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ABSTRACT

Ferroelectric domain wall (DW) based nano-electronics is an emerging new field of research. It is only recently with advancements in electron and atomic force microscopy instrumentation that the complex nature of these 2D entities can be probed. In this Research Update, the advances in aberration corrected scanning transmission electron microscopy applied to ferroelectric topological defects are summarized. We discuss sub-atomic imaging and diffraction techniques used to observe changes in polarization, chemical composition, charge density, and strain at DWs and vortices. We further highlight the current achievements in mapping the 3D nature of ferroelectric polar skyrmions and in situ biasing. This Review will focus on both the fundamental physics of DW and polar vortex formation and their dynamics. Finally, we discuss how electron spectroscopy can be used to relate the quantified structural distortions of polar topological entities to changes in their oxidation state and band structure.

I. INTRODUCTION

In the past 20 years, there has been a significant shift in interest within the ferroelectric community from domains to domain walls (DWs) as the active element for device applications. At almost the exact same time, commercially available aberration corrected scanning transmission electron microscopy (STEM) was achieved. This significant advancement in STEM enabled researchers to start analyzing the sub-atomic shifts at ferroelectric domain walls and polar interfaces, thus probing the fundamental physics at the spatial resolution of the DW itself. Previous theories regarding DW width, structure, and nucleation mechanisms are now regularly investigated experimentally via STEM. With further advances in STEM detectors, computing power, and post-processing, the previously suggested ideas such as complex polarization rotation at ferroelectric domain walls as seen in ferromagnetic DWs and room temperature ferroelectric skyrmions can now finally be proven experimentally.

The results from STEM characterization have made many impactful studies toward developing domain wall nanoelectronics. More specifically, this type of characterization is vital for optimizing thin film growth in terms of strain, thickness, and purity levels for specific DW type based devices. Substitutional doping in perovskite and manganite unit cells has been used to tune material properties such as magnetism and conductivity. Additional control of the domain formation is possible through epitaxial strain.

Atomic-level DW studies have understandably concentrated on the properties of unusual DWs in well-known ferroelectrics. Often these materials have been previously commercialized and thus have established growth processes, ground-state domain structures, and compatible dopants. We wish to highlight the opportunity of finding non-classical behavior and emergent phenomena by searching for new, improper ferroelectrics, which intrinsically contain charged domain walls. Such uncommon ferroelectrics are more...
Characterizing DW properties requires crossover of expertise between high-resolution electron microscopy techniques and ferroelectric properties. These properties offer challenges and opportunities for DW experiments. For example, the stability under the electron beam varies not only between different materials but also the type of DW and polar topological feature. Furthermore, while the crystal symmetry is the overriding energy consideration for DW orientation in bulk crystals, DW or vortex orientation in nanoscale samples such as TEM lamellae can vary significantly. These factors are important as the DW contrast is often the most accessible clue for understanding the overall domain structure and polarity. Thus, a careful understanding of TEM contrast mechanisms and the applicability of different polarization mapping techniques is crucial for DW studies.

In this Review, we discuss how aberration corrected STEM techniques can be used to obtain reliable maps of the polarization, electric fields, and charge distribution within ferroelectric DWs and other polar topologies such as vortices, and how to avoid the most common sources of error and artifacts attributed to these techniques. As detailed in Tables I and II, we have structured the review by physical scale and the associated electron microscopy techniques possible. We begin the review by describing how to identify the domain patterns in the bulk sample via scanning electron microscopy (SEM) and the most appropriate electron microscopy techniques to use with increasing magnification, leading to pico-meter characterization. As one of the most exciting aspects of ferroelectric topological entities is their mobility, we also detail the in situ biasing options to investigate their dynamics at the different magnifications. Finally, we highlight some of the most recent advances in STEM characterization methods for ferroelectrics such as visualizing electric charge density at sub-angstrom resolution and the benefits of coupling polarization characterization with electron energy loss spectroscopy (EELS) band structure analysis.

II. MICROSCALE: BULK SAMPLE DOMAIN PATTERN RESOLUTION

A. Scanning electron microscopy

SEM provides a platform for selective domain contrast imaging depending on the chosen detector via a non-destructive characterization technique of the entire bulk sample. With a secondary electron detector, c+ (polarization pointing out of the surface) and c− (polarization pointing into the surface) domains exhibit darker and brighter contrast, respectively, than the a domains. This is due to positively and negatively charged domain surfaces repelling and absorbing SEs, respectively, but is true only either (1) at an equilibrium voltage where the beam does not charge the sample or (2) during the first few seconds of imaging, before the beam has charged the sample. It is known as voltage contrast. At lower voltages, the sample is positively charged and thus bright, while at higher voltages the sample is negatively charged and dark. Varying the voltage allows the equilibrium to be found for each material. Voltage contrast also applies to the a domains where it has been used to study point defects for a-type head-to-head or tail-to-tail domain walls.

