 https://doi.org/10.1051/bioconf/202412907006

Towards in-situ 4D-STEM observation of texture evolution in nano-crystalline thin films

Dr. Mingjian Wu[1], Chang-Lin Hsieh[1], Daniel Stroppa[2], Philipp Pelz[1], Colin Ophus[3], Penghan Lu[4], Rafal Dunin-Borkowski[4], Christina Harreiss[1], Peter Denninger[1], Erdmann Spiecker[1]

[1]IMN & CENEM, FAU Erlangen-Nurnberg, Erlangen, Germany, [2]DECTRIS Ltd, Baden-Daettwil, Switzerland, [3]NCEM, Lawrence Berkeley National Laboratory, Berkeley, USA, [4]Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Juelich, Germany

Background incl. aims

Texture describes the preferred orientation of grains in crystalline materials, which dictates their anisotropic, for example, (opto-)electronic, thermal transport, and mechanical properties. The texture is evaluated conventionally by probing the reciprocal space using X-ray and/or electron diffraction methods, where spatial information, e.g., the orientation relationship of particular grains, is hardly accessible. Probing the local diffraction pattern with a focused electron beam, i.e., nano-beam diffraction (NBD) 4D-STEM, provides local structure information. Recent detector technology opened new possibilities to perform such experiments at ever-higher temporal resolution. In this contribution, we discuss the optimized conditions towards in-situ 4D-STEM observations of texture evolution in thin films by a combination of state-of-the-art fast direct electron detector (DED), dose-efficient experimental approach, and novel algorithms of data analysis.

Materials and methods

Two material systems, (I) a beam robust poly-crystalline gold thin film and (II) an extremely radiation-sensitive bulk hetero-junction (BHJ) blend used as active layers in organic solar cells serve as model samples in this study.
For poly-crystalline gold, we deposited 15 nm gold with PVD on the SiNx windows of MEMS heating chips (DENSsolutions Wildfire) and annealed the film in the TEM at 150^{o}C for 180 s while observing coarsening of the nano-crystalline structure. 4D-STEM experiments were carried out using a Thermo Fisher Scientific Spectra 200 TEM operated at 200 kV in a regular nano-beam diffraction setup and data was acquired using a DECTRIS ARINA detector. The orientation maps are then analyzed using the ACOM [1] routine within the py4DSTEM package and custom codes to streamline the output orientation matrix to the Orix package [2] for further evaluation of the texture evolution.

The BHJ thin film of nominal thickness of 80 nm comprises small molecule donor DRCN5T blended in fullerene acceptor PC71BM as reported earlier

[3,4]. The major challenge is the dose budget (< 5 e-/Å2 at room temperature) that limits the applicable probe current for structural elucidation.

Results and discussions

For gold nano-crystal thin film (Fig. 1a), despite being radiation robust, it remains very challenging to observe evolution at high spatial and temporal resolution with sufficient angular resolution and sampling in diffraction space for orientation determination. This is due to the high dimensions of data required and the limited dose rate at the single pixel level of DED detection. To overcome this limit, we realized that an appropriate convergence angle and camera length are the key factors (using a standard NBD setup) that control the reciprocal space coverage and sampling. It is important to balance DED saturation in the primary beam and sufficient SNR of weak Bragg disks for accurate disk detection and subsequent crystal orientation matching. With a larger convergence angle, a higher probe current at a given high speed of detector readout, thus a higher dose, can be applied. While a small convergence angle seems arguably to favor angular resolution for Bragg disks detection, it lowers the applicable probe current due to detector saturation, resulting in weaker Bragg disks fading in the diffuse scattering background. After optimizing conditions on our experimental platform, we found that time resolution of 5 – 10s and sub-3 nm sampling resolution (probe size <1 nm) for a statistically relevant field of view is realizable.

We further discuss strategies to improve the dose-effectiveness in terms of Bragg peak detection and eventually, in-situ 4D-STEM experiments supported by experimental results. These include (I) elastic energy filtering, (II) amplitude grating using patterned probe-defining aperture [1], and (III) applying precession-assisted 4D-STEM [5].

