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Nanomorphology of P3HT:PCBM-based organic solar cells analyzed by low-energy scanning transmission electron microscopy

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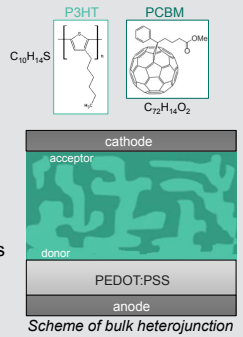
Introduction

- Strong correlation between efficiency of device and nanomorphology of absorber layer
- Photoactive layer: blend of donor P3HT (Poly(3-hexylthiophene) and acceptor PCBM ([6,6]-phenyl-C61-butyric acid methyl ester)
- Exciton dissociation only at interfaces
- Continuous pathways to electrodes necessary
  ➡ ideal morphology
- Morphology controlled by production processes (e.g. by thermal treatment) and influenced by material parameters (e.g. the molecular weight of the polymer)



Scheme of bulk heterojunction organic solar cell

Microscopical analysis:

- Conventional TEM: poor contrast for light materials with similar densities and mean atomic numbers
- Low-energy scanning transmission electron microscopy: high chemical contrast in high-angle annular dark-field (HAADF) STEM mode
  ➡ Study of the influence of annealing on P3HT:PCBM absorber layers using P3HT with different molecular weight

Samples

- P3HT:PCBM samples with a mixing ratio of 1:1
- P3HT with different molecular weights (20 kg/mol and 50 kg/mol)
- Annealing at 150 °C for up to 30 min
- Sample thickness of about 100 nm

References and Acknowledgements

[1] M.F.G. Klein et al., J. Polym. Sci. Pol. Phys. 50, 198 (2012).
[2] M. Pfaff et al., J. Microscopy 234, 31 (2011).
[3] M. Pfaff et al., Microsc. Microanal., accepted.

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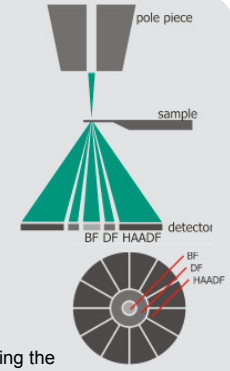
Techniques

Low-energy HAADF STEM:

- Electron energies ≤ 30 keV
- Imaging in the FEI Dual-Beam STRATA 400S equipped with a semiconductor STEM detector
- Detection angle range for HAADF: 0.2 - 0.7 rad
- Mean square scattering angle: $\overline{\theta^2} \propto \frac{Z^2 \cdot \rho \cdot t}{E^2 \cdot A}$

  Z: atomic number *A*: atomic mass number
  ρ: material density *t*: sample thickness
  E: electron energy

  ➡ **Contrast with high chemical sensitivity (Z-contrast)**

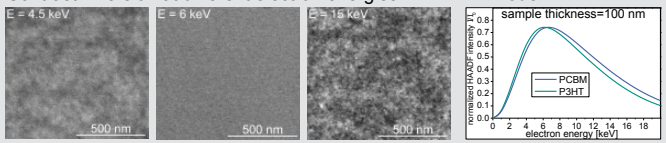


Capabilities of this technique already shown by imaging the morphology of P3HS(poly(3-hexylselenophene-2,5-diyl)):PCBM solar cells [1]

- TEM, electron diffraction
- Atomic Force Microscopy (AFM)

Interpretation of low-keV HAADF STEM images

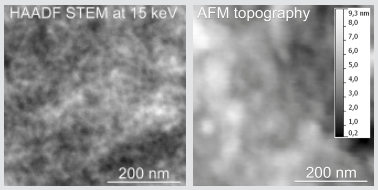
Contrast inversion at different electron energies in HAADF mode:



- Calculation of image intensity with semiempirical equation [2]
- Ideal electron energy depends on sample thickness and composition
- Decrease of resolution for reduced electron energy

Influence of thickness variations:

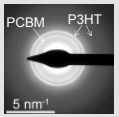
- Comparison with AFM images
- Large-scale lateral features due to thickness variations
- Small-scale features due to material contrast



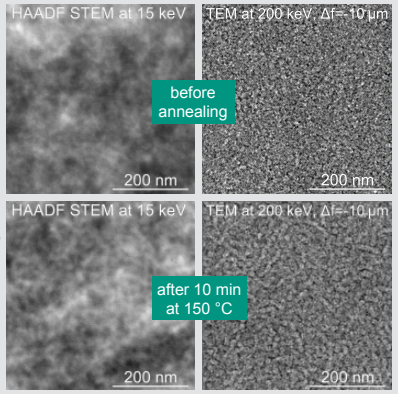
Results [3]

Samples with low molecular weight P3HT (20 kg/mol):

- Small globular features before annealing
- P3HT nanorods (dark contrast) form during annealing
- High contrast in low-keV STEM images
- TEM: Large defocus values for visualization of nanorods
  ➡ delocalization effects

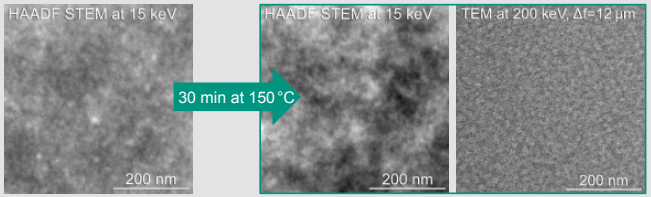


diffraction pattern of the annealed sample, showing distinct P3HT reflections



Samples with high molecular weight P3HT (50 kg/mol):

- Small globular features ➡ same size before and after annealing
- Increased roughness of annealed sample
- TEM: globular features cannot be recognized due to delocalization



Conclusions & Summary

- Low-keV STEM is well suited to image P3HT:PCBM absorber layers due to the high Z-contrast in HAADF mode
- In contrast to TEM even small globular structures can be resolved
- For image interpretation comparison with calculated HAADF STEM intensity and AFM topography images are necessary
- The morphology of P3HT:PCBM strongly depends on the molecular weight of P3HT ➡ P3HT nanorods only in the low-molecular-weight samples