Organic solar cells on indium tin oxide and aluminum doped zinc oxide anodes

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The authors compare organic solar cells using two different transparent conductive oxides as anode: indium tin oxide (ITO) and three kinds of aluminum doped zinc oxide (ZAO). These anodes with different work functions are used for small molecule photovoltaic devices based on an oligothiophene derivative as donor and fullerene C60 as acceptor molecule. It turns out that cells on ITO and ZAO have virtually identical properties. In particular, the authors demonstrate that the work function of the anode does not influence the $V_{oc}$ of the photovoltaic device due to the use of doped transport layers. © 2007 American Institute of Physics. [DOI: 10.1063/1.2771050]

Organic solar cells find increasing interest as a possible low-cost regenerative energy source. Tang1 presented in 1986 an efficient organic solar cell based on a donor-acceptor heterojunction realized with small molecules and having about 1% efficiency. A further improvement was reported in 1986 an efficient organic solar cell based on a donor-acceptor

levels to reduce energetic losses during exciton separation, as

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The authors compare organic solar cells using two different transparent conductive oxides as anode: indium tin oxide (ITO) and three kinds of aluminum doped zinc oxide (ZAO). These anodes with different work functions are used for small molecule photovoltaic devices based on an oligothiophene derivative as donor and fullerene C60 as acceptor molecule. It turns out that cells on ITO and ZAO have virtually identical properties. In particular, the authors demonstrate that the work function of the anode does not influence the $V_{oc}$ of the photovoltaic device due to the use of doped transport layers. © 2007 American Institute of Physics. [DOI: 10.1063/1.2771050]

However, for a broad application, organic solar cells have still to be significantly improved in terms of efficiency, stability, and cost. One aspect is to increase the open circuit voltage by using donors and acceptors with optimized energy levels to reduce energetic losses during excitation separation, as we have recently demonstrated by replacing the frequently used phthalocyanines with a new class of oligothiophene.2 These cells reach open circuit voltages of up to 1.0 V and high current densities, which is supported by the high absorption of the particular thiophene DCV5T (absorption coefficient $\alpha = 2.7 \times 10^5 \text{ cm}^{-1}$).

A key advantage of organic solar cells is the potential for low-cost production, supported by the possibility to fabricate them on flexible substrates such as plastic foils. However, organic solar cells (OSC) reported so far are usually based on indium tin oxide (ITO) anodes, which is a comparably expensive material. Therefore, cheaper anode materials such as polymers or alternative transparent conductive oxides have to be investigated. Recently, aluminum doped zinc oxide has been employed as transparent conductive oxide (TCO) for organic light emitting diodes8–10 and organic solar cells.11

In this letter, we show that organic solar cells based on aluminum doped zinc oxide as an alternative to indium tin oxide have comparable performance. We also demonstrate that the work functions of the anodes have no influence on the open circuit voltage of the cells. Finally, we demonstrate that comparatively rough etched substrates still allow to realize cells when doped transport layers are used.

