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Measuring Local Polarization by Differential Phase Contrast

S. Calderon V[1], Stephen D. Funni[1], Elizabeth C. Dickey[1]

[1.] Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA, USA.

Understanding the fundamental mechanisms giving rise to polarized states in materials and enabling their switching is critical for improving the next generation of functional electronic devices. Hence, in this work, we explore the use of the differential phase contrast (DPC) family of techniques in scanning transmission electron microscopy (STEM) to advance the determination of local polarization at atomic resolution. Although this methodology can be applied to a variety of systems, ZnO is studied as a prototype polar material. In fact, ZnO is currently being researched as a new ferroelectric material, when alloyed other oxides such as MgO [1], due to its high compatibility with the current silicon-manufacturing process for electronics.

ZnO has a wurtzite crystal structure, with a strong ionic character and a large spontaneous polarization along the c-direction. Taking advantage of such large spontaneous polarization and its simple theoretical calculation, we explore the accuracy of DPC-STEM (i.e. iDPC and dDPC) to measure the projected local polarization. A comparison between iDPC, dDPC and annular bright-field (ABF) is carried out using multislice simulations and validated by experimental images of ZnO oriented along [1 $1\bar{2}$0]. Two-dimensional vector pair correlation functions (vPCFs) [2] are used to calculate the overall polarization from simulated and experimental images, while assessing the influence of various microscope parameters on the accuracy of the polarization values measured from the images.

Multislice image simulations are carried out using Dr. Probe V1.9 software package [3]. Simulations are carried out using the frozen-phonon configuration with 900 variants to ensure convergence of each atomic position to the position in the atomic model. Images are simulated at 200 keV and 1 µm of spherical aberration, while varying the sample thickness, probe size and defocus values. The potential discretization is set at 144 pixels x 144 pixels (0.004 nm/pixel approximately) and the thickness of the slices is one atomic layer.

STEM experimental images are acquired in a ThermoFisher Titan-Themis operated at 200kV, using a four-segment annular detector (DF4), a probe convergence angle of 18 mrads and a camera length that resulted in inner and outer acceptance angles of 11 and 43 mrads. Orthogonal scan orientations are acquired to correct nonlinear drift distortions using the methodology described by Ophus et al [4].

The images are analysed using SingleOrigin Python module described by Funni et al [2] and available here (https://doi.org/10.1184/R1/14318765). Briefly, to locate the atomic-column positions in each image, a projected reference lattice generated from a crystallographic file is first registered to the image. This indexes the columns by sublattice and provides an initial guess for peak finding. Next, the atomic column positions are refined with 2D Gaussian fitting to give an accurate location.

Our results indicate that differentiated differential phase contrast (dDPC) is the most robust image modality to measure accurately local polarization, in relation to ABF and iDPC [5]. However, when segmented detectors are used, special care needs to be taken due to the non-symmetric contrast transfer of these detectors [6], which makes the images dependent on the sample orientation with respect to the

detectors, especially for thicker samples. We quantify the influence of sample thickness and probe defocus on the relative errors of the calculated polarization, showing that with optimal experimental conditions, the projected polarization for ZnO can be measured between 0.1 – 8 % accuracy using dDPC imaging, as shown in Figure 1a. Figure 1b shows the Zn-O vPCF, where detailed structural characteristics are revealed, including cell parameters, and displacements from a centrosymmetric reference lattice, which are used to calculated an average polarization of the experimental image.

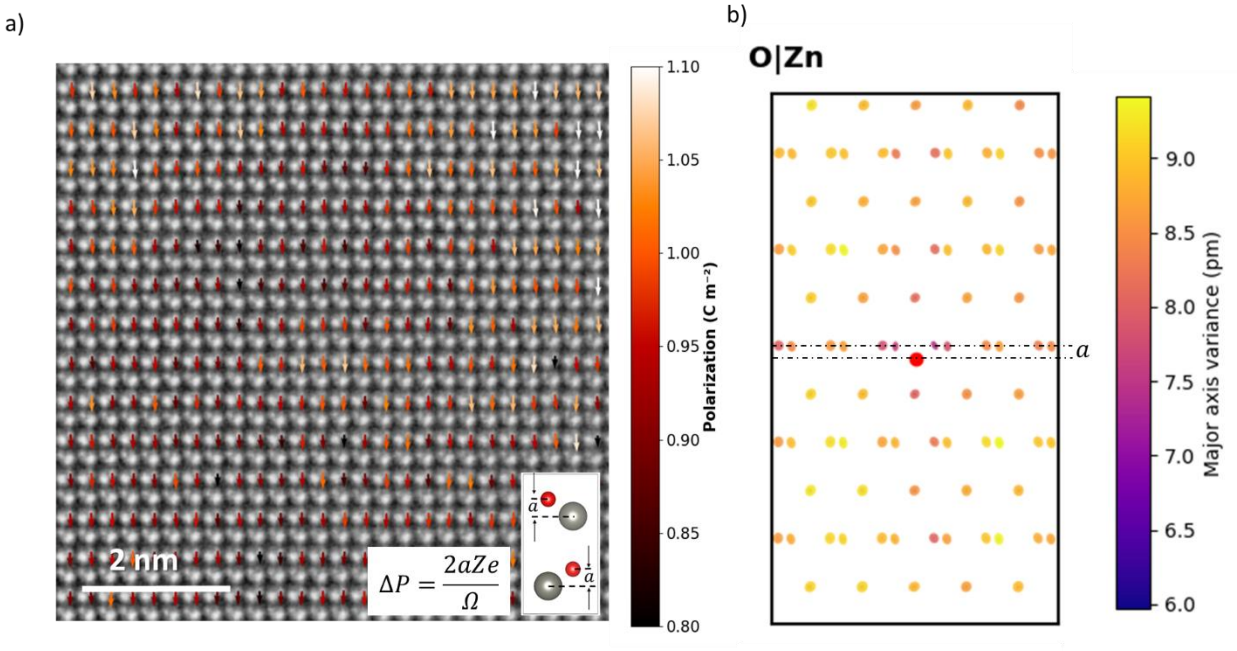

Figure 1. a) Experimental dDPC image overlapped with arrows representing the polarization calculated from each unit cell. The inset represents a ZnO wurtzite unit cell projected along $[1\bar{1}20]$ direction with the respective atomic displacement from a centrosymmetric ZnO phase. ΔP symbolizes the change in polarization, a is the atomic displacement, Z is the oxygen born effective charge, e the positive elementary charge and Ω is the volume of the unit cell. b) Experimental 2D Zn-O vector pair correlation function, where the atomic displacement (a) with respect to a centrosymmetric structure has been highlighted.

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