A systematic X-ray scattering study on bulk heterojunction P3HT:PCBM solar cells

S. Guo, M.A. Ruderer, E. Metwalli, M. Rawolle, J. Perlich[1], S.V. Roth[1], and P.Müller-Buschbaum

Technische Universität München, Lehrstuhl für Funktionelle Materialien, Physik-Department E13, James-Franck-Str. 1, D-85747 Garching, Germany

[1]HASYLAB at DESY, Notkestr. 85, D-22603 Hamburg, Germany

Relatively high performance polymer bulk heterojunction (BHJ) solar cells, based on a self-assembly phase separation of an electron-donating conjugated polymer P3HT (region-regular poly(3-hexythiophene)) and an electron-accepting fullerene PCBM (phenyl-C_{61}-butyric acid methyl ester), have become of great interests over the past decade. They offer a realization of low-cost, flexible, light renewable energy source. Although the efficiency of this kind of solar cells has been improving continuously and reached up to 7.7% [1], the in-depth knowledge about the inner morphology of these solar cells is still missing. Therefore we investigate the inner structural changes with GISAXS (grazing incidence small angle x-ray scattering) as a function of a multilayer stack build-up.

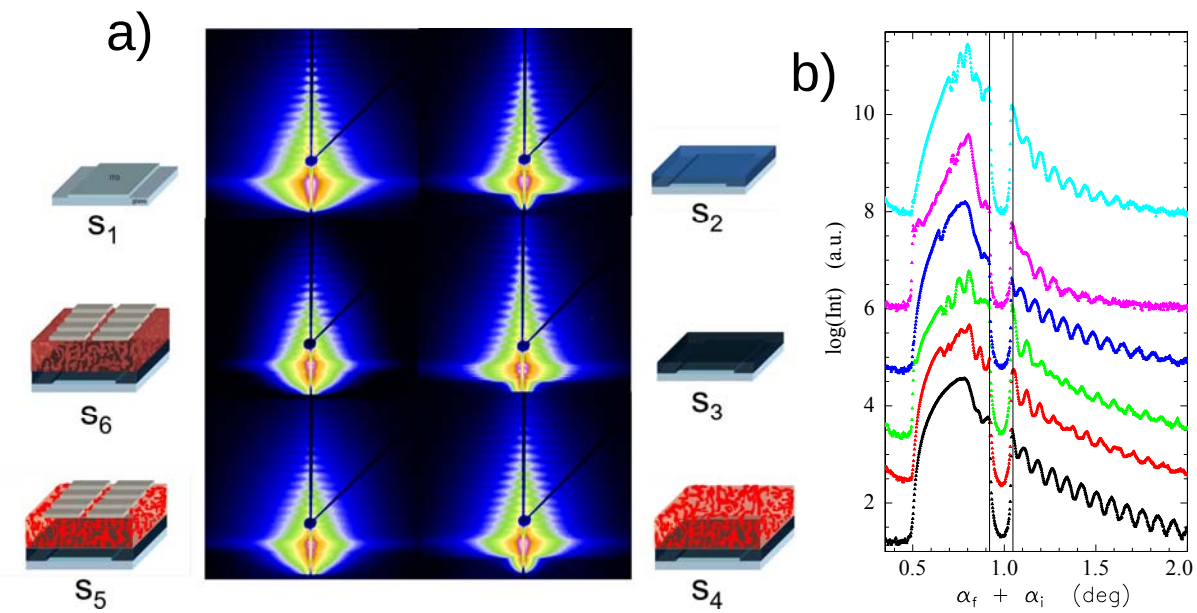

Figure 1: *a) 2d GISAXS images as a function of each preparation step of a BHJ solar cell (S_1: ITO substrate after chemical etching of the side area; S_2: additional ultra-thin PEDOT:PSS layer spin-coated from solution; S_3: annealed PEDOT:PSS layer; S_4: P3HT:PCBM spin-coated from 1,2-dichlorobenzene based solution; S_5: aluminium layer via thermal evaporation; S_6: post-treated solar cell annealed at inert atmosphere). b) detector cuts of the 2d intensity as a function of the detector angle $\alpha_i + \alpha_f$, the curves are shifted along the intensity axis for clarity.*

From the GISAXS measurement, molecular resolution of the buried interfaces of thin films or multilayer systems are obtained, without damaging the sample. As seen from the two-dimensional GISAXS images shown in Figure 1a, strong intensity oscillations are observed for all the probed samples. These intensity oscillations are caused by the rather rough ITO substrate surface, which roughness spectrum is replicated by the following thin films. To have a better understanding of the roughness correlation, as well as the lateral structure information, the analysis of detector cuts and out-of-plane cuts is required.

