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High work function transparent middle electrode for organic tandem solar cells

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The use of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) in combination with ZnO as middle electrode in solution-processed organic tandem solar cells requires a pH modification of the PEDOT:PSS dispersion. We demonstrate that this neutralization leads to a reduced work function of PEDOT:PSS, which does not affect the performance of polythiophene:fullerene solar cells, but results in a lower open-circuit voltage of devices based on a polyfluorene derivative with a higher ionization potential. The introduction of a thin layer of a perfluorinated ionomer recovers the anode work function and gives an open-circuit voltage of 1.92 V for a double junction polyfluorene-based solar cell. © 2010 American Institute of Physics. [doi:10.1063/1.3387863]

An attractive route toward more efficient polymer-based photovoltaics is to combine two or more cells with complementary absorption spectra in a multijunction device. Ideally these subcells should be interconnected by a fully solution-processed, conductive, and transparent middle contact. It has been demonstrated that such an electrode can be obtained by covering a layer of ZnO nanoparticles with a neutral pH dispersion of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS).1 The ZnO/neutral-PEDOT middle electrode was used in an all spin-coated tandem solar cell, of which the front cell consisted of a blend of a poly(phenylene vinylene) derivative as electron donor and [6,6]phenyl C61 butyric acid methyl ester (PCBM) as electron acceptor, whereas the back cell on top of the ZnO/neutral-PEDOT contact was made from poly(3-hexylthiophene) (P3HT) and PCBM. The pH modification of the PEDOT dispersion is needed to prevent the underlying ZnO layer from dissolving. However, ultraviolet photoemission spectroscopy studies have demonstrated that an increased pH of electronic grade PEDOT:PSS by addition of NaOH results in a decrease of the work function.2,3 For the back cell in Ref. 1, it was demonstrated that the neutral PEDOT:PSS middle anode still works as an Ohmic hole contact for P3HT, which has an ionization potential of 4.8 eV. An important question, however, is whether the neutral PEDOT:PSS is still able to form an Ohmic hole contact for polymers having high ionization potentials, e.g., polyfluorene derivatives. If this is not the case, a strong reduction in the open-circuit voltage is expected.4 The effect of a non-Ohmic hole contact for the back cell on the open-circuit voltage of a tandem device is depicted schematically in the simplified energy band diagram of Fig. 1. The maximum attainable open-circuit voltage of the back cell decreases when the work function of the middle anode is reduced, which results in an equal loss in the open-circuit voltage of the tandem device.

In this study the acidity of a highly conductive PEDOT:PSS dispersion (Clevios PH500, PEDOT:PSS ratio 1:2.5 by weight, H.C. Starck) was altered systematically by addition of a 1:8 dilution of 2-dimethylaminoethanol (DMAE, Aldrich) in water, as shown in Fig. 2. The obtained acidity ranged from pH 1.9 for unmodified PH500 to a slightly basic pH 8.5 after addition of 3.0 vol % DMAE:H2O. It is relevant to know to what extent the acidity of PEDOT:PSS should be modified in order to keep the underlying ZnO layer intact. As an indication, the ultraviolet-visible (UV-VIS) absorbance of a pristine ZnO layer at λ = 350 nm, as measured with a Perkin–Elmer Lambda 900 spectrophotometer, was compared to the absorbance of ZnO layers on which PEDOT:PSS of varying pH was applied via spin coating. Due to dissolution in acidic PEDOT:PSS, the absorbance of ZnO strongly decreased below pH 3. Additionally, a dramatic loss in wetting quality and film formation properties of PEDOT:PSS on ZnO was observed at low pH. When applied in multilayer solar cells using ZnO, the PEDOT:PSS dispersion should therefore have a pH ≥ 3.

