A Workflow for Imaging 2D Materials using 4D STEM-in-SEM

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The grain structure and orientation of polycrystalline two-dimensional (2D) materials modulates their thermal, mechanical, and electrical properties. Thus, to rationally control the properties of 2D materials, the as-synthesized grain structure of the 2D materials must be routinely and reliably measured. Although different methods can be used to spatially map the grain structure/orientation of 2D materials, electron diffraction methods are generally regarded as the 'ground truth' because they can resolve these characteristics on the nanometer length scale.

In this contribution, a four-dimensional (real-space and k-space) scanning transmission electron microscopy method for use in the scanning electron microscope (4D STEM-in-SEM) is described. This technique can map the structure/orientation of 2D materials on a wide range of length scales (10^{-2} m - 10^{-9} m). Briefly, a 30 keV focused electron beam is incident on the electron transparent 2D material. The electrons that transmit through the sample propagate in a field-free region and strike a phosphor screen forming a diffraction pattern. This (optical) diffraction pattern is then imaged onto a CCD camera. A home-built scan generator is used to raster the electron beam across the sample and trigger the storage of diffraction pattern images [1]. The low energy of the electron beam yields significant diffraction contrast while creating minimal knock-on damage [2].

Once collected, the output of a 4D STEM-in-SEM experiment can be regarded as a 'big' dataset which cannot be exhaustively inspected by humans – e.g., a single real-space scan (512 × 512) generates ~250000 diffraction patterns. We have developed a workflow based on a Fourier-space representation of the diffraction data to rapidly inspect 4D STEM-in-SEM data and extract information such as crystallographic orientation and identify distinct regions of the material (such as different thicknesses and interlayer rotations). A typical workflow for data inspection is as follows. First, since no de-scan coils exist in an SEM, the center of each diffraction pattern is located and de-scanned digitally. This step is particularly important for large fields-of-view. The diffraction pattern is then resampled to a polar grid, and the Fourier transform is applied to the angular coordinate. The transformed data can be visualized by creating colorized image of the amplitude and phase of the Fourier-space data. Since it can be reasonably assumed that the diffraction patterns of a 2D material are based on structures that have in-plane symmetry, we can initially restrict our inspection to just a few low-index Fourier components. These synthetic images allow a practical visualization of the 4D STEM-in-SEM dataset with minimal processing power and user time and can indicate what region/structures are present in the sample. Then a cross-correlation-based pattern matching approach can give higher quality orientation information. This Fourier representation may be a useful dimensionality reduction method when machine learning is used for further analysis.

Figure 1 shows examples of this Fourier based analysis applied to a graphene oxide sample. An image of the phase of a six-fold Fourier component is used to visualize the grain orientation, and the amplitude image to visualize multilayer structures. Figure 2 shows the technique applied to monolayer graphene. Inspection of the two-fold Fourier components unexpectedly reveals texture on the micrometer length

scale that was assigned as polymer residue from a wet-transfer step. Furthermore, the analysis showed that the polymer was oriented with respect to the graphene lattice [3]. The workflow described here leverages the symmetry of 2D materials and the efficiency of the FFT and may be particularly helpful when the S/N and processing power is not available/necessary to perform a more detailed analysis [4].

References:

[1] W.C. Lenthe et al., Ultramicroscopy **195** (2018), p. 93.
[2] R.F. Egerton, Micron **119** (2019), p. 72.
[3] M. Gulde et al., Science **345** (2014), p. 200.
[4] Y. Han et al., Nano Letters **18** (2018), p. 3746.

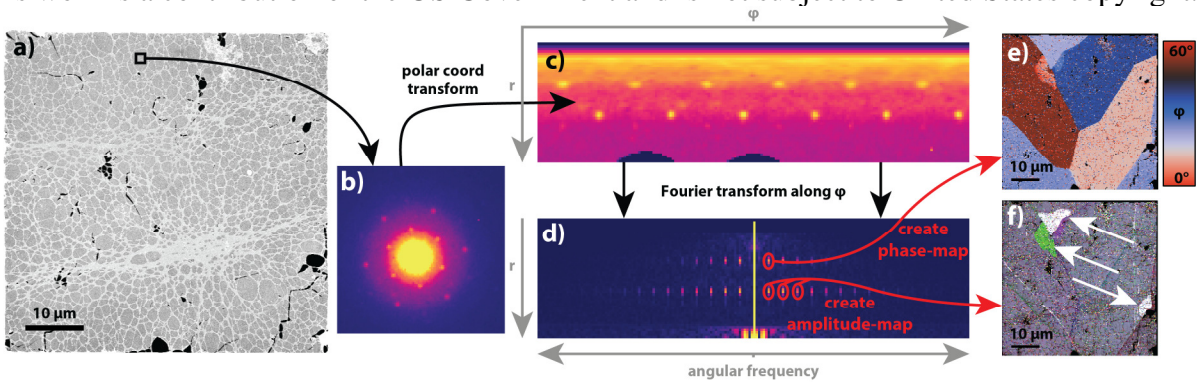

Figure 1. a) Secondary electron image of a mostly monolayer graphene oxide film on lacey carbon. b) A single diffraction pattern from a 4D STEM-in-SEM dataset. c) Diffraction pattern resampled to polar coordinates. d) Absolute value of the FFT (across φ) of the polar data. e) Colorized map of the phase of the circled Fourier component. f) Colorized map of the amplitudes of the circled Fourier components; distinct bilayer regions indicated with arrows.

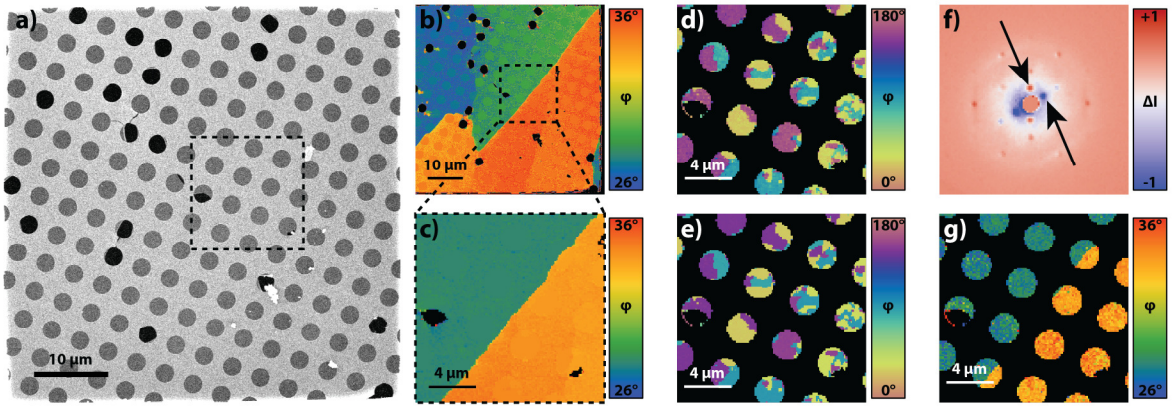

Figure 2. a) Secondary electron image of a supported monolayer graphene film. b) Colorized map of the phase of a six-fold Fourier component – i.e., graphene orientation. c) Zoomed-in orientation map derived using a cross-correlation approach. d) Colorized map of the phase of a two-fold Fourier component showing the texture of a polymer residue. e) Orientation map using a cross-correlation approach. f) The difference between the diffraction patterns in two polymer domains; the arrows indicate the polymer diffraction. g) The data in (e) *modulo* 60°, on the same colormap as (c), highlighting the orientation relationship.