The lattice rotation across the DWs and peak stress can be estimated by using the SEM based technique, electron backscatter diffraction (EBSD). Rather than precisely interpreting contrast, the knowledge of crystal orientation relative to the observed domain walls can often be sufficient to determine at least the polarization axes. For example, in tetragonal crystals, a DW along [110]pc means an a–a 90° DW and [100] means an a–c 90° DW angled 45° to the surface and wobbly or undefined curtain-like DWs mean c+/c− 180° DWs. If no DW contrast can be seen, ferroelastic domains can be identified by using EBSD to create a topology image similar to those often obtained by piezoresponse force microscopy. Mapping the approximate polarization in the SEM allows one to then target specific regions of interest for STEM characterization via combined (beam) SEM and focused ion beam (FIB) sample preparation.

SEM imaging techniques listed above can also be used to analyze the material within the FIB lamella and thus confirm if there are changes in the DW pattern after thinning. Piezoresponse force microscopy (PFM) and c-AFM mapping of the FIB lamella can also be done to quantify changes in polarization and conduction and relate these measurements back to the SEM imaging and diffraction. In general, epitaxial films and especially thin films are most likely to retain their domain structure because the domain formation is governed by nanoscale strain. Single crystals, on the other hand, are freer to adjust their domain structure to minimize their free energy during the lift-out and thinning of a lamella. This factor should be kept in mind when choosing the FIB lamella orientation, shape, thickness, and whether to include extra thin “windows.” Altering the FIB preparation techniques can result in drastically different strain throughout the lamella and thus DW pattern confinement effects. In this way, the local strain state of the lamella can be designed to preserve existing DWs or create new ones. Final thinning by argon ion milling requires additional consideration for ferroelectrics. The surface damage induced by gallium ion milling provides a polarizable “dead layer” on the surface, which makes c domains more easily stabilized but negates the need to form 180° c+/c− DWs for electrostatic screening. Thus, removing the dead layer with argon polishing may induce 180° c+/c− DWs, especially in “Z-cut” uniaxial crystals.

TABLE I. Summary of the review sections.

| RESOLUTION | TECHNIQUES |
|------------|------------|
| Microscale: Domain configuration | SEM, EBSD, FIB, TEM, 2 beam DF TEM, holography |
| Nanoscale: Domain analysis | STEM ADF, detector DPC, 4DSTEM (DPC, strain, phase) |
| Picoscale: Domain wall/vortex | Segmented detector DPC/idPC, aberration corrected STEM ADF, aberration corrected STEM ABF, 4DSTEM (ptychography, electric field, electrostatic potential) |
| Complementary techniques | DW dynamics induced by the electron beam, in situ TEM holders, EELS |

typically found as bulk single crystals rather than thin films. While there are relatively fixed and predictable DWs in thin films, samples cut from bulk single crystals can vary widely in the domain structure.