To assess the usability of the combined interlayers, we fabricated single and double junction P3HT:PCBM solar cells. The photoactive layers were spin coated from an 8

![FIG. 1. Simplified energy band diagram of a series-connected tandem bulk heterojunction solar cell under open-circuit conditions in two situations: (a) all electrodes provide an appropriate Ohmic contact and (b) a non-Ohmic hole contact of the top cell, due to a reduced work function of the anode, results in a reduction in open-circuit voltage ΔVoc of the tandem device. The indicated energy levels correspond to the HOMO position of the donor and the LUMO position of the acceptor. The subscripts F, B, and T stand for front, back, and tandem, respectively.](image-url)
The single layer device showed $FF=0.67$, and short-circuit current density $J_{sc}=22.6 \text{ A/m}^2$. The open-circuit voltage $V_{oc}$ is 1.10 V. However, using the ZnO/M-PH500 interlayer, we found a rather large spread in $V_{oc}$ for such devices with a maximum of only 1.5 V. This reduced $V_{oc}$ in the PF10TBT:PCBM cells is a direct consequence of the reduced work function of PH500 after neutralization. In order to further quantify this effect, the nondestructive Kelvin probe (KP) method was used to measure the work function of layers made from the series of modified PH500 dispersions with varying $pH$ on ITO in a nitrogen atmosphere. Subsequently, an 80 nm thick layer of PF10TBT:PCBM (1:4 by weight) was spin coated in air from a 3 mg/mL (polymer) solution in chlorobenzene, followed by thermal deposition of a LiF/Al cathode. The only intentional difference between the resulting photovoltaic devices was the acidity of the applied M-PH500 dispersion. The open-circuit voltage of each device was extracted from current-voltage (IV) measurements under illumination (again, $M=1.40$). The results of the KP and IV measurements are shown together as a function of $pH$ in Fig. 3. The work function strongly decreases with increasing $pH$. At $pH$ 3.4 it has dropped by more than 0.5 eV compared to that of unmodified PH500. This is consistent with the $V_{oc}$ loss from 2

mg/mL (polymer) solution of P3HT:PCBM (1:1 by weight) in chloroform. In the single junction cell and the front subcell of the double junction device, the active layers were applied on electronic grade PEDOT:PSS (Clevios VP AI4083, H.C. Starck). To form the interlayer in the double junction configuration, an 18 mg/mL acetonic dispersion of ZnO nanoparticles, synthesized as described elsewhere, and a modified PH500:DMAE dispersion at $pH$ 3.4 (hereafter referred to as M-PH500) were subsequently spin coated in air on top of the front P3HT:PCBM layer. Both interlayers were approximately 30 nm thick. One thermal annealing step at 140 °C was carried out in nitrogen atmosphere after all solution-processed layers were applied. A cathode consisting of 1 nm LiF and 100 nm Al was thermally deposited at $\sim 10^{-6}$ mbar. Current-voltage characteristics were performed with a Keithley 2400 SourceMeter under illumination from a Steuernagel SolarConstant 1200, corrected for spectral mismatch ($M=1.40$) (Ref. 7) and filtered with a GG385 UV filter, resulting in an incident light intensity equivalent to 0.9 sun. Contributions to the photocurrent from regions outside the test area were eliminated using illumination masks. The photovoltaic properties of the double junction solar cell are shown in Fig. 4: $V_{oc}=1.10$ V, fill factor $FF=0.67$, and short-circuit current density $J_{sc}=22.6 \text{ A/m}^2$. The single layer device showed $V_{oc}=0.55$ V, $FF=0.64$, and $J_{sc}=481 \text{ A/m}^2$. The rather low currents are due to the fact that thin P3HT:PCBM layers were used to allow a sufficient amount of light to reach the back cell. The addition of open-circuit voltages in the P3HT-based double junction device and the approximate power conversion efficiency of 1.9% for both cells clearly show that the ZnO/M-PH500 middle contact does not introduce any limitations to device performance.

