electron microscopy (TEM) cross-sectional image of the proposed ZAT-based inverted OSC. The thickness of the active layer (50 nm) is consistent with the thickness obtained from the ellipsometric measurement. A thin layer of TiO_x (ca. 5–10 nm) is clearly identified between the Ag film (15 nm) and the active layer. Its presence is further confirmed by Energy Dispersive Spectrometer (EDS) measurement presented in Fig. S3 of Supporting Information.

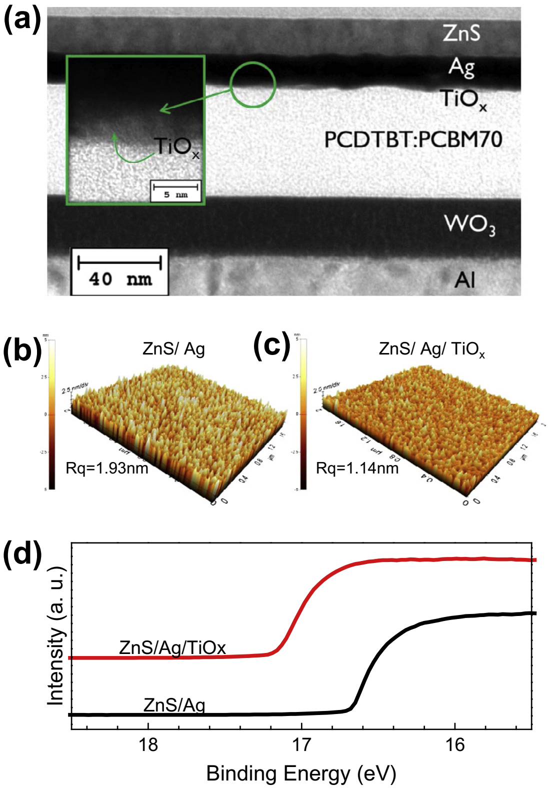

Fig. 1. (a) Cross-sectional bright-field TEM image of a ZAT-based organic solar cell. 3D AFM images for the top surface of (b) ZnS/Ag and (c) $ZnS/Ag/TiO_x$. (d) UPS data of Ag and Ag/TiO_x prepared on ZnS layers.