Imaging Polymer Crystallinity and Grain Boundaries with STEM ptychography

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The spatial atomic structure of crystalline grains in polyethylene naphthalate (PEN) is accessible for the first time with ptychographic imaging under low dose illumination. Ptychography also enables a three-dimensional (3D) study of the size and orientation relationship of grains.

The crystal structure and orientation in polymers, which depends on parameters including temperature, interfacial interactions and strain, will vary locally. To resolve the detailed microstructure, high resolution imaging is required because diffraction methods only generate average structural information from the characterization region. In a study of annealed thin films of PEN [1], crystalline domains were found to vary with the depth from a surface. Here, PEN is used as a model system to demonstrate high resolution imaging of polymer crystals.

High resolution imaging of polymers is limited by the low contrast generated by light elements and beam damage from the high-intensity illumination that used to get sufficient resolution. The low dose imaging techniques applied here are crucial to acquire data from the pristine structure before it is significantly altered by radiolysis. A thin polymer specimen can be treated as a weak phase object. When the electron probe scans through a thin specimen consisting of light elements, the amplitude is not expected to change significantly, while the phase contrast will offer more useful information.

Ptychography [2] is a dose efficient imaging technique with phase retrieval capacity by making used of a 4D STEM dataset. Figure 1 shows a ptychographic image of a grain in PEN. Many of the spatial frequencies present in the image, such as the (200) spacing, agree with previous models derived from X-ray diffraction studies [3]. Noticeable in Figure. 1, however, there are some details between the (200) planes that are not predicted from the previous model. This information can only be uncovered by direct imaging.

In addition, depth profiling can be obtained through a post-acquisition optical sectioning approach using the 4D dataset recorded in only one scan. This is very useful for beam sensitive materials. Grain boundaries can be directly observed from the reconstructed ptychographic images and 3-D detection of grain boundaries in PEN is possible with optical sectioning. It is found that there does not appear to be an amorphous layer in the boundary.

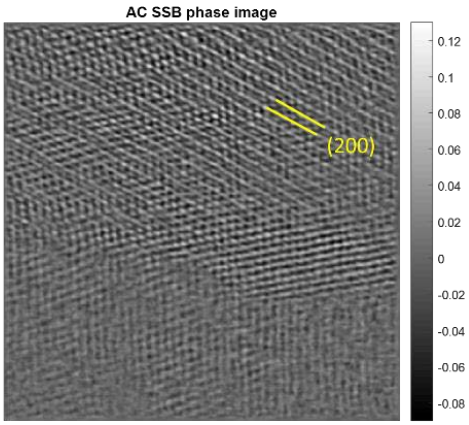

Figure 1. Ptychographic phase image of PEN crystallinity reveals conformational details. The structure between (200) planes are not observed in the images generated by the model that produced from XRD.

Reference

[1] Shinotsuka, K. et al. J. Appl. Polym. Sci. 133, (2016).
[2] Yang, H. et al. Nat. Commun. 7, 12532 (2016).
[3] Heuvel, et al. *Polymer (Guildf).* 41, 4249 (2000).