Recently, solar cells based on poly[9,9-didecanefluorene-alt-(bis-thienylene) benzothiadiazole] (PF10TBT) and PCBM with a power conversion efficiency of 4.2% were reported. The optical bandgap of PF10TBT is similar to that of P3HT but the energy levels of the highest occupied molecular orbital (HOMO, $-5.4 \text{ eV}$) and lowest unoccupied molecular orbital (LUMO, $-3.4 \text{ eV}$) result in a much smaller potential loss at the donor-acceptor interface and a higher open-circuit voltage of nearly 1 V. A series-connected double junction solar cell of PF10TBT:PCBM should thus produce a $V_{oc}$ close to 2 V. However, using the ZnO/M-PH500 interlayer, we found a rather large spread in $V_{oc}$ for such devices with a maximum of only 1.5 V. This reduced $V_{oc}$ in the PF10TBT:PCBM cells is a direct consequence of the reduced work function of PH500 after neutralization. In order to further quantify this effect, the nondestructive Kelvin probe (KP) method was used to measure the work function of layers made from the series of modified PH500 dispersions with varying $pH$ on ITO in a nitrogen atmosphere. Subsequently, an 80 nm thick layer of PF10TBT:PCBM (1:4 by weight) was spin coated in air from a 3 mg/mL (polymer) solution in chlorobenzene, followed by thermal deposition of a LiF/Al cathode. The only intentional difference between the resulting photovoltaic devices was the acidity of the applied M-PH500 dispersion. The open-circuit voltage of each device was extracted from current-voltage (IV) measurements under illumination (again, $M=1.40$). The results of the KP and IV measurements are shown together as a function of $pH$ in Fig. 3. The work function strongly decreases with increasing $pH$. At $pH$ 3.4 it has dropped by more than 0.5 eV compared to that of unmodified PH500. This is consistent with the $V_{oc}$ loss from 2
to 1.5 V in double junction cells made from PF10TBT:PCBM. An even further decrease of the work function is observed for higher pH. Clearly the open-circuit voltage of PF10TBT:PCBM cells follows the same trend and is reduced markedly by the pH-induced work function change. As a result the ZnO/M-PH500 middle electrode is only suited in combination with back cells based on a donor with an ionization potential of 4.8–4.9 eV, as P3HT.

In order for the back cell to produce the expected photovoltage, a method is needed to recover the function of the back cell anode. Electronic grade PEDOT:PSS can be reformulated by addition of a 5 wt% Nafion® perfluorinated resin solution in a water/alcohol mixture (Aldrich) to obtain a work function of 5.7 eV. Addition of a Nafion solution to PEDOT:PSS dispersions is considered less feasible, since it introduces an additional acidic component to the formulation. It is, however, possible to apply a thin Nafion-only layer that raises the work function of the underlying anode. Lee et al. have reported that the work function of ITO increases by 0.5 eV when covered with a thin Nafion layer. Moreover, using density-functional theory calculations, they showed that the ionization potentials of Nafion-like compounds are systematically higher than those of polyfluorene sulfonic acids. Here, we incorporate an interfacial layer of Nafion in a double junction solar cell of PF10TBT:PCBM, by spin coating Nafion perfluorinated resin solution, highly diluted in ethanol, on top of the M-PH500 (pH 3.4) anode before applying the second photoactive layer. An Ohmic hole contact between M-PH500 and PF10TBT has now been restored, without compromising the compatibility with the underlying ZnO layer. As shown in Fig. 4, this method results in a well-performing double junction PF10TBT:PCBM solar cell with an open-circuit voltage virtually twice as high as the single junction device. Altogether, the approximate power conversion efficiency of the double junction cell amounts to 4.5%, which is higher than that of the optimized single layer cell (4.0%). The physical origin of this effect will be discussed elsewhere.

In conclusion, we have modified the acidity of PEDOT:PSS to evaluate its use in multilayer polymer solar cells containing interlayers of ZnO nanoparticles. By addition of DMAE, the pH was varied from 1.9 to 8.5. The dispersions are compatible with ZnO for pH ≥ 3. Addition of open-circuit voltage and preservation of fill factor were demonstrated for a double junction P3HT:PCBM solar cell. The reduction in the work function of PEDOT:PSS upon neutralization, exceeding 0.5 eV, was shown to cause lower open-circuit voltages in solar cells based on a polyfluorene derivative with a higher ionization potential. An Ohmic hole contact was restored by inclusion of a thin layer of Nafion, which enabled the fabrication of double junction PF10TBT:PCBM cells with a Voc as high as 1.92 V.

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