Thin Solid Films 573 (2014) 14–17

Contents lists available at ScienceDirect

Thin Solid Films

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

Solution-processed silver nanowires as a transparent conducting electrode for air-stable inverted organic solar cells

Myungkwan Song [a], Jong-Kuk Kim [a], Shi-Young Yang [b,*], Jae-Wook Kang [b,*]

[a] Surface Technology Division, Korea Institute of Materials Science, Changwon 641-831, Republic of Korea
[b] The Graduate School of Flexible and Printable Electronics, Polymer BIN Fusion Research Center, Chonbuk National University, Jeonju 561-756, Republic of Korea

ARTICLE INFO

Article history:
Received 12 April 2014
Received in revised form 24 October 2014
Accepted 29 October 2014
Available online 5 November 2014

Keyword:
Silver nanowire
Transparent conducting electrode
Inverted organic solar cell
Solution process

ABSTRACT

Highly efficient and air-stable inverted organic solar cells (IOSCs) were fabricated using solution-processed silver nanowire electrodes. The electrodes showed a low sheet resistance of ~16 Ω sq^{-1} and a high transmittance of ~95% at a wavelength of 550 nm. A solution-processed ZnO buffer layer is typically used for electron transport and effective passivation of the surface of Ag NW electrodes. The device performance of the IOSCs that used these Ag NW electrodes, which were fabricated on a glass or plastic substrate, was >94% of that of devices containing indium tin oxide (ITO) electrodes. This indicates that solution-processed Ag NW electrode can replace commercialized ITO and can be utilized in roll-to-roll and large-area fabrication processes.

1. Introduction

Flexible organic solar cells (OSCs) have attracted significant interest because of their great potential as a green energy source due to their large area, light weight, superior mechanical flexibility, and low cost processing in roll-to-roll manufacturing [1–4]. Indium tin oxide (ITO), which is a commonly used material in transparent conductive electrodes (TCEs), is not suitable for use in transparent electrodes for the fabrication of flexible devices because it is brittle and cracks easily under bending stress [5,6]. Moreover, the production of ITO is costly and complex because of the use of various vacuum-based techniques [7,8]. There are several emerging transparent electrodes that have shown promise as a replacement for ITO such as carbon nanotubes [9–12], graphene [13–15], metal nanowires [16–25], and conducting polymers [26].

Among these materials, silver nanowires (Ag NWs) are considered one of the most promising TCEs due to their excellent solution compatibility, optical transparency, electrical conductivity, and mechanical flexibility. However, because the rough surface of Ag NW thin films is likely to cause short circuits in electronic devices, their surface morphology poses a major challenge for its application in flexible electronic devices. Recently, several attempts have been made to provide a solution to overcome this problem and to fabricate efficient OSCs by the overcoating of buffer layers such as poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) [22]. Although Ag NW-based flexible OSCs reportedly demonstrate good device performance and flexibility, devices with a conventional structure (TCE/PEDOT:PSS/active layer/Al) have a very short life-time in the absence of additional encapsulation. To increase stability, OSC has an inverted structure (TCE/electron selective layer/active layer/PEDOT:PSS/Ag) because the Ag anode has better oxidation resistance than the Al cathode used in conventional OSCs [27–31]. In inverted OSCs (IOSCs), zinc oxide (ZnO) is one of the most widely studied materials due to its promising optical, electrical, and optoelectronic properties. The formation of a ZnO interfacial layer between the active layer and TCE in IOSCs is an important process for enhancing the selectivity of the contact [30,31]. In this paper, we report air-stable IOSCs using solution-processed Ag NW transparent electrodes fabricated using a blend of poly(3-hexylthiophene) (P3HT)/[6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM). These TCEs showed a low sheet resistance (R_{sheet}) of ~16 Ω sq^{-1} and a high optical transmittance of ~95% at a wavelength of 550 nm ($T_{550\ nm}$). The power conversion efficiency (PCE) of the IOSCs utilizing Ag NW electrodes, which were fabricated on a glass or plastic substrate, was >94% of the value of devices with ITO electrodes.

