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Applications of low-energy STEM for the investigation of carbon-based materials for organic solar cells

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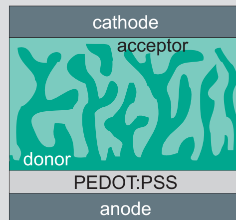
Introduction

Organic solar cells

- Strong correlation between efficiency of organic solar cell and nanomorphology of absorber layer
- Exciton dissociation only at donor-acceptor interfaces
- Continous pathways to electrodes necessary
  ➜ ideal morphology
- Morphology controlled by production processes and material parameters



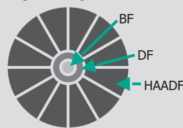
Scheme of bulk heterojunction organic solar cell

Microscopical analysis

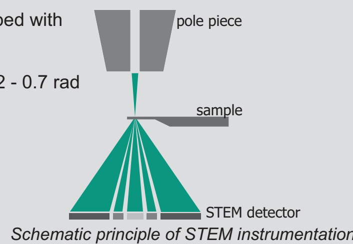
- Conventional TEM: poor contrast for light-weight materials with similar densities and mean atomic numbers
- Low-energy scanning transmission electron microscopy: high chemical contrast (Z-contrast) in the high-angle annular dark-field (HAADF) STEM mode

Instrumentation

- FEI Dual-Beam STRATA 400S equipped with a semiconductor STEM detector
- Electron energies: 3 - 30 keV
- Detection angle range for HAADF: 0.2 - 0.7 rad



Schematic STEM detector layout



Schematic principle of STEM instrumentation

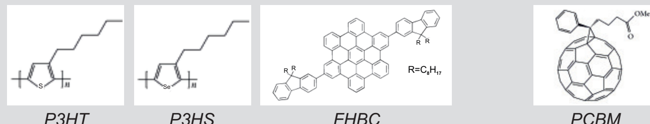
Samples

Donors:

- Poly(3-hexylthiophene-2,5-diyl) (P3HT)
- Poly(3-hexylselenophene-2,5-diyl) (P3HS)
- Fluorenyl hexa-*peri*-hexabenzocoronene (FHBC) [1]

Acceptor:

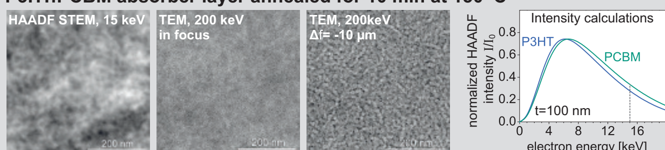
- [6,6]-phenyl-C61-butyric acid methyl ester (PCBM)



P3HT P3HS FHBC PCBM

Comparison with TEM [2]

P3HT:PCBM absorber layer annealed for 10 min at 150 °C



- High contrast between P3HT and PCBM domains in the HAADF STEM image
- HAADF intensity calculations: P3HT appears darker than PCBM for 15 keV
- No structural features in the in-focus TEM image due to small difference in mass thickness
- Large defocus values necessary to reveal elongated structures in TEM
  ➜ Reduced resolution and strong delocalization of image information
  ➜ Accurate size determination and image interpretation difficult

References and acknowledgement

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[3] M. Pfaff et al., J. Microsc. 243 (2011) p. 31
[4]W. Bothe, Handbuch der Physik 22.2, Springer (1933) p.1
[5] M.F.G. Klein et al., J. Polym. Sci. Pol. Phys. 50 (2012) p. 198

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Calculation of the HAADF STEM intensity [3]

- Angular distribution of the transmitted electrons: $\frac{I(\theta)}{I_0} = \frac{d\Omega}{2\pi\overline{\theta^2}} e^{-\theta^2/2\overline{\theta^2}}$

$I(\theta)$: Intensity scattered into the angle θ
I_0: Intensity of incident electrons
$\overline{\theta^2}$: mean quadratic scattering angle

Integration over the detection angle range θ_1–θ_2

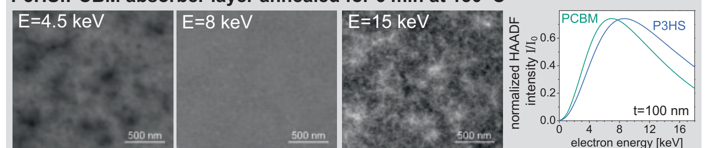
- Normalized HAADF STEM intensity: $\frac{I_{HAADF}}{I_0} = e^{-\theta_1^2/2\overline{\theta^2}} - e^{-\theta_2^2/2\overline{\theta^2}}$

- Mean quadratic scattering angle according to Bothe [4] with an adapted prefactor: $\overline{\theta^2} = 9.15 \cdot 10^9 \left(\frac{Z}{E}\right)^2 \frac{\rho t}{A}$ [rad^2]
  ➜ valid for light materials, low electron energies and high scattering angles

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

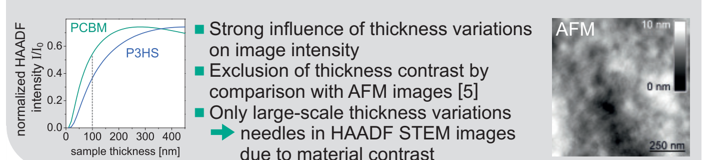
Interpreation of low-energy HAADF STEM images

P3HS:PCBM absorber layer annealed for 6 min at 150 °C



- Contrast inversion at different electron energies in HAADF mode
- Calculation of image intensity
  ➜ Bright needle-like structures at 15 keV are composed of P3HS [5]
- Reduced resolution at 4.5 keV ➜ needle-like structures cannot be resolved
- Ideal electron energy depends on sample thickness and composition

Intensity calculations for 15 keV depending on the sample thickness:



- Strong influence of thickness variations on image intensity
- Exclusion of thickness contrast by comparison with AFM images [5]
- Only large-scale thickness variations
  ➜ needles in HAADF STEM images due to material contrast

Thickness and material density determination

- Well-definded relation between density ρ, sample thickness t and electron energy E at the intensity maximum for homogeneous samples with known composition:

$$\rho \cdot t = \frac{\theta_1^2 - \theta_2^2}{4\ln(\theta_1/\theta_2)} \cdot \frac{A}{Z^2 \cdot 9.15 \cdot 10^9} \cdot E^2 \quad (1)$$

θ_1 and θ_2: inner and outer detection angle
Z: atomic number A: atomic mass number

- Variation of the electron energy until thickness contrast is minimized
  ➜ Energy E of HAADF intensity maximum
  ➜ Denisty ρ or thickness t can be calculated with Eq. (1)

Thickness determination:

- Sample with well-known composition and density needed

Density determination:

- Set of samples with different known thicknesses for enhanced quality and reliability of the measurement

➜ error smaller than 10%

Determination of FHBC density:

- FHBC films with different thicknesses
- Plot of the sample thickness vs. the electron energy at the maximum HAADF STEM intensity
- Prefactor of the quadratic fit function yields density

➜ $\rho = 1.04 \pm 0.29$ kg/m^3

Summary

- Low-energy HAADF STEM is well suited to image absorber layers of organic solar cells due to high Z-contrast in the HAADF mode
- Optimum electron energy depends on sample thickness and composition
- Image interpretation requires comparison with calculated HAADF STEM intensities
- Semiempirical formalism enables thickness and density determination with an error below 10 %