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Highly efficient organic multi-junction solar cells with a thiophene based donor material

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The efficiency of organic solar cells can be increased by serial stacked subcells even upon using the same absorber material. For the multi-junction devices presented here, we use the small molecule donor material DCV5T-Me. The subcell currents were matched by optical transfer matrix simulation, allowing an efficiency increase from 8.3% for a single junction up to 9.7% for a triple junction cell. The external quantum efficiency of the subcells, measured under appropriate light bias illumination, is spectrally shifted due to the microcavity of the complete stack, resulting in a broadband response and an increased cell current. The increase of the power conversion efficiency upon device stacking is even stronger for large area cells due to higher influence of the resistance of the indium tin oxide anode, emphasizing the advantage of multi-junction devices for large-area applications.

Organic photovoltaics (OPV) have great potential for future renewable energy generation due to a cheap and low temperature production process, low material consumption, possibility of semi-transparency, and the processing on flexible and light weight substrates.1,2 These properties offer a broad field of applications such as building or automotive integrated photovoltaics3 or cells integrated in clothing. Organic dyes can have high absorption coefficients which allow very thin photoactive layers of a few nanometers. However, the absorption is spectrally rather narrow, so that much light is lost for current generation in the solar cell. To overcome this problem, the use of the multi-junction concept of stacking multiple sub-cells in series is generally used. Ideally, the sub-cells contain spectrally complementary absorber materials to harvest photons over a wide spectral range,4–6 resulting in an increased power conversion efficiency (PCE).5–8 However, also with the same absorber material in the sub-cells, an increased cell performance can be reached. There are two aspects which make this approach attractive for organic solar cells: (i) the thickness of the absorber layer is often limited by transport properties and (ii) electrodes often have too high resistances, which is less detrimental if multi-junction cells with lower currents are used.

In this Letter, we present fully vacuum deposited, highly efficient multi-junction organic solar cells with the absorber material DCV5T-Me in all sub-cells and doped transport layers for a lossless charge transport in between. The absorber with a thin film peak absorption in the green region at 584 nm is used as donor in combination with C60 as acceptor. The high efficiency of this material set in bulk heterojunction (BHJ) devices12 is due to efficient charge separation and transport properties in combination with high voltages. Furthermore, the extinction coefficient of DCV5T-Me is exceptionally high for small molecular materials (k = 1.5 at 582 nm, see Fig. 1). The layer thicknesses of the multi-junction architectures are optically optimized for maximum cell performance by a transfer matrix algorithm.9

All devices are deposited by thermal evaporation onto indium tin oxide (ITO) coated (90 nm with 26 Ω sq and 84% transparency), structured glass substrates (TFD, USA) in a high vacuum chamber (K. J. Lesker, UK) with a base pressure around 10−5 mbar. The devices are encapsulated immediately after preparation under nitrogen atmosphere using epoxy glue and glass lids. The overlap between the ITO anode and the evaporated aluminum top electrode forms the photoactive cell area of 6.20 mm² for small pixels and 136.5 mm² for large pixels on our samples. As exciton reflecting and charge blocking layer surrounding the BHJ, we use undoped layers of the electron transporting fullerene C60 and the hole transporting material 9,9-bis[4-(N,N-bis-
biphenyl-4-yl-amino)phenyl]-9H-fluorene (BPAPF). To place the absorbing layers in the optical field maxima, we follow the p-i-n concept with transparent doped charge transport layers to reach high conductivities in the range of $10^{-5}$–$10^{-3}$ S/cm for a lossless charge transport.\textsuperscript{10} For the n-type layers (electron transport layer (ETL)), we choose N,N-Bis(2-fluoren-2-yl)-3-phenylhexyltetraline carboxylic diimide (Bis-Hfl-NTCDI)\textsuperscript{11} as transparent matrix material doped by 7 wt. % of tetrakis(1,3,4,6,7,8-hexahydro-2H-pyrimidin-1,2- dipyrimidinato)ditungsten (II) (W2(hpp)4). For the p-type layers (hole transport layer (HTL)), the transparent matrix material BPAPF doped with 10 wt. % NDP9 (Novaled AG). To enhance the charge extraction at the aluminum contact and at the charge conversion contacts, we additionally use the energetically favorable hole transport material N,N'-((Diphenyl-N,N'-bis)9,9-dimethyl-fluorene-2-yl)-benzidine (BF-DPB) with a higher ionization potential of 5.3 eV compared to 5.6 eV for BPAPF. Furthermore, we use a 1 nm thick pure p-dopant layer of NDP9 at the aluminum electrode to obtain an ohmic contact at interface.

For solar cell characterization, we use measurement masks to minimize edge effects and for an exact definition of the photoactive area, resulting in 2.78 mm\textsuperscript{2} for small pixels and 113.65 mm\textsuperscript{2} for large pixels. The external quantum efficiency (EQE) was detected with a lock-in amplifier (Signal Recovery SR 7265) under monochromatic illumination (Oriel Xe Arc-Lamp Apex Illuminator combined with Cornerstone 260 1/4 m monochromator (Newport, USA)), using a calibrated mono-crystalline silicon reference diode (Hamamatsu S1337, Fraunhofer ISE). For bias light illumination of the samples during the EQE measurement, we use monochromatic high power LEDs (Luxeon and Roithner, spectral half width 20–35 nm). The current voltage characteristics (IV) are measured spectrally mismatch corrected using the experimental and simulated EQE spectra,\textsuperscript{14} giving values of IQE = 0.5 for the intrinsic C60 layer (i-C60).