2. Experimental details

The Ag NW films were prepared using a spin-coating process on precleaned glass or polyether sulfone (PES, 188 μm thickness, i-components Co., Ltd.) substrates. PES substrates were attached to a supporting glass substrate using carbon tape. An as-received dispersion containing Ag NWs (Cambrios ClearOhm Ink) was spin-coated for 40 s at a speed of 1000 rpm. The formed Ag NW films were annealed at 120 °C for 5 min in a glove box filled with nitrogen, resulting in ~55-nm-thick films. The ITO/PES films were vacuum-sputtered in our

* Corresponding authors.
E-mail addresses: yangsy@jbnu.ac.kr (S.-Y. Yang), jwkang@jbnu.ac.kr (J.-W. Kang).

http://dx.doi.org/10.1016/j.tsf.2014.10.098
0040-6090/

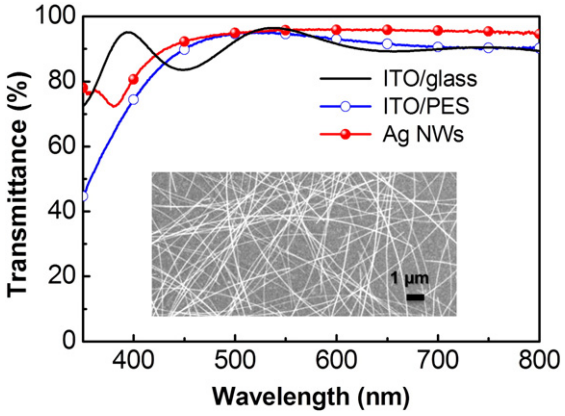

Fig. 1. Transmittances of the Ag NW and ITO films. Inset: SEM image of an Ag NW film with R_{sheet} ~ 16 Ω sq^{-1}.

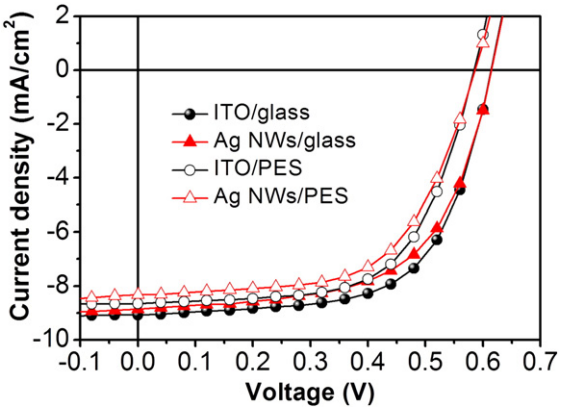

Fig. 2. Characteristic *J–V* curves of IOSCs fabricated on Ag NW and ITO electrodes under AM 1.5 G illumination (100 mW cm^{-2}).

laboratory, and the ITO/glass film was commercially obtained (Shinhan SNP Co., Ltd, $T_{550\ nm}$ ~ 96% at R_{sheet} ~ 10 Ω sq^{-1}). The ITO/PES films were formed by depositing an ~100-nm-thick layer of ITO ($T_{550\ nm}$ ~ 94% at R_{sheet} ~ 50 Ω sq^{-1}) on a PES substrate by radio-frequency (RF) superimposed DC magnetron sputtering [6]. 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. The scanning electron microscopy (SEM) micrographs were obtained using a JSM-6700 F field emission scanning electron microscope at a voltage of 5.0 kV.

The IOSCs were fabricated using Ag NW film-coated glass and PES substrates or ITO film-coated glass and PES substrates. The ZnO solution was spin-cast on top of the various TCEs. The ZnO films were annealed at 150 °C for 10 min in air, resulting in ~40-nm-thick films. The ZnO sol–gel solution was prepared using zinc acetate (16.40 mg, Aldrich) dissolved in 2-methoxyethanol (100 ml, Aldrich) mixed by 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 and vigorous stirring.

