Gradient ZnPc:C_{60} Absorption Layers in Small Molecule Solar Cells

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Introduction

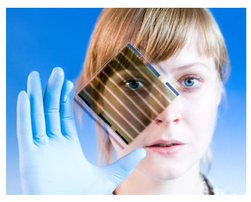

Figure 1. Thin film organic solar cells show their potential for transparent window application.

The field of organic electronics is rapidly developing and new applications and products are on the brink of being commercial available. The main reasons for the widespread interest in organic semiconducting materials is their potential for low cost processing, the adjustability of organic molecules with respect to their properties, and the compatibility with flexible substrates.
However, for organic solar cells to enter the market, the efficiency has to be further increased.

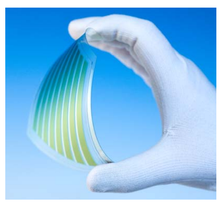

Figure 2. Due to weak interaction forces between the organic molecules, organic solar cells can easily be processed on flexible substrates.

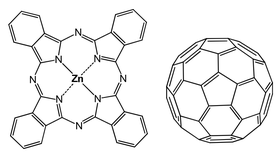

Figure 3. The donor molecule Zinc phthalocyanine (ZnPc) and the acceptor molecule fullerene C_{60}, which are commonly used absorber materials.

Motivation

Since the first organic solar cell consisting of a two-layered donor-acceptor system (1) was realized in 1985 by Tang,[1] huge progress in research could be achieved. This work determined the importance of the hetero-junction surface of the donor and acceptor material in respect of the device efficiency. Consequently, blended donor-acceptor layers (2) were processed and yielded better solar cell performance.[2] In order to prevent the quenching of excitons at the interface between the absorber layer and the cathode, an exciton blocking layer (EBL) was additionally introduced (3).[3] A major drawback of organic semiconductors is their low conductivity, which can be circumvented by the PiN-like architecture (4) for organic solar cells.[4] Here, a p-doped hole transporting layer (HTL) and an n-doped electron transporting layer are used to transfer the charges from the intrinsic absorption layer towards the electrodes.
Figure 1. depicts the historical development in research of organic solar cells based on vaporizable molecules. This progress shows that the solar cell efficiency grew corresponding to the complexity of the cell architecture.[5]

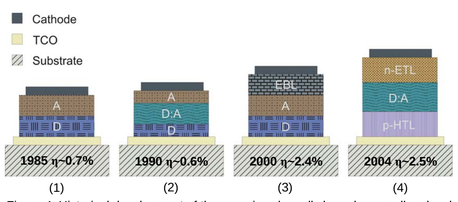

Figure 4. Historical development of the organic solar cells based on small molecules.

Since the realization of the PiN-concept resulted in efficient solar cells with high reproducibility, we try to transfer this structure to the intrinsic absorption layer by processing this film with a graded distribution of the donor and acceptor material. According to the data presented in figure 5, this modification of the donor-acceptor concentration within the absorber layer would result in a variation of the charge carrier mobility. With an enhancement of the donor molecule concentration towards the HTL, the hole mobility should increase further the closer the hole moves to its transporting layer. This phenomenon should occur for the electron mobility in respect to the ETL as well.

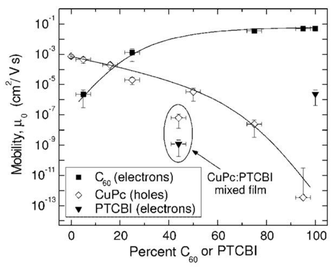

Figure 5. Graphical presentation of the charge carrier density in dependence on the concentration of the acceptor in the blended donor-acceptor layer. These results were taken from literature. [6]

Device Fabrication of the Test and Reference Cell

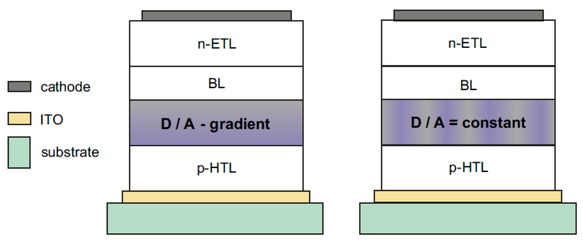

Figure 6. Solar cell architecture for the used experiments. On a indium tin oxide (ITO) coated substrate a p-doped HTL layer, an intrinsic absorber.(AL), an exciton blocking layer and an electron transporting layer (ETL) were deposited.