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| Technique                                      | Experience   | Common artifacts                                                                 | Advantages                                                                                                           | Disadvantages                                                                                     |
|-----------------------------------------------|--------------|----------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|
| **Microscale: Domain configuration**          |              |                                                                                  |                                                                                                                      |                                                                                                    |
| SEM                                           | Beginner     | Surface charging causes contrast reversal                                         | Large area analysis, ease-of-use                                                                                  | Requires contrast interpretation, not all DWs visible, surface only, limited polarization information |
| EBSD                                          | Intermediate | Scanning distortions when using long dwell times and large areas                   | Large area analysis, crystal orientation information                                                               | Limited polarization information                                                                     |
| Low magnification TEM                         | Beginner     | Dislocations, and bending contours appear similar to DWs                           | Quick, large area analysis                                                                                         | Limited polarization information, DWs must cause strain to show diffraction contrast               |
| 2-beam DFTEM                                   | Intermediate | Diffraction contrast, tilt sensitive                                              | Large area analysis, identifying the domain configuration                                                          | Time consuming, tilt sensitive, multiple images, and prior knowledge required for polarization interpretation |
| Holography                                    | Advanced     | Diffraction contrast                                                              | Large area analysis                                                                                               | Requires specific hardware, difficult post-processing                                             |
| **Nanoscale: Domain analysis**                |              |                                                                                  |                                                                                                                      |                                                                                                    |
| STEM DPC segmented detector                   | Intermediate | De-scan imperfection causing a diffraction pattern shift, diffraction contrast     | Quick, real-time, detailed polarization information                                                               | Requires microscope re-alignment to transition from domain-scale analysis to DW analysis, segmented detector required |
| Low magnification STEM ADF                    | Beginner     | Image becomes coherent at too-low collection angles, contrast reversal             | DWs exhibit strain-related contrast, can quickly transition from DW identification to DW analysis                   | Very little quantitative knowledge gained at low magnification                                        |
| GPA/Fourier masking                            | Beginner     | Noise related artifacts                                                            | Quick, requires only lattice resolution images, can give specific polarization information                          | Prior knowledge of unit cells for each domain needed                                               |
| Microprobe 4DSTEM                              | Advanced     | Processing artifacts, de-scan imperfection                                        | Detailed structural information and polarization direction can be captured over a large area                        | Post-processing required, acquisition time can be minutes long                                      |
| Technique | Experience | Common artifacts | Advantages | Disadvantages |
|-----------|------------|------------------|------------|---------------|
| Picoscale: Domain wall/vortex | STEM ADF | Intermediate | Tilt sensitive, scan distortions | Real-time, simultaneous EELS possible, relatively insensitive to strain, Z contrast provides chemical information | Post-processing and previous knowledge of polarization needed, cannot image light and heavy atoms together |
| | STEM ABF | Advanced | Contrast reversal, tilt sensitive | Complimentary to HAADF for imaging light elements | Post-processing required to determine polarization, coherent image contrast is sensitive to focus and thickness |
| | Segmented detector DPC | Intermediate | Defects, boundaries, thickness gradients | Real-time, picoscale electric field and charge density maps | Segmented detector required or post-processing from the 4DSTEM dataset |
| | Segmented detector iDPC | Intermediate | De-scan imperfection, tilt sensitive | Real-time, linear Z contrast allows light and heavy elements to be captured in one image, simultaneous EELS | Segmented detector required or post-processing from the 4DSTEM dataset |
| | Nanoprobe 4DSTEM | Advanced | CoM maps sensitive only to atomic potentials can be interpreted as the electric field, de-scan imperfection | Picoscale electric field and charge density maps can be measured, iDPC, ADF, and ABF imaging can be reconstructed, complementary structural information | Requires samples <7 nm and intensive post-processing. Requires commercial software for polarization mapping not yet available |
| | Ptychography | Advanced | De-scan imperfection | Dose efficient, highest spatial resolution possible | Image must be reconstructed from the 4DSTEM dataset |
| Complementary techniques | In situ holders | Advanced | Required applied V different to bulk | Physical and chemical characterization of dynamics | Difficult sample preparation |
| | Electron beam induced dynamics | Intermediate | Scan distortions | Flexible in situ applied electric field experimental possibilities | Only samples with a coercive field below the possible electric field of the STEM beam |
| | EELS | Advanced | Background subtraction and signal window chosen by user, delocalization, Cherenkov losses for low energies | Chemical information from core-loss EELS, density-of-states information for low-loss EELS | Post-processing required, modeling usually required for quantitative analysis |
More recently, studies have shown that the SEM probe can also be used to induce domains, switch their polarization direction, and even move the DWs. Kianirad et al. detailed the motion of the DW can be controlled via the dose rate, total dose, and scan direction, as shown in Fig. 1. Sections IV A and IV B will discuss the TEM/STEM based in situ biasing DW dynamic techniques.

III. NANOSCALE: DOMAIN RESOLUTION

A. Low magnification transmission electron microscopy

Before high resolution (HR)-STEM analysis of a DW can be carried out, the desired DW must first be found and the polarization in the surrounding domains identified. Diffraction contrast in low-magnification TEM can be used initially to see the domain structure of the lamella as a whole. If the aim is to monitor domains over a large area, then specific modes of TEM can be used. Tilting to a two-beam dark field condition can isolate intensity from a specific diffraction spot. In ferroelectric crystals, some diffraction spots break Friedel’s law and can be used to directly relate the image intensity to the polarization direction (Fig. 2). The drawback is that multiple images must be carefully acquired under different conditions to map the polarity of the entire domain structure (Fig. 2). More simply, an off-centered objective aperture will enhance diffraction contrast at low-medium magnification TEM to detect any subtle DWs present, which is particularly useful for in situ studies.