In the detector cuts shown in figure 1b, the specular reflected x-ray beam is shielded by a beamstop to protect the detector (at $\alpha_i + \alpha_f = 1.02°$). The peaks on the left side of the beam stop area are the Yoneda peaks, which are material dependent features and originate from dynamical effects. Strong oscillations are observed on the right side of the beam stop area for all probed samples due to

roughness correlation originated from the ITO substrate. In addition, the beats in the diffusely scattered intensity for the samples S_2 and S_3 indicate a similar thickness between ITO and PEDOT:PSS layer, which is around 85 nm given by x-ray reflectivity measurement.

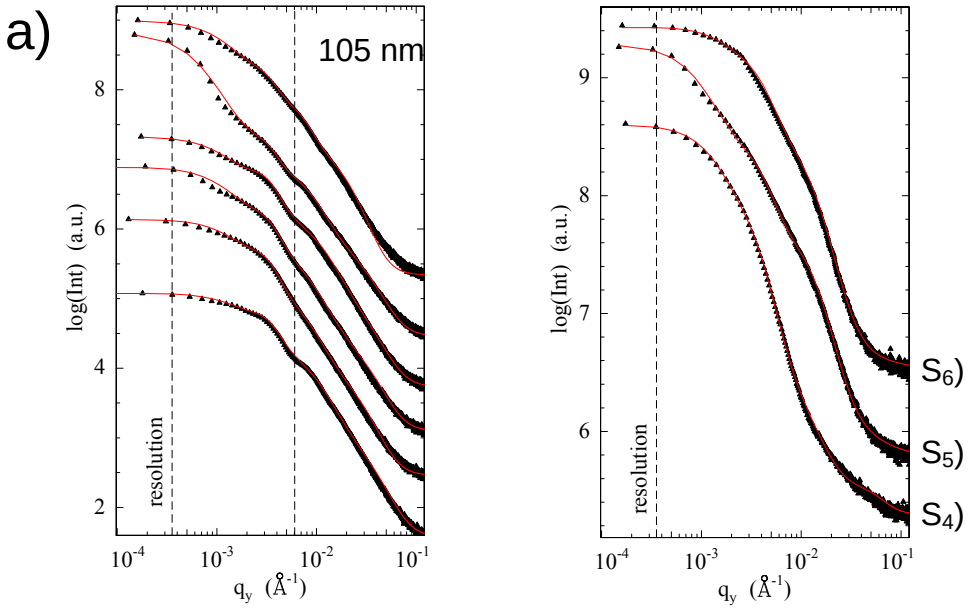

Figure 2: *Out-of-plane cuts taken at the critical angles of a) ITO (S_1 to S_6 from bottom to top) and b) P3HT (only S_4, S_5 and S_6 as indicated). The data are shown with symbols and the fits based on the effective surface approximation with (red) solid lines. For clarity, the curves are shifted along the intensity axis.*

Lateral structural information is gained from the out-of-plane cuts (see figure 2). Fitting of the data is performed within the model of the effective surface approximation. As a result, the lateral structure size of ITO stays constant (105 nm) during the additional layers built-up on top. However, the size of P3HT domains increase slightly from 70 nm (S_4, S_5) to 75 nm (S_6) as seen in Figure 2b due to thermal treatment in the inert gas, which leads to the more optimized phase separation. Therefore, much higher efficiency is achieved as shown in Table 1.

	I_{sc} (mA/cm^2)	U_{oc} (V)	FF (%)	η(%)	A (mm^2)
as-spun	5.60	-0.56	48.51	1.52	0.14
annealed	7.81	-0.60	54.59	2.54	0.14

Table 1. I-V parameters of the solar cells: the short circuit current I_{sc}, the open circuit voltage U_{oc}, fill factor FF, power conversion efficiency η, and effective area A.

In summary, the efficiency of BHJ 1,2-dichlorobenzene based-P3HT:PCBM solar cells is improved by the applied treatment [2]. The roughness correlation and the inner structure information are revealed via the serial GISAXS study, showing that the roughness of the ITO substrate has a strong influence on the morphology of the following layers, which directly determines the final power conversion efficiency of the solar cell. Further investigations about this system are still ongoing.

References

[1] H.-Y. Chen, J.i Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu and G. Li, *Nat. Photonics*. **3**, 649 (2009).

[2] S. Guo, M.A. Ruderer, E. Metwalli, M. Rawolle, J. Perlich, S. V. Roth and P. Müller-Buschbaum. In preparation.