On an indium tin oxide (ITO) coated glass substrate a p-doped hole transporting layer (HTL), an intrinsic absorber layer (AL) consisting of ZnPc and C_{60}, an exciton blocking layer (BL), an n-doped electron transporting layer (ETL) as well as Al were deposited *via* thermal evaporation in a high vacuum deposition chamber from Bestec. Each substrate was structured with 4 active areas of different sizes (from 1.23 mm^2 to 79.63 mm^2).
In order to deposit a defined structure of the absorber layers (ALs) with ZnPc and C_{60}, rates were monitored with quartz crystal sensors and regulated by a deposition controller (Inficon). The variation of both rates was determined by a macro program using the Bestec tool software. Figure 6 shows the device architecture for the experiment with either a graded and a homogenous processed absorption layer.

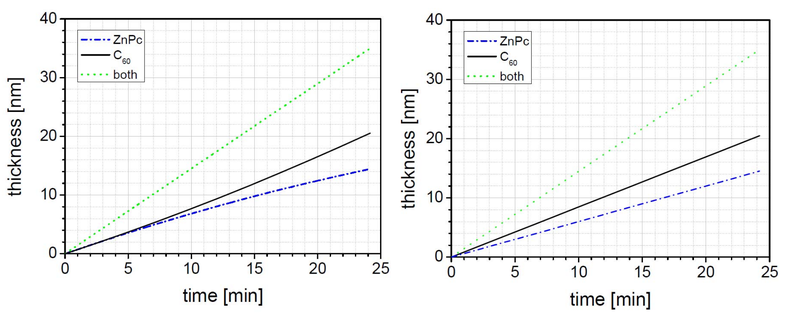

Figure 7. Thickness monitoring of the graded grown (left) and the homogenously grown (right) absorber layers.

Whereas the composition of the test (cell A) and reference layer (cell B) is for each time during the deposition always different (blue for the part of ZnPc, black for the part of C_{60}), the sum thickness (green) remains equal. For comparison of the solar cell performance the overall composition of the absorption layer was kept identical. In order to realize the gradient-like structure of the absorber layer, the rates were decreased (ZnPc) and increased linearly (C_{60}) every 5 nm.
Because of the low run-to-run reproducibility which originates from the changing pressure and material quality, it is important to process a reference cell in each run to compare the results and to draw a conclusion.

Characterization of the Solar Cells

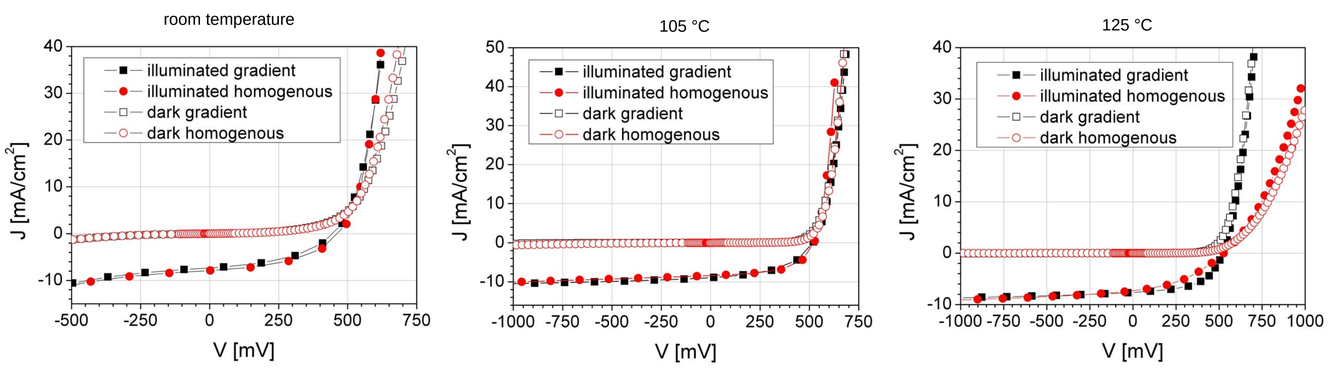

Figure 8. J-V curves of the test cell (black squares) with a graded absorption layer and the reference cell (red circles) in dependence of the substrate temperature. The curves were measured under illumination (filled symbols) and in the dark (open symbols).

$$\eta = \frac{J_{SC} \times V_{OC} \times FF}{P_0}$$

η..... efficiency
J_{SC} .. short circuit current density
V_{OC}...open circuit voltage
FF... filling factor
P_0... power of the incident light

J-V curves were measured with a sun simulator using an AM 1.5 global reference spectrum and an irradiance of 1000 W/m^2 at a cell temperature of 25 °C.