B. Scanning transmission electron microscopy

STEM imaging relies on collecting electrons that have passed through a thin sample by a scanned beam. This imaging technique has two main differences in comparison to conventional TEM: (1) The detector is placed in the backfocal plane where the diffraction space information is held and (2) the intensity of each pixel in a STEM image is collected separately, allowing highly specific, localized information to be isolated from adjacent areas. STEM annual dark field (ADF) imaging uses a doughnut-shaped annular detector. The high angle annular dark field (HAADF) collects highly scattered electrons, thus providing useful images of heavier atoms differentiated by intensity. The annular bright field (ABF) collects weakly scattered electrons and is particularly useful for imaging lighter elements. In comparison to TEM, STEM imaging is less impacted by diffraction contrast, and thus, it can be difficult to identify domains with small spontaneous strain differences. To maximize diffraction contrast and identify domains in the sample, microprobe STEM can be used at the cost of atomic resolution capabilities. Alternatively, it is recommended to use an inner collection angle of the annular detector very close to the convergence angle, low angle-annular dark field (LAADF). Using LAADF gives the added advantage of quickly transitioning from low to high resolution STEM without realignment. In this way, much of the polarity for individual domains can be identified based on DW orientations relative to the crystal structure. However, when investigating unconventional DW configurations or novel materials, interpreting the DW contrast to make a "most-plausible domain polarization" map can be overly simplistic, and more in-depth techniques are required.

Geometric phase analysis (GPA) allows quantitative strain maps to be determined for any lattice resolution image. Conventional TEM atomic resolution images are sensitive to thickness changes and subject to contrast reversal, making large-area strain mapping sometimes problematic. Conversely, STEM is relatively insensitive to surface defects, thickness changes, and sample tilts. STEM allows fields-of-view of over 100 nm to be strain-mapped.
narrowing down the possible polarization for each domain to two opposite directions. The direction of lattice rotation across PbTiO$_3$ DWs, for example, can be used to fingerprint the exact polarization in each domain and, by extension, the entire domain structure. Thus, GPA strain and rotation maps have been used extensively to map the domain structure in various investigations of PbTiO$_3$. GPA fingerprinting of polarization should be possible for other ferroelectrics exhibiting lattice rotation at DWs, e.g., LiNbO$_3$ and BiFO$_3$.

By masking fast Fourier transforms (FFTs), domain mapping can be further simplified. Rather than displaying relative changes in spacing/strain as GPA does, FFT masking displays the location in the image of specific spacings/strain states. Thus, while it cannot be used to identify small strain changes or produce rotation maps, FFT masking allows specific “superlattice” or unique structural spacings that characterize individual domains or DWs to be identified in a real-space image. These unique atomic spacings are especially prevalent in non-perovskite ferroelectrics with complex unit cells. Boracites, for example, have a unique superlattice reflection related to the polarization axis in the domain. FFT masking is further useful for cryogenic investigations such as those on charge-ordered manganites, where the sample drift is an issue because it is subject to the same flexible image conditions as GPA.

C. 4DSTEM for strain measurements

As the domain and DW formation depends on nanoscale strain, it is vital to investigate the coupling of polarization to spontaneous strain around DWs and within the 2D features itself. FFT and GPA can be used to map out the strain states of the domains. However, the quantification of strain states by these methods is only possible if the region in the field of view is highly strained. The electron diffraction patterns collected from 4DSTEM datasets allow researchers to measure very low changes in strain percentages using patterned probes and even weakly scattering 2D materials using direct electron detectors. Another advantage of using 4DSTEM strain mapping for ferroelectric materials is the flexibility in the possible magnifications while retaining high precision. This is vital for investigating the internal strain measurements of individual ferroelectric DWs and vortices at the picoscale while being able to relate these measurements back to the bulk domain configuration of the TEM lamella. It is important to note that there is a slight trade-off between the resolution in real and reciprocal space; however, with advancements in beam shaping, beam tilting (precision electron diffraction), probe patterning, camera speeds, and improved data processing, this limitation is becoming less of an issue.

