

Determination of Thin-Film Ferroelectric Polarity at the Nanoscale

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The properties of thin-film ferroelectric materials depend on the spatial arrangement (domain patterns) of the ferroelectric polarization. Transmission electron microscopy has been used successfully for the analysis of specimen polarity of bulk materials [1] and thin films [2]; however, determining the direction of polarity (such as across 180° domain boundaries) is challenging when unit cell distortions are small, such as in BaTiO₃. And while convergent beam electron diffraction (CBED) can distinguish between 90° and 180° domain walls [3], typical beam size on the order of 10 nm limits utility for examining nanoscale variations of the ferroelectric polarization in thin-film materials.

In this presentation, we establish that position averaged convergent beam electron diffraction (PACBED) allows for determination of the polarity in ferroelectric materials. The PACBED technique uses a scanned Ångström-sized electron probe in STEM to form patterns that exhibit high sensitivity to specimen thickness, tilt, and crystal structure polarity [4]. We will demonstrate that PACBED allows for ferroelectric polarity determination even when unit-cell distortions are smaller than what can be measured using real-space imaging techniques. The sensitivity of the technique is demonstrated by examining a thin-film of BaTiO₃ grown by molecular beam epitaxy on SrTiO₃ where the polar distortion is only ~ 4 pm. Further, we will show that the method is compatible with the electron optical settings and specimen thicknesses used in atomic resolution STEM imaging.

Fig. 1 shows a simulated polar BaTiO₃ PACBED pattern. The pattern exhibits asymmetric intensity, particularly in the lobes at the top and bottom of the central disk, due to non-centrosymmetry of the unit-cell (see figure for orientation). Fig. 2 shows magnified top and bottom lobes as a function of specimen thickness where asymmetry is detectable by visual inspection over a range of specimen thicknesses. Validation of the technique is provided in Fig. 3 where excellent agreement is demonstrated between an experimental PACBED pattern of a BaTiO₃ thin-film, acquired from a ~ 5 × 5 unit-cell region, and a corresponding simulation. We will also show that the *a* and *c* directions of a tetragonal unit cell can also be distinguished. When this information is combined with the asymmetric lobe intensity, separation of unit-cell distortions *and* polarity is made possible. For example, cases where a tetragonal film may not necessarily be polar can be investigated with PACBED patterns. Finally, we will also address the influence of specimen tilt on the PACBED intensity distribution for polar materials.

References

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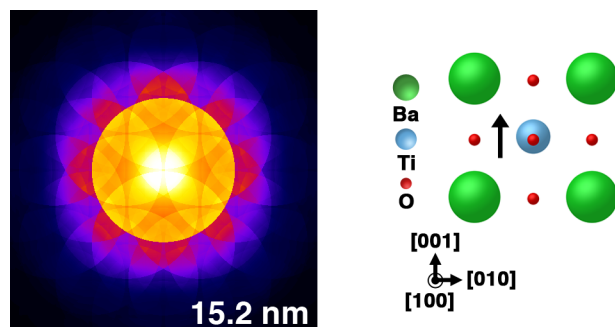


FIG. 1. Simulated PACBED pattern of BaTiO₃ with corresponding orientation of the unit-cell.

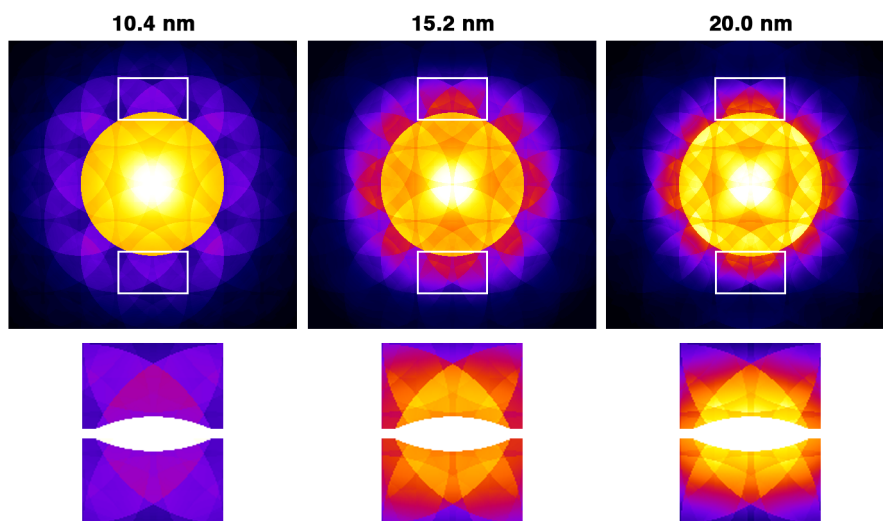


FIG. 2. (top) Simulated PACBED patterns of BaTiO₃ as function of thickness (bottom) Magnified lobes of the PACBED patterns, as indicated, where image intensities have been adjusted to accentuate the lobe asymmetry.

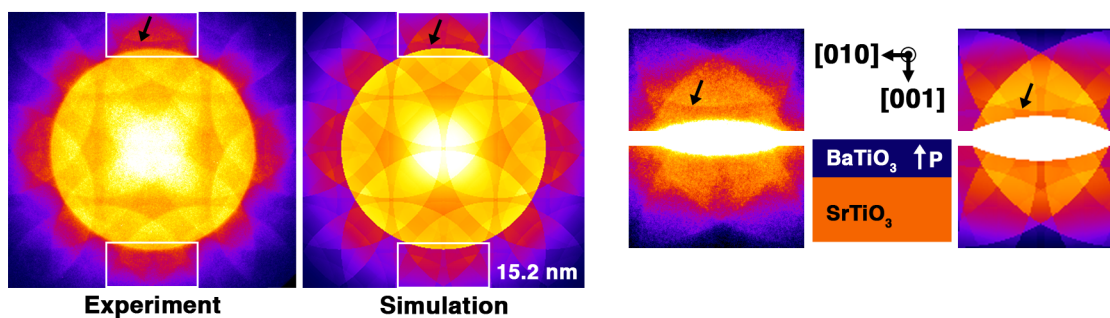


FIG. 3. (left) Experimental and simulated PACBED patterns of a 15.2 nm thick BaTiO₃ thin-film sample (right) Comparison of the top and bottom lobes extracted from experiment and simulations. Inset shows the orientation of the BaTiO₃ thin-film ferroelectric polarization relative to the substrate.