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Letter

Progress towards fully spray-coated semitransparent inverted organic solar cells with a silver nanowire electrode

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ABSTRACT

We demonstrated a fully spray-coated semitransparent organic solar cell, from the lowermost organic layer to the uppermost top electrode. The fabricated devices based on a poly (3-hexylthiophene):[6,6]-phenyl-C61 butyric acid methyl ester (P3HT:PCBM) are semitransparent (~70% transparency at long wavelength beyond 650 nm), fully spray-coated from organic layer to top electrode, highly efficient (~80% of that of a device with a conventional metal electrode).

1. Introduction

Organic solar cells (OSCs) are considered a promising solar cell technology, because of the tunability of the electronic and optical properties of organic semiconductors, and the potential for low-cost roll-to-roll manufacturing with solution-based printing process [1–7]. OSCs have been intensely investigated for their potential for making unique advances for broader applications. Several such applications would be enabled by high performance transparent devices, including building-integrated photovoltaic cells (BIPV), and integrated PV chargers for portable electronics. Recently, many research efforts have been made toward demonstrating visibly transparent or semitransparent OSCs [7–13]. Transparent conducting electrodes, such as thin metal films [13], metal oxide films [12], metal nanowire [7–9], and conducting polymers [10,11], have been deposited onto photoactive layer, to demonstrate transparent or semitransparent OSCs. However, these demonstrations often result in low transmittance, or low device efficiency. Recently, transparent conducting electrodes (TCEs) based on silver nanowires (Ag NWs) have been shown to provide high flexibility; while providing transmittances and sheet resistance at the level of indium tin oxide (ITO) [14,15]. Several groups have demonstrated solution processed Ag NW films in OSCs, using them as a bottom or a top electrode, and achieving comparable power conversation efficiencies (PCEs) to ITO-based devices [16–19]. Virtually all devices reported to date, however, were fabricated by using the conventional spin-coating method. The development of fully solution-processed devices, based on roll-to-roll compatible process, would greatly enhance the industrial viability of OSC technology. To date, spray-coating has been used to successfully coat layer of photoactive polymers, metal oxides and metal electrodes, demonstrating that it can be used to fabricate OSCs [11,20–24].

To realize the fully printing processed OSCs, an inverted architecture is normally used to avoid the vacuum process used for the deposition of the low-work-function metal cathode such as Al and Ca. In the inverted organic solar cells (IOSCs) applications, a high work-function anode, such as Ag and Au, is used to collect holes; and an

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electron-selective layer onto ITO is used to collect electrons [25,26]. The fully spray-coating process with a device structure of ITO/electron-selective layer/photoactive layer/hole-selective layer/top electrode is a very promising technique for fulfilling this requirement, owing to its simplicity and low-cost. One critical issue in the fabrication process of semitransparent IOSCs is how to form a high work function and semitransparent top electrode using a solution process, without damaging the device performance. Although a few attempts to spray-coat metal nanowires [7,8], metal nanoparticles [27-29], and conducting polymers [11] as top electrode have been successful, our approach is to use fully spray-coated IOSCs, from the lowermost electron-selective layer, to the uppermost semitransparent top electrode. Further, to demonstrate semitransparent devices, the see-through transmittance can be adjusted, by controlling the thickness of Ag NWs electrode. In this study, a spray-coating process is presented for the fabrication of semitransparent IOSCs. The fabricated device, based on a poly (3-hexylthiophene):[6,6]-phenyl-C61 butyric acid methyl ester (P3HT:PCBM), is semitransparent (~70% transparency at long wavelength beyond 650 nm), fully spray-coated, highly efficient (~80% of that of a device with a conventional metal electrode) and air-stable (~80% retention of original efficiency after 30 days).