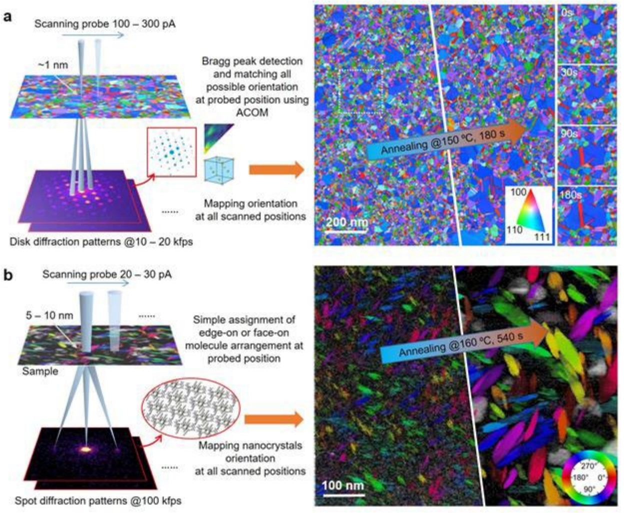
Finally, we were able to visualize the grain orientation from optimized, standard NBD 4D-STEM datasets and track the evolution of texture evolution of a defined ROI from the early stage on. We observed the growth of <111> oriented grains at the cost of neighboring high-index oriented grains (Fig. 1a). The 4D-STEM datasets allow grain orientation relationships to be analyzed qualitatively as well as quantitatively, shedding light on the complex interplay between various factors including types of grain boundaries, defects, and even local strain.

In the case of extremely dose-budget limited scenarios like the molecular nano-crystallites in the BHJ, the ultimate Bragg peak detectability is limited by the Poisson noise of the scattered electrons that strike on detector pixels. Therefore, the focused electron diffraction pattern is advantageous. Inspired by earlier work of ultra-high angular resolution ω-q mapping [P. Midgley, Ultramicroscopy 76(1999) 91], we established a dose-efficient approach, 4D-scanning confocal electron diffraction (4D-SCED), to study the texture structure, i.e., face-on and edge-on domains, of nano-crystallites of the donor in the BHJ (Fig. 1b). 4D-SCED applies defocused pencil beam illumination on the sample and combines a confocal electron optic setup with a pixelated detector to record focused spot-like diffraction patterns. The defocused illumination reduces the dose and generates a homogenous beam-specimen interaction. At the same time, the confocal optics generates spot-like diffraction signals, boosting both the signal-to-noise ratio and signal-to-background ratio even in Poisson noise-limited scenarios [4]. We demonstrated a quasi-in-situ observation of the molecular nanocrystallites' structural evolution during an annealing experiment using a CMOS detector [3] (Fig. 1b). We further discussed new avenues to further reduce dose, improve experimental speed (temporal resolution) and throughput using a fast hybrid pixel detector, and advantage of the frame-based detector over the current generation of event-based detector for these applications [4].

Conclusion

In the study of nano-crystalline structural evolution, the achievable temporal resolution of in-situ 4D-STEM experiments is dose-limited at detection saturation level, independent of sample radiation resistance. Besides calling for further improvements of detectors, we present and discuss several experimental strategies for both beam robust and beam sensitive samples to optimize conditions to spare the meaningful dose to Bragg signal detectability and structural determination.

Graphic:



Keywords:

4D-STEM, in-situ, texture, thin film.

Reference:

[1] Ophus, C., et. al., Microsc. Microanal., 28 (2022), 390–403.
[2] Johnstone, D. et. al., J. Appl. Crystallogr., 53 (2020) 1293
[3] Wu, M., et. al., Nat. Comm., 13 (2022), 2911.
[4] Wu, M., et. al., J. of Phys: Mater., 6 (2023), 045008.
[5] Midgley, P., Eggeman, A., IUCrJ. 2 (2015) 126