Table 1. Key values of organic solar cells in dependence on the substrate temperature. Cell A and B correspond to the test cell with a gradient (ZnPc (50→33%) : C_{60} (50→67%)) and the reference cell with a homogenously blended absorption layer (ZnPc (42%) : C_{60} (58%)), respectively. The thickness of the absorber layer was set to 35 nm.

Cell	Substrate temperature	V_{OC} [mV]	J_{SC} [mA/cm²]	FF [%]	η [%]
A	room temperature	446.92 (±17.97)	6.25 (±0.22)	40.44 (±1.43)	1.13 (±0.11)
B		488.35 (±10.12)	7.28 (±0.23)	47.18 (±2.43)	1.67 (±0.10)
A	85 °C	525.11 (±3.77)	8.91 (±0.22)	50.53 (±7.98)	2.37 (±0.36)
B		530.37 (±3.80)	8.41 (±0.14)	58.42 (±0.14)	2.58 (±0.03)
A	105 °C	534.13 (±3.78)	8.11 (±0.30)	57.43 (±2.53)	2.48 (±0.09)
B		536.13 (±5.94)	8.52 (±0.37)	54.84 (±2.32)	2.50 (±0.12)
A	125 °C	535.20 (±4.60)	7.50 (±0.60)	50.00 (±6.10)	2.01 (±0.30)
B		532.30 (±3.40)	7.40 (±0.50)	41.30 (±5.10)	1.65 (±0.30)

Table 2. Key values of the organic solar cells in dependence on the gradient strength. Cell A and B correspond to the test and reference cell, respectively. The absorption layer thickness was set to 35 nm and the substrate was kept at a temperature of 125 °C.

Cell	Absorber layer	V_{OC} [mV]	J_{SC} [mA/cm²]	FF [%]	η [%]
A	(39-33%)	548.98 (±3.77)	6.39 (±0.42)	44.34 (±1.37)	2.37±0.36
B	36%	546.67 (±3.82)	7.02 (±0.93)	41.75 (±0.14)	2.58±0.03
A	(50-33%)	534.13±3.78	8.11 ±0.30	57.43±2.53	2.48±0.09
B	41.5%	536.13±5.94	8.52 ±0.37	54.84±2.32	2.50±0.12
A	(66-33%)	535.2±4.60	7.50 ±0.60	50.00±6.10	2.01±0.30
B	50%	532.3 ±3.40	7.40 ±0.50	41.30±5.10	1.65±0.30

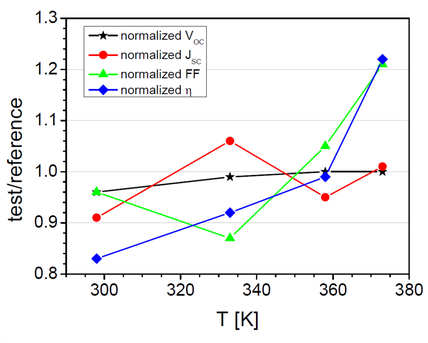

Figure 9. Normalized key values in dependence on the substrate temperature.

- At room temperature the gradient-like structure reduces the performance of the solar cell
- At higher substrate temperature this influence reverses
- The higher the substrate temperature, the better are the graded organic solar cells than the homogenous reference cells
- The stronger the gradient is, the better are the graded organic solar cells than their reference cells

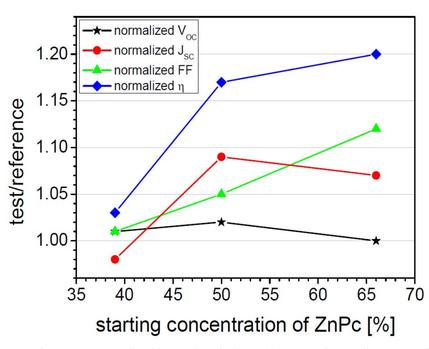

Figure 10. Normalized key values in dependence on the gradient strength. The final concentration of ZnPc was 33%.