D. STEM DPC and phase related techniques

STEM differential phase contrast (DPC) and center of mass (CoM) imaging have become the tool of choice for visualizing internal electric and magnetic fields. Beam deflections due to internal fields were initially detected by single detectors using Fresnel and Foucault imaging, but it was a delicate, time-consuming, and difficult-to-control task to produce interpretable image contrast. In contrast, the development of quadrant annular detectors allowed multidirectional beam shifts to be interpreted from a single acquisition. Images detecting shifts in a STEM BF disk partially overlapping an annular quadrant detector are generally referred to as DPC. When studies identified that redistribution of intensity within the BF diffraction disk could also contribute to the contrast in DPC images, it became recognized that the contrast is finally determined by the CoM of the BF disk. Thus, the terminology of CoM imaging was introduced. However, while the CoM can be approximated from quadrant detectors, it can be more accurately measured by recording the entire BF disk, as in 4DSTEM. Hence, polarization maps constructed from 4DSTEM datasets are also referred to as CoM imaging.

When mapping polarization in a ferroelectric domain via DPC, one is trying to measure the effect of net electric field ($E$) in the sample. In the absence of any external biasing, this means the spontaneous polarization ($P_s$) minus the depolarization ($D$) caused by the screening charge at DWs, as explained by the following equation:

$$D = \varepsilon_r \varepsilon_0 E + P_s,$$

(1)
and the change in $D$, $E$, and $P_s$ moving across a DW is related to the screening charge ($\rho_s$) by

$$\nabla \cdot D = e_0 e_\lambda \nabla \cdot E + \nabla \cdot P_s = \rho_s. \tag{2}$$

As detailed by MacLaren et al.,\textsuperscript{69} when the DW is fully screened,

$$E = \nabla \cdot E = 0$$

and

$$\rho_s = \nabla \cdot P_s,$$

$2P_s$ for a $180^\circ$ DW, where the DW is perpendicular to $P_s$.

In most examples of ferroelectric DPC studies, there is a measured electric field, and thus, the polarization is not fully screened. Equation (2) also means that taking the differential of DPC maps to map the charge density measures the net of (bound charge due to polarization) – (screening charge). It is important to clarify that maps of $e_0 e_\lambda \nabla \cdot E$ represent the unscreened portion of the bound charge at the DW, not the local free charge density ($\rho_f$). However, $\rho_f$ at the DW can be calculated by adding the differential of the DPC map to $\nabla \cdot P_s$, [from Eq. (2)]\textsuperscript{69} $\nabla \cdot P_s$ may need to be calculated using phase-field simulations for complex DWs.\textsuperscript{70,71}

When the electric field gradient is greater than the probe size, as is the case for nanoscale electric fields across domains vs an electron probe, the effect is purely a beam deflection.\textsuperscript{72,73} It is recommended to use microprobe STEM with a small convergence angle $\alpha$ of ~1 mrad to increase sensitivity to small deflections. Under the kinematical (single scattering) approximation, the deflection angle ($\theta$) is expressed as

$$\theta(r) = C_{HT}[\nabla_r U_s(r) \cdot t(r) + U_s(r) \cdot \nabla_r t(r) + U_i \cdot \nabla_r i(r)], \tag{3}$$

where $C_{HT} = \frac{\epsilon (k_s + k_c)}{k_s (3 k_s + k_c)}$ is the interaction constant that corrects for relativity.

$E_e$ is the electron energy, $e$ is the elementary charge, $\lambda$ is the electron wavelength, $E_r$ is the electron rest energy, $U_i$ is the mean inner potential,\textsuperscript{74} $U_s$ is the (additional) electrostatic potential, $t$ is the thickness, and $\nabla_r t$ is the local thickness gradient. When there is no electrostatic potential, $U_s = 0$, Eq. (3) can be used to measure the mean inner potential or the thickness gradient of a sample.\textsuperscript{75} More importantly, for ferroelectrics, when there is a uniform thickness, Eq. (3) can quantify the net electric field ($E = \nabla_r U_s$) from the measured beam deflection $\theta$.

Typical electric field strengths are 3–4 orders of magnitude smaller than atomic potential gradients at 0.1 V/nm–1 V/nm. Thus, increasing the relative sample thickness either physically or by using a lower accelerating voltage is recommended to increase the deflection angle and thus the sensitivity.\textsuperscript{76} The deflection angle can be measured directly via 4DSTEM, but DPC maps require normalization by the sum of the quadrants and calibration for quantitative interpretation.\textsuperscript{77} Some of the sources of error are channelling effects, strong diffracting conditions exciting asymmetric Friedel’s pairs, and smaller potential gradients (defects or interfaces), causing asymmetry within the BF disk. Each of these can cause artifacts in a CoM-derived electric field map from DPC or 4DSTEM data. Normalization and tilting away from zone axis to achieve quasi-kinematical conditions can mitigate these effects, and a vacuum dataset can correct for scanning-induced beam shifts if de-scan settings are imperfect.\textsuperscript{78}