As substrates, either ITO, obtained from Thin Film Devices Inc. (Anaheim, CA) or different aluminum doped zinc oxide (ZAO) coated glass substrates are used. The ZAO 1 substrates are produced at Fraunhofer IPMS, Dresden by direct current (dc) magnetron sputtering,10 using a ZnO target with 2 wt % Al2O3. The ZAO 2 and ZAO 3 (FZ Jülich) are fabricated by radio frequency (rf) magnetron sputtering.12 A doping ratio of 1 wt % Al2O3 in ZnO is used. In an attempt to achieve a better light injection into the OSC, the ZAO 3 is additionally etched for approximately 25 s in diluted hydrochloric acid (0.5% HCl).13 The surface roughness of the TCOs is obtained from $10 \times 10 \mu \text{m}^2$ images recorded with an atomic force microscope (in tapping mode) from Digital Instruments. The photovoltaic cells have an average area of $4 \times 70 \text{mm}^2$ and are evaporated in a UHV multichamber system (typical pressure of $10^{-8} - 10^{-7} \text{ mbar}$). For the $p$-doped hole transport layer, $N,N'$-di(naphthalen-1-yl)-$N,N'$-diphenyl-benzidine (NPD) or 4,4',4''-(tris(2-naphthyl)phenylamino)-triphenylamine (TNATA) are used, with a proprietary acceptor dopant from Novaled AG, Dresden (doping ratio of approximately 20 mol % in NPD and 6 mol % in TNATA, respectively). $\alpha,\alpha'$-bis(2,2-dicyanovinyl)-quinqueithiophene with ethyl groups as side chains (DCV5T-Et) is used as donor and Buckminster fullerene C60 as acceptor material. The cathode is formed by using a thin layer of 4,7-diphenyl-1,10-phenanthroline (BPhen) and aluminum. NPD, TNATA, C60, and BPhen are cleaned by thermal gradient sublimation before evaporation. DCV5T-Et and the acceptor dopant are used as received. Current-voltage measurements are carried out in a nitrogen glovebox using a source measurement unit 236 (Keithley) and taken under a sun simulator (Hoenle) calibrated with an outdoor reference cell provided by the Fraunhofer Institut für...
Solare Energiesysteme ISE (Freiburg, Germany).

The transmission of the substrates is presented in Fig. 1. For ITO, ZAO 1, and ZAO 2, a Shimadzu spectrometer was used. For ZAO 3, the transmission of a comparable substrate having a thickness of approximately 600 nm is shown (using a Perkin Elmer spectrometer); to avoid light scattering and internal light trapping an index matching fluid was used. All substrates show a high transmission in the visible spectral region. The thicknesses are given by the company for ITO, ZAO 1, and ZAO 2. The sheet resistances of the substrates obtained from a four-contact measurement technique (substrate geometry taken into account) are as follows: ITO: 42 Ω/sq, ZAO 1: 34 Ω/sq, ZAO 2: 8 Ω/sq, and ZAO 3: 27 Ω/sq.

The solar cells are based on an oligothiophene derivative (DCV5T-Et) as donor and C₆₀ as acceptor molecule. The absorption of this oligothiophene is similar to the derivative we introduced earlier with a high absorption between 500 and 650 nm and a maximum at around 570 nm. In comparison to the oligothiophene [α,α′-bis(2,2-dicyanovinyl)-quinquethiophene; DCV5T] used in the butyl-side chains are changed to ethyl groups in this derivative to provide a more flexible molecule with less decomposition during evaporation.

FIG. 1. Transmission of the different anode substrates: ITO (solid line), ZAO 1 (dotted line), ZAO 2 (line with open circles), and ZAO 3 (dashed line); transmission for an approximately 600 nm thick substrate is shown. ZAO 1 is produced using dc magnetron sputtering, ZAO 2 and ZAO 3 with rf sputtering. ZAO 3 has been etched with HCl.

FIG. 2. (Color online) AFM images of the different substrates used for roughness determination (size of 10×10 μm²): (a) ITO (z scale of 21.8 nm), (b) ZAO 1 (z scale of 36.8 nm), (c) ZAO 2 (z scale of 9.5 nm), and (d) ZAO 3 (z scale of 285.3 nm). The ITO shows some spikes, whereas the surface of the ZAO 1 and ZAO 2 is very smooth.

FIG. 3. J-V curves of photovoltaic cells (measured at 1–1.2 sun) using ITO (cell A, solid line), ZAO 1 (cell B, dotted line), ZAO 2 (cell C, line with open circles), and ZAO 3 (cell D, dashed line) as anode material. All cells reach the same Voc and comparable FF. The lower current density in cell D is a result of a thick p-doped hole transport layer, which absorbs a small amount of the incoming light as confirmed in optical simulation.