The P3HT:PCBM blend solution was prepared at a 1:1 mass ratio in 1,2-dichlorobenzene (20 mg/ml P3HT and 20 mg/ml PCBM). The active material was then coated onto the ZnO layer with an average thickness of ~250 nm using a spin-coating process (spin speed of 600 rpm for 40 s) in a glove box. Subsequently, solvent evaporation was performed for 2 h, and pre-annealing was carried out at 150 °C for 20 min in a glove box. A buffer layer of poly(3,4-ethylenedioxylenethiophene) (PEDOT-PSS, Baytron P):isopropyl alcohol (IPA) (PEDOT-PSS:IPA = 1:2) was prepared using a spin coater after passing through a 0.45 μm filter with a thickness of ~40 nm. The coated PEDOT-PSS film was dried at 150 °C for 1 min on a hot plate in a glove box. Finally, a 120-nm-thick Ag electrode was deposited on the PEDOT:PSS layer by thermal evaporation at 4×10^{-4} Pa. The effective area of the active layer for the solar cell prepared in this approach was 0.38 cm^2, which was determined using a shadow mask. The current density–voltage (*J–V*) characteristics of the IOSC were measured under AM 1.5 simulated illumination at an intensity of 100 mW cm^{-2} (Pecell Technologies Inc., PEC-L11). The intensity of the sunlight illumination was calibrated using a standard Si photodiode detector with a KG-5 filter [3,6]. The *J–V* curves were recorded automatically using a Keithley SMU 2410 source meter by illuminating the prepared IOSC. The quantum efficiency measurement system used to determine the incident photon to current conversion efficiency (IPCE) spectra (Oriel IQE-200) used a 250 W quartz tungsten halogen (QTH) lamp as the light source and contained a monochromator, an optical chopper, a lock-in amplifier, and a calibrated silicon photodetector [6,22].

3. Results and discussion

Fig. 1 shows the transmittance spectra of the Ag NW and ITO electrodes. When evaluating transparent metal NW electrodes for solar cell applications, the diffusive transmittance is more important than the specular transmittance. The random nature of the Ag NWs leads to substantial scattering of incident light. Additionally, the large scattering of the Ag NWs enhances the solar cell performance due to an effective increase in the light path length in the photoactive layer.

For the Ag NW film, the diffusive transmittance was greater than the specular transmittance, which is in accordance with previously reported results [22,25]. However, the specular and diffusive transmittances of the ITO films were almost the same. The diffusive transmittance of the Ag NW electrodes was $T_{550\ nm}$ ~ 95% with R_{sheet} ~ 16 Ω sq^{-1}, which is comparable to that commercially available ITO electrodes on glass ($T_{550\ nm}$ ~ 96%, R_{sheet} ~ 10 Ω sq^{-1}) and much improved compared to ITO/PES ($T_{550\ nm}$ ~ 94%, R_{sheet} ~ 50 Ω sq^{-1}). The inset in Fig. 1 shows a scanning electron microscopy (SEM) image of an Ag NW film fabricated on a PES substrate. The nature of randomly dispersed Ag NWs leads to protrusions produced by overlapping wires that are about two or three times higher than the diameter of the nanowires (approximately 25 nm). In this case, the surface roughness of the Ag NWs is not suitable for the application of thin film OSCs, where the thickness of each layer is less than 250 nm. This rough surface may induce device failure due to power shortage [22]. The subsequent coating of a solution-processed ZnO buffer layer reduces the surface roughness of the Ag NWs from

Table 1
Photovoltaic characteristics of the IOSCs under AM 1.5 G illumination (100 mW cm^{-2}). The values are the average of five samples. The shunt resistance (R_{sh}) and series resistance (R_s) of the IOSCs were estimated by fitting of the dark *J–V* curves.

	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF* (%)	R_{sh} (Ω cm^2)	R_s (Ω cm^2)	PCE (%)
ITO/glass	9.11 ± 0.03	0.61 ± 0.02	61.65 ± 0.03	1.00×10^4	6.32	3.46 ± 0.07
Ag NWs/glass	8.89 ± 0.03	0.61 ± 0.01	59.56 ± 0.01	8.62×10^3	6.86	3.25 ± 0.02
ITO/PES	8.49 ± 0.17	0.59 ± 0.01	61.01 ± 0.02	6.81×10^3	7.20	3.05 ± 0.10
Ag NWs/PES	8.42 ± 0.11	0.58 ± 0.10	59.76 ± 0.01	6.00×10^3	7.45	2.96 ± 0.03