



Doped hole transport layers processed from solution: Planarization and bridging the voids in noncontinuous silver nanowire electrodes



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ABSTRACT

We report about solution-processing of a doped small molecule hole transport layer (s-HTL) comprising of N,N'-((diphenyl-N,N'-bis)-9,9-dimethyl-fluoren-2-yl)-benzidine (BF-DPB) as matrix and the p-dopant "NDP9" in the non-halogenated solvent tetrahydrofuran (THF). We show that the doping process is already happening in solution and stays effective after coating. Conductivities achieved with this process are comparable to those reached by thermal co-evaporation under high vacuum, which is the usual deposition method for this material. Applied as planarization layer onto AgNW films with best performance values of $15 \Omega/\square$ and 83.5% total transmission including the substrate, the s-HTL is proving its ability to sufficiently smoothen the initially rough AgNW topography. We analyze the necessary lateral conductivity to bridge micrometer-large voids in the mesh, as they are inherent in nanowire network electrodes. In combination with zinc phthalocyanine:C₆₀ organic solar cells, a s-HTL conductivity less than $1 \times 10^{-4} \text{ S/cm}$ can lead to decreased device performance with a loss greater than 10% for nanowires with 90 nm diameter and the associated mesh width. Furthermore, we demonstrate more efficient vacuum-deposited p-i-n solar cells with an oligothiophene (DCV5T-Me) as donor, C₆₀ as acceptor. They exhibit power conversion efficiencies up to 4.4% on AgNW bottom electrodes with s-HTL, compared to 4.1% on ITO with s-HTL as reference device.

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1. Introduction

Indium tin oxide (ITO) as transparent conductive oxide (TCO) is frequently used as transparent conductor for display technology and optoelectronic devices such as organic light emitting diodes (OLEDs) and organic photovoltaics (OPV) [1–4]. It shows excellent optical and electrical properties [5] and is an industry proven technology.

In view of using cheap mass production technologies for large area OLED and OPV devices like roll-to-roll coating with solution-based deposition techniques (e.g. inkjet-printing or spray-coating) on temperature sensitive polymer substrates, plasma deposition of ITO is a likely technology bottleneck.

TCOs are stiff and brittle materials which could exhibit cracks when deposited and bended on flexible substrates like PET or PEN

[6,7] and especially indium is a rare element [8,9]. Therefore, new flexible and low-cost transparent electrode technologies are investigated as alternatives.

Much actual research is focused on new electrode technologies from either carbon-based (e.g. highly conductive PEDOT:PSS, graphene or carbon nanotubes) or metal-based materials like metal grids and metal thin films [10–14].

A promising approach of the latter class are percolation networks made of randomly oriented metal nanowires, whereby most publications deal with copper or silver nanowires (AgNW) [15–18]. They exhibit high conductivity with simultaneously high optical transmittance in the visible light spectrum and show mechanical robustness to bending and stretching [19–21].

The AgNW electrodes have a fundamentally different microscopic structure than common TCOs. TCO electrodes form a uniform, closed layer. A charge carrier needs to travel only in vertical direction through a device to reach the highly conductive electrode. This pathway is in most OPV charge carrier transport layers not more than 100 nm. In contrast, AgNW electrodes exhibit voids

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between the wires which can be in the range of square micrometers. These voids need to be filled by the transport layer. A charge carrier located above such a void needs to travel through the organic layer filling in vertical and lateral direction to reach the nanowire network. These higher distances entail higher requirements on the conductivity of the charge carrier transport layer, and, if not fulfilled, may worsen the macroscopic performance of an OPV device. Although the AgNW electrodes exhibit superior performance to ITO electrodes, the electrodes surface roughness plays a critical role for a successful implementation as bottom electrode in organic thin film devices. Devices are often shunted in case of non-planarized AgNW bottom electrodes.

For planarization, mainly two different routes using solution-based deposition techniques were chosen in literature: On one hand, the AgNW film was deposited on glass, buried in a thick polymer layer (e.g. polyimide, PVA) [22–24] and then separated from the glass substrate. Consequently, the plane underside is now the surface for following organic layers. On the other hand, spin- or spray-coated conductive polymers like PEDOT:PSS [17,20] or metal oxides (e.g. zinc oxide or titanium oxide) [25–27] were deposited as subsequent layer, smoothing the nanowire topography. In both cases, the treatment improved the wire-to-wire-junctions and additionally the network conductivity without the need for further high temperature processes [28].

We report on using small molecule materials as a promising addition to the latter route. Their electrical properties can be improved and controlled easily by doping. Although these molecules are usually vacuum deposited, OPVs with spin-coated small molecule absorbing layers show high power conversion efficiencies as well [29–31]. As only spiro-OMeTAD is currently known in literature as solution-processable and dopeable small molecule hole transport layer [32], we fulfill a demand for more publications in this field.

Our present work is introducing the solution processing of a doped small molecule hole transport layer (s-HTL) comprising of N,N'-((diphenyl-N,N'-bis)9,9,-dimethyl-fluoren-2-yl)-benzidine (BF-DPB) as host and the Novald p-dopant "NDP9" with the intention of planarizing AgNW electrodes with a best performance of $15 \Omega/\square$ at 83.5% total transmission, measured at 550 nm wavelength.

We show, that these layers exhibit similar conductivity values of 3×10^{-4} S/cm for solution processing as thermally deposited layers from the same materials (e-HTL). We investigate the interplay between the highly conductive AgNW network structure and the low conductive HTL filling. By using the well studied zinc phthalocyanine:C₆₀ system, a strong dependence of OPV device performance on the HTL conductivity – adjusted by the doping concentration – can be assigned to the nanowire network voids in the square micrometer range. These voids necessitate a minimum HTL conductivity of around 1×10^{-4} S/cm for contained device performance.

