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Letter

High fill factor polymer solar cells comprising a transparent, low temperature solution processed doped metal oxide/metal nanowire composite electrode

Tobias Stubhan [a,*], Johannes Krantz [a], Ning Li [a], Fei Guo [a], Ivan Litzov [a], Matthias Steidl [a], Moses Richter [a], Gebhard J. Matt [a], Christoph J. Brabec [a,b]

[a] Institute of Materials for Electronics and Energy Technology (I-MEET), Friedrich-Alexander-University Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany
[b] Bavarian Center for Applied Energy Research (ZAE Bayern), Am Weichselgarten 7,91058 Erlangen, Germany

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ABSTRACT

In this paper we report on the replacement for the commonly used ITO electrode material by a low temperature solution processed silver nanowire/(doped) metal oxide composite. Devices employing silver nanowires (AgNWs)/buffer layer electrodes with a photoactive layer of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61} butyric acid methyl ester (PCBM) are showing a comparable performance to the ITO reference cell with fill factors (FF) of over 62% and a power conversion efficiency of ~2.7%. Zinc oxide (ZnO) and highly conductive Al doped ZnO (AZO) are used as buffer layer. AgNW devices without a buffer layer have a high open circuit voltage (V_{OC}) but the FF and the short circuit current density (j_{SC}) are substantially lower. Overall it is demonstrated that AgNWs and the low temperature solution process of the buffer layer are an attractive device concept towards an indium free organic solar cell.

1. Introduction

Solution processed electrodes are required for large scale printed organic photovoltaics (OPV) and generally organic electronics [1]. The key requirements are high transparency and conductivity at the same time, but various further properties like stability and low temperature deposition also need to be fulfilled. Graphene sheets [1–4], carbon nanotubes [1,5–7], transparent conductive oxide nanoparticles and -rods [1,8], conducting polymers [1,9–11] and printed metal grids [1,12] were already proposed as possible alternatives. Due to the low sheet resistance, high transmittance and solution processing, silver nanowires (AgNWs) are considered as highly promising candidates to replace brittle and expensive sputtered indium–tin-oxide (ITO) [13–18].

The AgNW percolation type electrode needs to be filled with a buffer layer to smooth out the roughness, to adjust the work function and provide charge selectivity. N-type metal oxides like ZnO and TiO_x are a suitable and stable material group, that find wide application as n-type buffer layers in OPV [19–25]. The application of TiO_x and intrinsic ZnO as buffer layers for AgNWs are already reported [13,17]. Leem et al. successfully applied TiO_x as buffer layer for an electrode using NWs from Cambrios Technologies Corporation with comparable properties to those NWs used in this study [17]. The typical size of the NWs was a few tens of nanometers in diameter and a few tens of micrometers in length. One further report uses intrinsic zinc oxide to fill a network comprising rather thick (~80 nm) and short (~6 μm) AgNWs [13]. Because of the high roughness of this electrode, a very thick active layer (400 nm) is needed to reduce shunts. This is not applicable to most new high performance polymers, as most of them require active layer thicknesses in the range 70–130 nm [26–28]. Consequently we choose a just 100 nm thick P3HT:PCBM active layer for our devices.

Lately various reports on doped ZnO appeared that demonstrated its advantages over intrinsic zinc oxide [20,25,29,30–33]. The performance of solar cells using an approx. 100 nm thick intrinsic ZnO buffer layer on planar ITO electrodes is reduced significantly compared to a thin buffer layer. In contrast, doped zinc oxide layers allow a film thickness above 100 nm while maintaining high performance [29,33]. Puetz et al. reported the combination of indium doped zinc oxide and (high-workfunction) silver as efficient cathode [31].

In this report we demonstrate low temperature, solution processed AgNW/(doped) metal oxide electrodes with excellent functionality. We compare doped and intrinsic zinc oxide buffer layers for this percolation type electrode. In contrast to planar ITO electrodes we find that the performance of intrinsic and doped

* Corresponding author. Tel.: +49 9131/85 27634; fax: +49 9131/85 28495.
E-mail address: tobias.stubhan@ww.uni-erlangen.de (T. Stubhan).

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zinc oxide is quite comparable when combined with nanowire electrodes.

2. Experimental

2.1. Synthesis of Al doped ZnO

Al doped ZnO: $Zn(Ac)_2 \times 2H_2O$ (2.17 g) and $Al(NO_3)_3 \times 9H_2O$ (0.037 g) were mixed in 100 mL of ethanol. The composite was heated up to 80 °C for 3 h and afterwards filtered through a 0.45 μm filter to remove insoluble materials. The route is adopted from Søndergaard et al. [30]. Zinc oxide was synthesized adopting a literature route as published earlier [20,29].

2.2. Device processing

The inverted photovoltaic devices were processed and characterized in ambient atmosphere unless stated otherwise. Reference devices were processed on pre-structured ITO coated glass substrates (as obtained from Osram, 12.3 Ω/□). AgNW based devices were processed on float glass slides. The AgNW film was deposited via doctor blading and annealed at 140 °C for 15 min resulting into a low sheet resistance of 7 Ω/□.