2. Experimental

Semitransparent IOSCs were fabricated on patterned ITO-coated glass substrates (sheet resistance ~10 ohm/sqr.) of 2.5 × 2.5 cm^2 size, which were first cleaned in an ultrasonic bath containing acetone, and then boiled in isopropyl alcohol. The substrates were then dried in an oven, and treated with UV–ozone for 5 min. The spray-coating system uses two nozzles, as the core and cladding. The core nozzle was connected to an injection pump for the coating solution, and the cladding nozzle was linked to compressed N_2 gas. The spray-coating conditions in air atmosphere were optimized to minimize the surface roughness by varying the solution injection rate, N_2 gas flow rate, and printing speed [11,30]. First, a thin film of zinc oxide (ZnO) was spray-coated onto the ITO glass substrate from a ZnO sol–gel solution, and annealed at 300 °C for 20 min in air, resulting in a thickness of ~40 nm. The ZnO sol–gel solution was prepared using zinc acetate (16.40 mg, Aldrich) dissolved in 2-methoxyethanol (100 ml, Aldrich) using a magnetic stirrer. Ethanolamine (5 ml, Aldrich) was then added and the resulting solution was kept at 60 °C for 1 h under ambient conditions with vigorous stirring. Second, a P3HT:PCBM blended solution prepared at 1:1 mass ratio in 1,2-dichlorobenzene (10 mg/ml P3HT and 10 mg/ml PCBM) was spray-coated onto the ZnO layer with a thickness of ~270 nm, and annealed at 150 °C for 20 min in a glove box. A buffer layer of PEDOT:PSS (AI4083, H.C. Stark): isopropyl alcohol (IPA) (PEDOT:PSS:IPA = 1:6) was prepared using spray-coating onto the P3HT:PCBM layer with a thickness of ~40 nm at the temperature of ~80 °C. The coated PEDOT:PSS film was annealed at 150 °C for 1 min in a glove box. Finally, an as-received dispersion containing Ag NW (Cambrios ClearOhm Ink) was spray-coated on the PEDOT:PSS layer, and annealed at 120 °C for 5 min, in a glove box. In the spray-coating of the Ag NWs electrode, a shadow mask was used to cover the PEDOT:PSS layer, to form cell areas of 0.36 cm^2. Detailed information of the optimized spray-coating conditions for ZnO, P3HT:PCBM, and PEDOT:PSS layer can be found elsewhere [30]. In an opaque control device, the ~40-nm-thick ZnO, ~270-nm-thick P3HT:PCBM and ~40-nm-thick PEDOT:PSS layers were fully spray-coated. Finally, a 120-nm-thick Ag electrode was evaporated at 3×10^{-6} Torr. The fabricated IOSCs was characterized using restricted illumination by inserting a shadow mask to eliminate excess photocurrent from conductive PEDOT:PSS layer [30]. The current–voltage (J–V) characteristics were measured under AM 1.5 simulated illumination, with an intensity of 100 mW/cm^2 (Pecell Technologies Inc., PEC-L11 model). The intensity of sunlight illumination was calibrated using a standard Si photodiode detector with a KG-5 filter. The J–V curves were recorded automatically with a Keithley SMU 2400 source meter, by illuminating the IOSCs. The quantum efficiency measurement system (Oriel IQE-200) used to determine the incident-photon-to-charge-carrier efficiency (IPCE) comprised a 250 W quartz-tungsten-halogen (QTH) lamp as the light source, a monochromator, an optical chopper, a lock-in amplifier, and a calibrated silicon photodetector. The layer thickness was measured using a surface profiler (KLA-Tencor, P-11). The specular and diffusive transmittance spectra were measured over the wavelengths between 300 and 800 nm by UV–visible spectrophotometry (Varian, Cary 5000). Specular transmittance is measured by detecting only light that comes out of the sample parallel to the incident light. The diffusive transmittance only differs from specular transmittance in that diffusive transmittance includes all forward scattered light measured using an integrating sphere. The film thicknesses, sheet resistances, and optical transmittances were measured using a surface profiler (Alpha Step P-11, Tencor Instruments), a four-point probe system (Mitsubishi Chemical Corporation), and a UV–vis spectrophotometer (Cary 5000, Varian), respectively.

3. Results and discussion

To increase Ag NW thickness for application in device top electrodes, a multi-layer coating process was investigated to further lower the sheet resistance of the films, resulting in thickness that increased from ~35 to ~400 nm with the number of sprayings. As shown in Fig. 1(a), the thickness of Ag NW film was linearly proportional to the number of spray-coatings. The inset of Fig. 1(a) shows that the Ag NWs in the network were uniformly distributed and randomly oriented over the entire coating area with an average diameter of approximately 25 nm and an average length of a few tens of micrometers. Fig. 1(b) and (c) shows the behavior of transmittance and sheet resistance as a function of the thickness of the spray-coated Ag NW electrode. We determined the diffusive (T_{diff}) and specular (T_{spec}) transmittance spectra of Ag NW electrodes coated on PEDOT:PSS/glass substrates over