Finally, we employ a more efficient oligothiophene-based donor material with C₆₀ as acceptor to show a maximum power conversion efficiency of 4.4% on a nanowire bottom electrode, compared to 4.1% on ITO with same solution-processed s-HTL and 5.4% for a fully evaporated device on ITO as reference.

2. Experimental

BK7 glass and ITO prestructured substrates ($2.5 \times 2.5 \text{ cm}^2$, Schott, Mainz, Germany) were cleaned sequentially with n-methylpyrrolidone, deionized water and ethanol and treated with oxygen plasma for 10 min (Harrick Plasma, NY, USA).

A dispersion of silver nanowires in ethanol (BlueNano, Charlotte (NC), USA) with a mean diameter of 90 nm (NW-90) or 35 nm (NW-

35) was diluted, deposited and structured as described elsewhere [28]. To achieve highly conductive AgNW layers, the as-sprayed samples were heated 90 min at 210 °C and 30 min at 140 °C on a heating plate in ambient atmosphere for NW-90 and NW-35, respectively. The electrodes exhibit electrical (corresponding to sheet resistance R_S) and optical (corresponding to total transmission at 550 nm wavelength T_{550}) properties, which range from $R_S = (15\text{--}35)\Omega/\square$ with $T_{550} = (83.5\text{--}86.5)\%$ and $(45\pm 5)\Omega/\square$ with $T_{550} = 85\%$ for NW-35. The ITO substrates used in this study exhibit $R_S = 26\Omega/\square$ at $T_{550} = 82\%$.

N,N'-((Diphenyl-N,N'-bis)9,9,-dimethyl-fluoren-2-yl)-benzidine (BF-DPB, Synthron, Wolfen, Germany) as matrix and 2,2'-(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F6-TCNNQ) or Novald Dopant NDP9 (Novald AG, Germany) as p-dopant were dissolved separately in tetrahydrofuran (anhydrous THF > 99.9% with 250 ppm butylhydroxytoluene as stabilizer, Sigma Aldrich, Germany) and annealed on a hotplate at 55 °C. BF-DPB was sonicated for 5 min and then blended with the NDP9 solution, so that a final concentration of 10 mg/ml was reached. Due to light-sensitivity of NDP9 in THF, dissolving and spin coating was performed in UV-light-protected nitrogen-filled glovebox. Spin coating was performed at 1000/min for 45 s, followed by heating at 55 °C for 10 min. Layer thickness was 100 ± 10 nm for all spin-coated layers and 30 ± 3 nm for vacuum-deposited layers of BF-DPB:NDP9, if not stated otherwise.

Organic solar cells were made using a single-chamber thermal evaporation system with a base pressure of 1×10^{-8} mbar (Lesker, Hastings, UK). Listed materials, BF-DPB and NDP9 were used as supplied or purified by a gradient sublimation, at least twice: C₆₀, ZnPc (CreaPhys, Dresden, Germany), 2,2'-((3,4-dimethyl-2,2:5,2:5,2:5-quinquethiophene)-5,5-diyl)bis(methanylylidene)dimalononitrile (DCV5T-Me) (Synthron, Wolfen, Germany), 4,7-diphenyl-1,10-phenanthroline (BPhen) (ABCR, Germany), tetrakis(1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidinato)dichromium (Cr₂(hpp)₄), 9,9-bis[4-(N,N-bis-biphenyl-4-yl-amino)phenyl]-9H-fluorene (BPAPF) (Lumtec, Hsin-Chu, Taiwan), aluminum (Lesker, Hastings, UK).

Device architectures were p-i-n stacks with the following layer sequence (absorber layer underlined, bracket values are nm): glass/ITO or AgNW/e-HTL [30] or s-HTL [100]/ ZnPc : C₆₀ (1:2) [30]/C₆₀ [30]/BPhen [6]/Al [100] and glass/ITO or AgNW/e-HTL [90] or s-HTL [100]/NDP9 [1]/BPAPF:NDP9 (10 wt%) [5]/BPAPF [5]/DCV5T-Me [5]/DCV5T-Me : C₆₀ (2:1)[40 at 80 °C substrate temperature]/C₆₀ [20]/C₆₀:Cr₂(hpp)₄ (4 wt%) [15]/Al [100].

Transmission measurements were carried out using a UV–Vis–NIR photospectrometer with integrating sphere unit (Shimadzu, Japan). All transmission values are stated including the glass substrate, exhibiting a transmission of 92% as single piece. Solvent spectra were taken using a quartz glass cuvette and a cuvette filled with THF as reference with 1 cm optical path length respectively. Sheet resistance was determined using a four point probe setup (Lucas Labs, USA).

Layer thicknesses were measured with a profilometer Dektak 150 (Veeco Instruments, Plainview, USA).

For measuring the HTL conductivity, 60 nm of silver were thermally deposited in vacuum through a shadow mask to create interdigitated fingers with a total of 111 mm channel length and 0.5 mm channel width. The target material was deposited on top. The resistance was measured with a SourceMeter[®] Instrument 2400 (Keithley, Ohio, USA) (SMU) for e-HTL in-situ and for s-HTL after deposition. Finally, the conductivity was calculated in respect to the layer thickness.

Scanning electron microscope (SEM) images were taken with DSM 982 (Carl Zeiss, Jena, Germany).

Atomic force microscope images were taken in tapping mode

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