Soft Matter, Polymers, Composites

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

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High-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) is a promising technique for imaging carbon-based materials for organic solar cells because it provides a particularly sensitive composition (Z-)contrast at low electron energies. Furthermore, low-keV STEM can be generally applied to quantify thickness or material density of the investigated samples if the composition of the material is known.

The experiments were carried out with the field-emission-gun scanning electron microscope of a dual-beam FEI Strata400S. A standard semiconductor STEM detector with several ring-like segments was used which is positioned below the sample. Pronounced atomic-number contrast can be obtained in the high-angle annular dark-field (HAADF) STEM mode where only electrons are collected which are scattered into high angles after interaction with the nucleus of the sample atoms. This leads to a strong Z-contrast which is even more pronounced at low electron energies. For comparison, transmission electron microscopy (TEM) images were taken with a Philips CM 200 FEG/ST microscope at 200 keV.

The low-keV HAADF STEM intensity is not only sensitive towards the chemical composition but depends also on the sample thickness and primary electron energy. The energy dependence is demonstrated by Figures 1a-c which shows HAADF STEM images taken at different electron energies of an approximately 100 nm-thin film containing a blend of poly-(3-hexylselenophene-2,5-diyl):C61-butyric acid methyl ester (P3HS:PCBM), which is a material system for photoactive layers in organic solar cells [1]. A contrast inversion is clearly visible by comparing Figures 1a and 1c. To interpret the images a semiempirical formalism for the calculation of the HAADF STEM image intensity was developed [2]. The calculated intensities of PCBM and P3HS are plotted in Figure 2 as a function of the electron energy assuming a 100 nm-thin film. The contrast inversion is well predicted. The intensities show a characteristic maximum at about 8 keV which corresponds to minimum contrast between PCBM and P3HS (Figure 1b). On the basis of the calculations, the bright needle-like structures in Figure 1c are composed of P3HS. A degradation of resolution is visible in the image taken at 4.5 keV (Figure 1a) which suggests the choice of an electron energy higher than the contrast inversion energy for optimized imaging conditions.

Figure 3 shows a comparison of a 15 keV HAADF STEM image and two conventional bright-field TEM images. The sample consists of a blend of poly-(3-hexylthiophene-2,5-diyl):[6,6]-phenyl C61-butyric acid methyl ester (P3HT:PCBM). High contrast between the P3HT and PCBM domains is obtained in the 15 keV HAADF STEM image (Figure 3a). Simulations of the P3HT and PCBM HAADF STEM intensities in analogy to Figure 2 show that P3HT exhibits a lower intensity compared to PCBM. In contrast, in-focus bright-field TEM (Figure 3b) does not provide any structural features due to the small difference of mass thickness of the compounds. Large defocus values (Figure 3c) reveal some contrast. However, large defocus values degrade the resolution to a few nanometers and lead to strong delocalization of the image information which impedes the interpretation of the TEM images and the accurate size determination of the structural features [3].

The semiempirical formalism is not only useful for image interpretation or for the evaluation of optimum imaging conditions, it can be also used to determine either the sample thickness or the density of the sample material for a material with known composition. For this purpose the energy-dependent maximum of the HAADF STEM intensity is exploited. At the intensity maximum a well-defined relation exists between electron energy E, sample thickness t, density ρ, atomic number Z and atomic mass number A given by $t = f \cdot (A \cdot E^2)/(\rho \cdot Z^2)$, whereby the factor f depends on the collection angles of the HAADF detector. Experimentally, the intensity maximum is determined by varying the electron energy until the contrast due to thickness variations is minimized. This is exemplified by the determination of the density of fluorenyl hexa-peri-hexabenzocoronene (FHBC) [4] which is not known up to now. In principle it is sufficient to determine the contrast inversion energy for only one sample with a precisely known thickness. To enhance the quality and the reliability of the

measurement it is nevertheless useful to examine a set of samples with different known thicknesses. Figure 4 shows a plot of the sample thickness vs. the electron energy at contrast inversion, i.e. the energy at the maximum HAADF STEM intensity, for several FHBC films with different thicknesses. The density was then calculated from the prefactor of the quadratic fit function resulting in a value of 1.04±0.29 kg/m³.