Characterization of the Absorption Layer

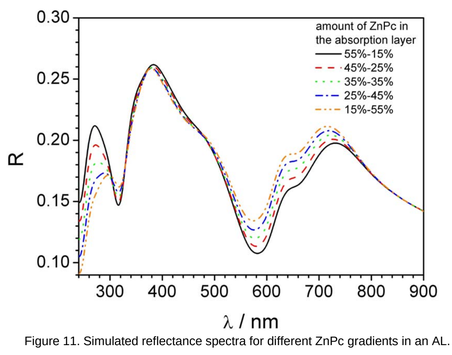

Figure 11. Simulated reflectance spectra for different ZnPc gradients in an AL.

Reflectance spectra can be used to characterize the absorption layers optically. By usage of the software VASE, measured spectra can be fitted with different models to determine the layer thickness and its composition as depicted in Figure 11.

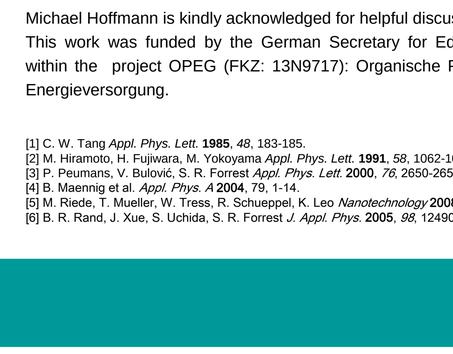

Figure 12. Reflectance spectrum of the test and reference AL and their fits. The EMA (effective medium approximation) model describes a homogenous distribution of both materials, ZnPc and C_{60}. The graded model includes additionally a gradient.

Table 3. Amount and distribution of ZnPc in the AL according to reflectance measurements and their used fits.

Structure of the AL	EMA model	graded model
graded	35.2% (±1.1%)	45.8-25.5% (±0.7%)
Homogenous	39.7% (±1.2%)	40.9-38.5% (±0.6%)

Figure 13. Relative spectral response spectra for samples processed at different temperatures. For comparison the spectra were normalized at the first peak.

- The contribution of the ZnPc absorption (550-800 nm) for the J_{SC} increases with higher temperature
- Spectral response spectra from samples processed at room temperature are identical in shape
- At increased temperature, the difference in shape becomes more distinctive at the ZnPc absorption bands

Summary and Conclusions

- Organic solar cells featuring an absorption layer with either a gradient-like or homogenously blended structure were realized and characterized
- OSCs exhibiting a graded absorption layer in several variations resulted always in lower efficiencies than their homogenous analogues if the devices were processed under ambient temperature
- The negative influence of the graded structuring disappeared when the substrate was heated and revealed at 125 °C in a better performance than the homogenous reference cell
- This temperature effect is attributed to the formation of micro crystals and the improvement of the percolation paths for the donor and acceptor material when the substrate was heated
- The stronger the absorption layer was graded at a substrate temperature of 125 °C, the better were the solar cell with a gradient containing absorption layer than their corresponding reference cells
- The shape of the spectral response spectra suggests that the charge transport improves at increased substrate temperature stronger than the conventionally processed organic solar cells

Acknowledgement and References

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[1] C. W. Tang *Appl. Phys. Lett.* **1985**, *48*, 183-185.
[2] M. Hiramoto, H. Fujiwara, M. Yokoyama *Appl. Phys. Lett.* **1991**, *58*, 1062-1064.
[3] P. Peumans, V. Bulović, S. R. Forrest *Appl. Phys. Lett.* **2000**, *76*, 2650-2652.
[4] B. Maennig et al. *Appl. Phys. A* **2004**, 79, 1-14.
[5] M. Riede, T. Mueller, W. Tress, R. Schueppel, K. Leo *Nanotechnology* **2008**, *19*, 1-12.
[6] B. R. Rand, J. Xue, S. Uchida, S. R. Forrest *J. Appl. Phys.* **2005**, *98*, 124902.