Correlative STEM and SEM Imaging of PTB7:PC$_{71}$BM-Based Photoactive Layers in a Scanning Electron Microscope

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Lowering the electron energy from values ≥ 80 keV in standard STEM experiments to ≤ 30 keV in scanning electron microscopes equipped with a STEM detector leads to the suppression of knock-on damage and contrast enhancement due to the increased scattering probability. The latter is favorable to distinguish weakly scattering materials with similar densities and average atomic numbers. Another advantage of scanning electron microscopes is the inherent availability of surface topography imaging by secondary electron (SE) SEM imaging, which can be used in a correlative manner in combination with STEM, i.e., SEM and STEM images are acquired in parallel revealing bulk structure and surface topography from exactly the same specimen region [1]. This is important because STEM contrast can be influenced by topography effects and SE SEM images support the interpretation of STEM images.

The PTB7:PC$_{71}$BM system is a well-studied material system for bulk-heterojunction absorber layers of organic solar cells, which consist of an interpenetrating network of domains of donors (PTB7) and acceptors (PC$_{71}$BM). The photovoltaic performance is strongly influenced by the nanomorphology of the absorber layer [2], which is often investigated by TEM. However, the materials suffer from electron-beam damage and low contrast at high electron energies.

In this work, we apply correlative STEM/SEM in a scanning electron microscope (≤ 30 keV) to image the nanomorphology of PTB7:PC$_{71}$BM absorber layers after deposition from o-xylene and the process additive 1,8-diiodooctane (DIO) [3]. To understand contrast formation, 30 keV cross-section HAADF- and BF-STEM images of alternating pure PTB7 and PC$_{71}$BM layers in a wedge-shaped specimen were analyzed (Figure 1a,b). Intensity line profiles (Figures 1c,d) were acquired along the arrows in Figure 1a,b which point into the direction of increasing specimen thickness t. The HAADF-STEM intensity (normalized with respect to the intensity of the incident electron beam) of PTB7 and PC$_{71}$BM is plotted as a function of t in Figure 1c, which shows maxima and a corresponding contrast inversion between PTB7 and PC$_{71}$BM at a thickness of 470 ± 10 nm. Below this thickness, the PC$_{71}$BM appears brighter than PTB7 while PC$_{71}$BM is darker at larger t. The BF-STEM intensity (Figure 1d) is lower for PC$_{71}$BM at all t values, and its intensity decreases strongly up to 100 nm sample thickness. Due to the thickness dependence of the STEM contrast at 30 keV, correlatively taken SE SEM topography images yield information on t changes and are useful to distinguish PTB7 and PC$_{71}$BM.

The results show that the thin-film nanomophology depends strongly on the DIO concentration in the earlier PTB7:PC$_{71}$BM solution. Omitting DIO during deposition, the absorber layer forms a "hill"-like topography (Figure 2a). Exploiting the information in Figures 1c,d for phase assignment in the HAADF- and BF-STEM images (Figures 2c,d), the hill-like regions are large PC$_{71}$BM domains (~200-500 nm) which are surrounded by PTB7. In contrast, upon addition of 3 % DIO, the surface of the absorber layer flattens upon film formation (Figure 2d). Hence, thickness effects can be ignored in STEM images

(Figure 2e,f) and material contrast dominates. The $PC_{71}BM$ domains dramatically decrease in size to ~10-20 nm and form aggregates with a size of tens of nanometers which are either $PC_{71}BM$-rich or $PC_{71}BM$-poor both in lateral (Figures 2e,f) and vertical directions (as can be inferred from cross-section images not shown here). The small-scale phase separation with domain sizes in the order of the exciton diffusion length leads to a strongly enhanced photovoltaic performance [3]. Our results suggest that low-energy correlative SEM and STEM is well suited image beam-sensitive, weakly scattering, and complex organic materials [4]. It is also promising for biological samples.

References:

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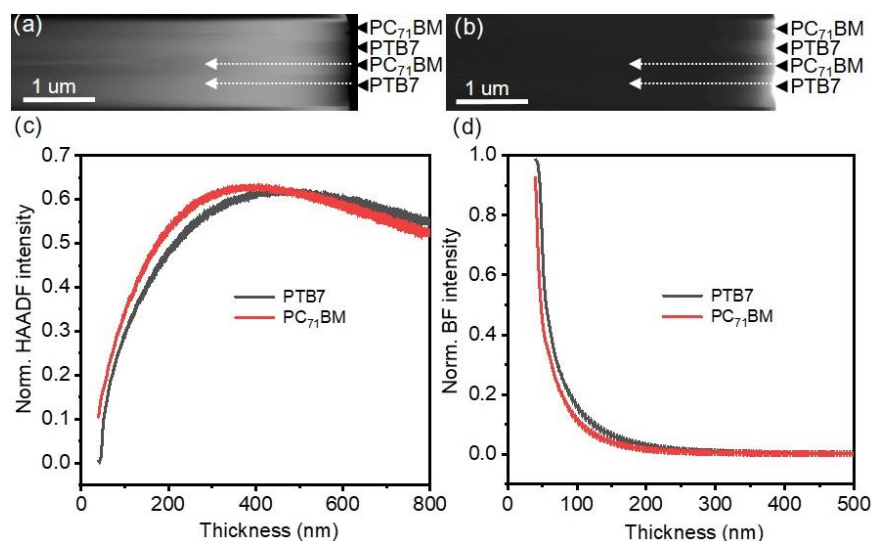
Figure 1. Cross-section (a) HAADF- and (b) BF-STEM images of alternating pure PTB7 and $PC_{71}BM$ layers in a wedge-shaped specimen. (c,d) Intensity line profiles as a function of the specimen thickness acquired along the arrows in (a,b) for PTB7 and $PC_{71}BM$ in (c) HAADF- and (d) BF-STEM, respectively.
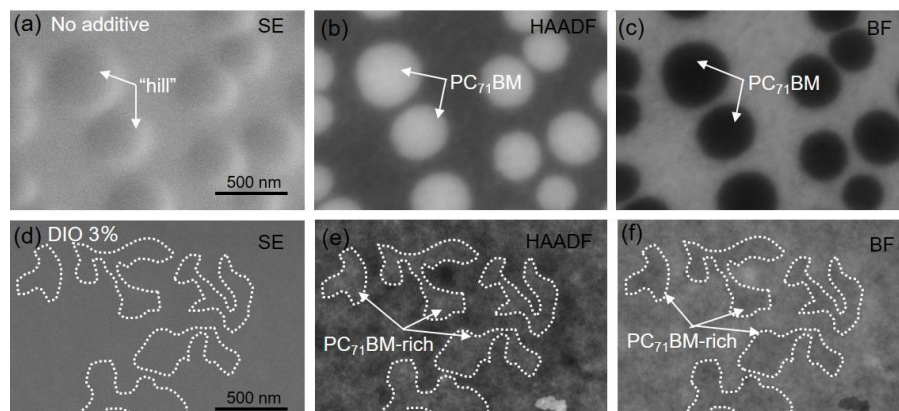

Figure 2. Plan-view correlative SEM, HAADF- and BF-STEM images of PTB7:$PC_{71}BM$ absorber layers (a-c) without DIO and (d-f) with 3% DIO.