 https://doi.org/10.1051/bioconf/202412907021

Texture analysis of radiation sensitive organic films: Comparative study by electron diffraction tomography and GIWAXS

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Background incl. aims

Texture describes the preferred orientation of grains in crystalline materials. For characterization of texture, the reciprocal space is conventionally investigated in diffraction experiments using electrons, X-rays or neutrons as probes. In polycrystalline thin films texture is an important characteristic of the microstructure determining anisotropic properties like, e.g., charge carrier transport in bulk heterojunction (BHJ) organic solar cells (OSC). Gracing incidence wide angle X-ray scattering (GIWAXS) is a well-established method for texture analysis of OSCs, however, real space information is only indirectly accessible as averaging measure (e.g. grain size or coherence length). In contrast, electrons as probe in transmission electron microscopes (TEM) provide direct access to both real and reciprocal space while additionally delivering analytical signals for local chemical analysis. However, due to the challenge of radiation damage, electron diffraction is not well explored for OSCs. In this work we show that electron diffraction tomography (EDT) can be used to investigate the reciprocal space of polycrystalline thin films in 3D, providing information on texture comparable to results obtained with GIWAXS.

Methods

We chose two radiation sensitive BHJ OSC active layers as model sample systems. Both OSCs contain $PC_{71}BM$ as fullerene acceptor, but differ in that the donor component is a small molecule (DRCN5T) in one case and the classical polymer P3HT in the other. Large-area plan-view samples of the active layer were prepared by floating off the spin-coated film from the substrate and transferring it to a TEM grid. Real space information on the nanomorphology of the donor and acceptor phases was obtained using STEM-EELS or EFTEM as exemplary shown for the DRCN5T/$PC_{71}BM$ system in Fig. 1a.

For EDT we acquired tilt series of zero-loss energy filtered SAED patterns across a tilt range of ±70° using a single-axis tomography holder (Fig. 1b). Energy filtering is necessary to suppress inelastic scattering background in particular at small scattering angles, which is critical to reveal crystallographic information on the small molecule/polymer crystallites with their nm-sized unit cells. To minimize effects of radiation damage, each diffraction pattern was acquired at a fresh sample area with electron dose well below the evaluated critical dose. From the SAED tilt series the 3D diffraction space was reconstructed with a home-developed code for 3D reciprocal space filling which is based on polar transformations (Fig. 1c). Furthermore, azimuthal averaging of the volume around qz axis was performed to obtain qr-qz reciprocal space maps for direct comparison with GIWAXS data.

Results

The qr-qz reciprocal space maps derived from EDT and GIWAXS are exemplarily depicted side-by-side in Fig. 1d for the DRCN5T/$PC_{71}BM$ film. They show excellent agreement, indicating that not only GIWAXS but also EDT is perfectly suited for texture analysis of such radiation sensitive organic films. Moreover, direct comparison of different line profiles extracted from the reciprocal space maps reveal even quantitative matching of EDT and GIWAXS data. Interestingly, the EDT data show a better signal-to-noise ratio, in particular regarding the in-plane reciprocal information, which is difficult to access with GIWAXS. From the reciprocal space maps, it can be seen that the π-stacking of the small molecules in the DRCN5T crystallites exhibit preferred edge-on and face-on orientation in the fibre like nanomorphology revealed by STEM-EELS. Quantitative evaluation of the diffraction peak characteristics yields comparable structural information in terms of crystal coherence length, mosaicity, etc..

Conclusion

In summary, we demonstrate that the texture of radiation sensitive OSC thin films can be investigated using EDT yielding results in quantitative agreement with GIWAXS. Combining EDT with real space characterization using high-resolution and analytical TEM methods provides great opportunities for a more comprehensive and in-depth analysis of OSC thin films. Furthermore, the application of the presented methodology to state-of-the-art, non-fullerene OSC systems consisting of PM6:Y6 is in progress and will be covered in the conference contribution.

Graphic:

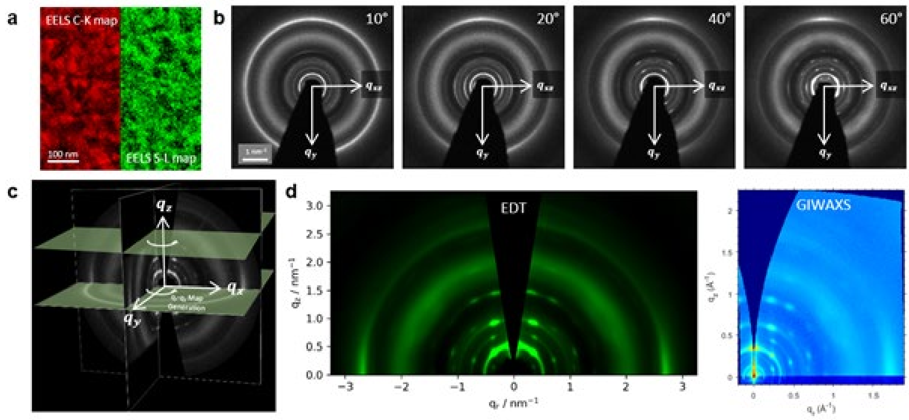

Figure 1: Characterization of DRCN5T:$PC_{71}BM$ BHJ OSC. (a) STEM-EELS dataset showing the nanomorphology. (b) Exemplary EF-SAED patterns out of the acquired tilt series. (c) Reconstructed 3D reciprocal space featuring the azimuthal integration for obtaining (d) the q_r-q_z map for comparison to GIWAXS measurements (left: EDT data, right: GIWAXS data).

Keywords:

Thin-film texture, EDT, OSC, GIWAXS