The cells have the following layer sequence (thicknesses in brackets, values in nanometers): TCO/Au (1)/p-doped-NPD (10)/NPD (5)/DCV5T-Et (10)/C₆₀ (40)/BPhen (6)/Al (100) with ITO as TCO in cell A and ZAO 1 in cell B and TCO/Au (1)/p-doped TNATA/p-doped-NPD (10)/NPD (5)/DCV5T-Et (10)/C₆₀ (40)/BPhen (6)/Al (100) using ZAO 2 as TCO and 30 nm p-doped TNATA in cell C, and ZAO 3 and 150 nm p-doped TNATA in cell D. The additional p-doped TNATA layer in cell D does not influence the shape of the J-V curve. In cell D, the thick TNATA layer is needed to avoid shorts due to the large surface roughness of the ZAO 3. The J-V curves of the solar cells are shown in Fig. 3, additionally the characteristic parameters are given in Table I. The current densities in Table I are normalized for a sun intensity of 100 mW/cm² for a better comparison.

For the ITO, we estimate a work function of ~4.6 eV as previously measured with ultraviolet photoelectron spectroscopy (UPS) for substrates from the same company. The work function of aluminum doped zinc oxide depends strongly on the amount of doping. Therefore, a number of different values have been published in the last few years. For the ZAO 1, we determine the work function to be approximately ~4.5 eV using kelvin probe microscopy. We estimate a different work function for the ZAO 2 and ZAO 3, respectively, due to a lower doping ratio of Al₂O₃ in ZnO compared to the ZAO 1.

All photovoltaic cells reach nearly the same open circuit voltage of approximately 1.0 V. We determine a highest occupied molecular orbital (HOMO) of the oligothiophene using UPS of approximately ~5.6 eV. Although a large energy difference of the HOMO between the oligothiophene and the TCO exists, the doped transport layer in between allows a quasi-Ohmic contact, as shown previously. The current densities of all solar cells are comparable. From optical simulation we assume a reduced current density (approximately 9.2%) of cell D (ZAO 3) compared to cell C (ZAO 2) caused by the absorption of the thick TNATA layer. All cells have nearly the same fill factor FF. The efficiencies of the cells are estimated and corrected for the spectral mismatch of our sun simulator to the AM1.5 sun spectrum, as presented in Ref. 7. We determine the external quantum efficiency spectrum of cell C and cell D with a homemade setup and convolute these spectra with the AM1.5 sun spectrum to estimate the current density of these cells under these conditions. The corrected current densities are used in the efficiency calculation. Comparing the cells presented here,
cell C shows a higher forward current than the other cells. This might be a result of the lower sheet resistance $R_s$ of this substrate. The estimated series resistance $R_s$ of the device is a result of a fit by using

$$I = I_s \left( \exp \left( \frac{e(U - R_s I)}{nkT} - 1 \right) \right),$$

(1)

to model the $I-V$ curves in the dark between 0.9 and 1.5 V. Here, $n$ represents an ideality factor (introduced for diodes) and $I_s$ a constant similar to a saturation current of an inorganic solar cell. All three values were taken as variable in this fit and the series resistance is presented in Table I. The lower $R_s$ of cell C might be a result of a lower sheet resistance of the TCO, in agreement with its larger thickness. The higher series resistance in cell D is possibly caused by the higher surface roughness of this substrate.

In conclusion, small molecule organic solar cells using ZAO as an alternative TCO for the anode are presented. The open circuit voltage in these cells is defined by the Fermi levels of the free charge carriers in the photovoltaic materials; the work function of the TCO does not influence this value when using doped materials on top of the anode. This aspect is an additional advantage of using doped transport materials.

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<table>
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<th>Cell</th>
<th>$V_{oc}$ (V)</th>
<th>$j_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>Est. $\eta$ (%)</th>
<th>Calc. $R_s$ ((\Omega\ cm^2))</th>
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