The following layers were processed identically on ITO and AgNWs. The samples with a buffer layer contain a layer of ZnO or AZO deposited from solution via doctor blading. The annealing of ZnO and AZO was achieved by heating the samples to 140 °C for 10 min. P3HT was purchased from Merck and technical grade PCBM from Solenne. Both semiconductors were separately dissolved in chlorobenzene at a concentration of 2 wt% and stirred for at least 1 h at 60 °C before being blended in a volume ratio of 1:1. The blended solution was stirred for at least another hour at 60 °C before used. The approx. 100 nm thick active layer was deposited via doctor blading. PEDOT:PSS (Clevios PH) from H.C. Starck was diluted in isopropyl alcohol (1:5 volume ratio) before being deposited via doctor blading. The samples were brought into a glovebox and the whole stack was annealed at 140 °C for 5 min on a hot plate. Afterwards a 100 nm thick Ag layer was thermally evaporated to form the top electrode, before the devices were annealed at 140 °C for 5 min again. The active area of the investigated devices was 10.4 mm^2. Current density–voltage (j–V) characteristics were measured with a source measurement unit from BoTest. Illumination was provided by an OrielSol 1A solar simulator with AM 1.5 G spectra at 0.1 W/cm^2.

Table 1
Key parameter set of investigated devices with different cathode configurations (cathode-P3HT: PCBM–PEDOT: PSS–Ag).

Device	V_{OC} (mV)	j_{SC} (mA/cm^2)	PCE (%)	FF (%)	R_S (Ω cm^2)	R_{Shunt} (kΩ cm^2)
AgNW	545	−6.52	1.65	46.4	1.3	13
ITO–AZO	569	−8.57	3.17	64.7	0.3	47
AgNW–AZO	548	−7.86	2.68	62.3	1.3	51
ITO–ZnO	592	−7.77	2.87	62.3	0.3	18
AgNW–ZnO	556	−7.34	2.46	60.2	1.0	14

3. Results and discussion

Fig. 1 shows the AFM images of the AgNWs and AgNWs covered by the AZO layer. The metal oxide nanoparticles enclose the nanowires. Thereby the AZO film smoothens out the roughness of the AgNW electrode from RMS of over 10 nm to around 4 nm and generates a rolling-hill morphology without the sharper edges and ridges observed for the pure AgNW film.

The j–V characteristics of the investigated devices are shown in Fig. 2 and the corresponding key parameters are listed in Table 1. Interestingly in contrast to the previous report of Leem et al. [17], we found that the reference device with only AgNWs performs already quite well. The V_{OC} is already comparable to the cells with buffer layer. This is explained by the quite low work function (WF) of 4.4 eV measured by a Kelvin Probe setup (KP Technology Ltd., SKP5050). The low WF matches the lowest unoccupied molecular orbital (LUMO) of PCBM well. But as the bare AgNW electrode lacks selectivity and is quite rough, the FF of the device is low at 46.4%, the j_{SC} 6.52 mA/cm^2 and the PCE 1.65%.

When a ZnO or an AZO buffer layer is used the FFs are largely increased to 60.2 and 62.3%. The j_{SC}s are also enhanced to −7.34 and −7.86 mA/cm^2 leading to PCEs of 2.46% and 2.68%. These results are quite comparable to the reference devices on ITO substrates. There are only slightly better values for the FF (~2% (absolute)), V_{OC} (~20–45 mV) and j_{SC} (~0.4–0.7 mA/cm^2) of the ITO based devices leading to 0.4–0.5% (absolute) higher PCE. Efficient inverted solar cells based on AgNWs are achieved using

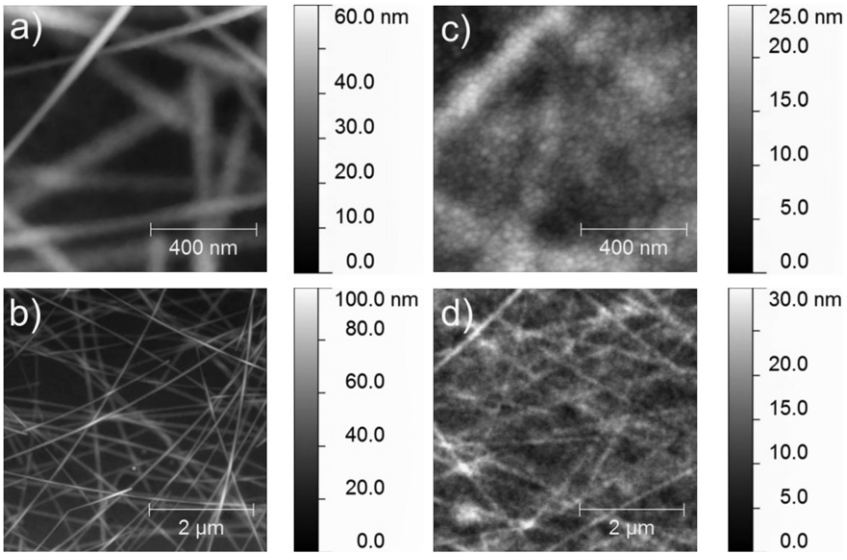

Fig. 1. (a) and (b) displays the surface topography of the AgNW films (RMS: ~11–15 nm) and (c) and (d) shows the surface of the AgNWs covered by the AZO layer (RMS ~4 nm).