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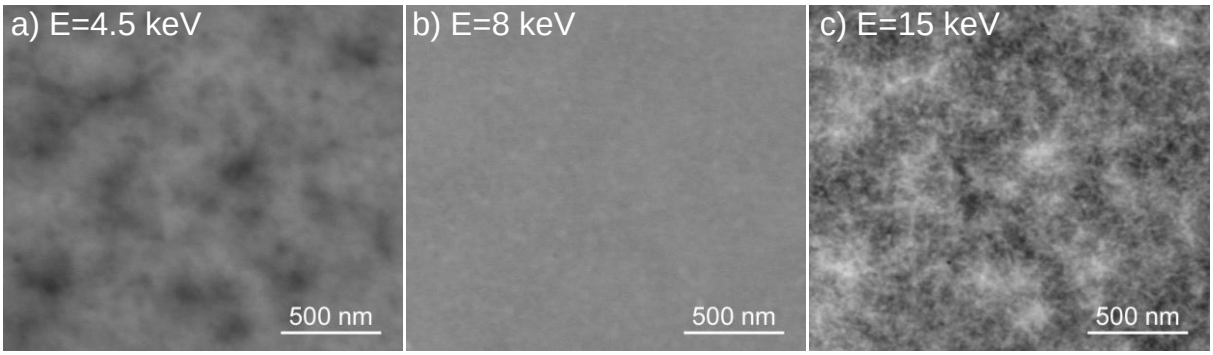

Figure 1. a)-c) HAADF STEM images of a P3HS:PCBM film taken at different electron energies, which show contrast inversion.

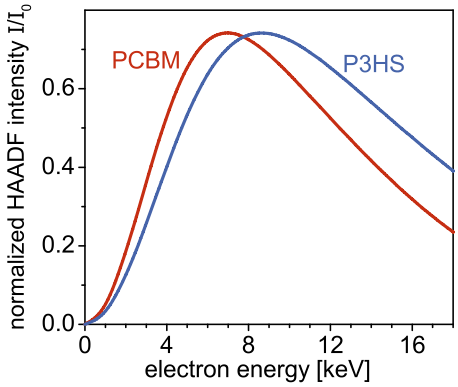

Figure 2. HAADF STEM intensity normalized with the intensity of the incident electrons calculated for 100 nm-thin films of P3HS and PCBM.

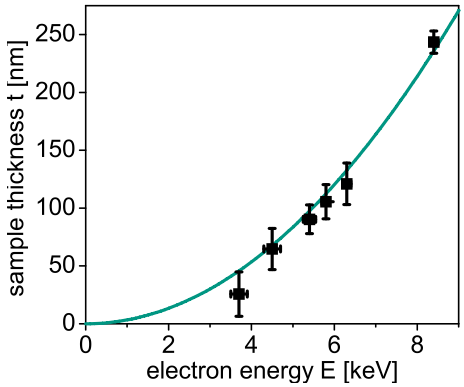

Figure 4. Relation between sample thickness and electron energy for different pure FHBC films at the intensity maximum (contrast inversion point).

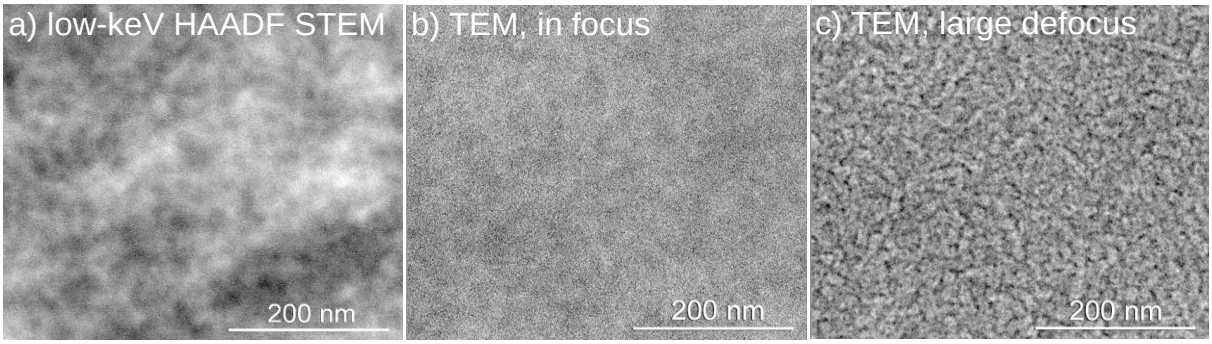

Figure 3. a) HAADF STEM image of a P3HT:PCBM film taken at 15 keV; b) In-focus TEM image taken at 200 keV; c) TEM image with an underfocus of 10 µm. (The images are taken at different sample positions.)