The experimentally optimized single junction stack is shown in Fig. 1, reaching a calibrated efficiency of 8.3% PCE. From the absorption spectra of donor and acceptor, the peak at 350 nm can be associated to absorption in the fullerene, whereas the oligothiophene derivative shows strong absorption around 600 nm. The contributions of donor and acceptor absorption to the photocurrent in the device are obtained from optical transfer matrix simulations\textsuperscript{9} using the spectral constants (n and k) previously determined, using identical preparation conditions (substrate temperature, mixing ratio, and deposition rate). The internal quantum efficiency is obtained by matching the experimental and simulated EQE spectra,\textsuperscript{14} giving values of IQE = 0.84 for the BHJ layer and IQE = 0.5 for the intrinsic C60 layer (i-C60). The lower IQE for the i-C60 layer is reasonable because excitons generated within i-C60 have to diffuse through the whole layer to the donor interface before charge separation can occur.

With the obtained IQE of the active layer, several multi-junction configurations have been modeled by stacking the same absorber system on top of each other. By tuning the thickness of the transparent and highly conductive charge transport layers described above, the absorbers can be placed in the maxima of the optical field with very low parasitic absorption losses in the HTL and the ETL. The thicknesses of the photoactive layers must be adjusted to obtain similar photocurrent generation in all subcells of the series circuit. For maximization and matching of the subcell photocurrents, we use an asymptotic convergence algorithm that varies all deposition conditions (substrate temperature, mixing ratio, and deposition rate).
charges. Therefore, the absorber layer thicknesses must be limited to the thickness obtained experimentally for single junction solar cells with optimized efficiency. With this limitation, the multi-junction optimization returns the optimized thicknesses for the highest FF-Jsc product.

In this way, the optimal stacks for tandem and triple configurations are found, shown in Figs. 2 and 3. For the optimal tandem stack, the photoactive layers are placed in the first and second maximum of the optical field between the electrodes. For this reason, both BHJ layers have still the same thickness of 35 nm, where the maximal FF-Jsc product for each subcell is reached. In the optimized triple junction case, two subcells are positioned in the first optical maximum and the third again in the second field maximum. Therefore, the thickness of the front subcell is only 27 nm to share the photon absorption in the first optical maximum with the second subcell, whereas the third subcell placed in the second field maximum is much thicker (43 nm) to generate the same photocurrent for current matching.

In order to separately address each subcell in the EQE measurements, we use monochromatic bias illumination of the sample and bias voltages. The bias wavelength is appropriately chosen (regions with different spectral responses of the subcells) to flood the unaddressed subcells with charge carriers (higher spectral response at the bias wavelength), resulting in the desired current limitation by the investigated subcell. For the tandem device, we use LEDs with 405 nm and 525 nm wavelength for subcell separation (Fig. 2). For the triple cell, we use LEDs with 405 nm, 525 nm, and 680 nm wavelength where two subcells are biased at the same time (Fig. 3). For the certification measurements at Fraunhofer ISE, similar results are obtained by using a spectrally tunable sun simulator. For both the tandem and the triple junction device, we obtain good agreement between the measured subcell EQE and the simulated curves (Figs. 2 and 3), using the same IQE values calculated from the single stack for all subcells.

For a more quantitative performance analysis, the certified STC fingerprints of the I-V characteristics of the single, tandem, and triple devices are plotted in Fig. 4. The Jsc decreases with the number of junctions due to the strong spectral response overlap, i.e., photon sharing of the subcells containing the same absorber. However, we make use of the strong micro cavity effect inside the device allowing to
spectrally shift the response of the subcells compared to the single junction device despite using the same absorber material. Therefore, we obtain a spectral broadening of the multi-junction response resulting in an overall improvement in the total photocurrent, noticeable when comparing the higher currents of the multi-junctions with the single junction $I_{sc}$ divided by the junction number. The multi-junction $V_{oc}$ reaches nearly the sum of the subcell voltages, indicating an almost lossless charge transport via the charge conversion interfaces and the doped transport layers. Due to the shift of the I-V curves to higher voltages and lower currents for the multi-junction devices, we obtain a more favorable $V_{oc}/I_{sc}$ ratio and, therefore, by itself higher fill factors, which is a further advantage of such stacked devices. For these reasons, the efficiency of the small area devices is finally increased from 8.3% for the single stack to 9.6% for the tandem stack and 9.7% for the triple junction device, respectively.

Going to larger area devices, we obtain only a minute reduction of the photocurrent, whereas $V_{oc}$ even slightly increases. The largest difference is obtained in the FF, which drops significantly in the single junction device due to resistive losses over the ITO electrode. However, with regard to the production of solar modules, the lower currents at higher voltage in multi-junction devices demonstrate great advantage over the single junction cells with a FF which is only 2% smaller for the large area triple junction device. Finally, the PCE of the large area triple junction device of 9.5% is only slightly smaller than that of the small area device (9.7%), underlining the clear advantage for large module applications.

In conclusion, we present pronounced performance improvement up to 9.7% power conversion efficiency by stacking subcells with the same absorber material DCVST-Me to form multi-junction solar cells. This value is the highest efficiency for small molecule organic solar cells with disclosed active materials up to date. A spectrally broader photon harvesting is obtained due to spectral shifts of each subcell response induced by the micro cavity effect. The optimized active layer and spacer thicknesses are simulated using optical transfer matrix simulations. Although we use the same absorber for all subcells, the EQE can be measured independently using monochromatic bias light and bias voltage. From the consistency of experiment and simulation, the algorithm proves to be a powerful tool for the optimization of multi-junction devices. With respect to solar module applications, the increased fill factor on large areas in serially connected multi-junction devices underlines the benefit of such junction stacking even upon using only one absorbing material.

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