The best practice for measuring E-fields is to use microprobe STEM with an objective aperture blocking all diffraacted beams and place the BF disk just inside the inner detector radius (DPC) or inner virtual detector radius (4DSTEM).\textsuperscript{74,79,80} Thus, there is no signal/overlap of the BF disk in the absence of a long-range potential gradient and the CoM can be ignored to focus on the differential signal intensity. Such artifact-free ferroelectric DPC maps should then resemble magnetic field maps with DWs appearing as black boundaries between uniformly colored domains.\textsuperscript{74}

For researchers investigating multiferroic domain walls and needing to correlate the electric and magnetic fields in a single multiferroic, the sample should be achievable by changing the accelerating voltage between, e.g., 60 kV and 300 kV. At 60 kV, the sample appears approximately seven times thicker to the electron beam, increasing the deflection due to the electric field. Meanwhile, the electron velocity is reduced by ~43%, decreasing the deflection due to the magnetic field proportionally. The electric field DPC map can be acquired at 60 kV, and then, the voltage changed to 300 kV, changing the contributions to the beam deflection by an order of magnitude, to measure a DPC map of the (perpendicular) magnetic field. Thus, it should be possible to map out both the magnetic and electric field transitions across magnetolectric domain walls.

IV. PICSACLE: DOMAIN WALL AND POLAR VORTEX RESOLUTION

A. Aberration corrected transmission electron microscopy

Aberration corrected TEM was first used by Jia et al.\textsuperscript{1} to image the change in investigation of the cation–oxygen dipoles per unit

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**FIG. 3.** The panoramic view of nesting tetragonal and monoclinic domains viewed along the [110]T direction. The yellow dotted lines trace the boundaries between the tetragonal and monoclinic phases, and the white dotted lines trace the domain walls in the monoclinic phase. The phase and domain boundaries are differentiated by mapping the relative displacements of $O_2$ columns (red arrows) with respect to centers of the nearest neighboring Zr/Ti columns over the whole image. Scale bar: 1 nm. (b)–(d) Enlarged view of the relative displacements of the $O_2$ columns in domains M-I, T-I, and M-II in (a). The colored circles overlapped on the images denote different column types: Pb/O1—yellow, Zr/Ti—blue, and $O_2$—red. The vertical dashed and solid lines indicate positions of the Zr/Ti columns and centers of their nearest neighbors. The relative displacements of $O_2$ columns with respect to these centers can be directly identified in this way.\textsuperscript{85}
cell at ferroelectric DWs. By using the negative spherical-aberration imaging,\(^{28,29}\) they were able to experimentally quantify the large difference in atomic displacement at charged vs uncharged DWs. This type of imaging technique has been used to confirm non-classical ferroelectric allowed polarization theories such as dipole continuous rotation in vortex structures,\(^{83}\) unique cycloidal polarization order,\(^{84}\) and Néel-like polarization in ferroelectric DWs,\(^{85}\) as shown in Fig. 3. However, atomic resolution TEM imaging is hindered by the inability to map out the lighter elements in more complex unit cells of other materials, and the atomic resolution imaging is sensitive to thickness changes and subject to contrast reversal. In this Review, we will focus on advances in aberration corrected atomic resolution STEM imaging and other STEM techniques such as 4DSTEM.

B. Aberration corrected scanning transmission electron microscopy

With the development of aberration correctors, STEM imaging modes can be used to identify atomic column positions down to a precision of 3 pm–5 pm.\(^{86–89}\) Thus, for ABO
3 perovskite ferroelectrics, HAADF can identify the heavier “A” and “B” site atoms, while ABF can be used to see the displacements or rotations of oxygen octahedra (Fig. 4).\(^{90–96}\) These complimentary aspects of high resolution (HR) STEM are crucial as the positions of all atoms in the unit cell must be measured to determine the displacements with respect to the paraelectric phase and thus the net polarity. For some more complex unit cells, STEM ABF is not able to resolve all the positions of the lighter elements. More recently, a segmented ADF detector integrated differential phase contrast (iDPC) imaging

![Simulated annular bright-field scanning transmission electron microscopy (ABF-STEM) images along the zone axis of [11̄0] for a–a–a– (a) and [101] for a–b+a– (b) OOR patterns. (c) and (g) show the ABF-STEM images of the 2.6 nm-thick CaTiO
3 (111) film along the zone axis of [11̄0], measured using 80-keV (c) and 200-keV (g) electron kinetic energy. (d) and (h) display the maps of OOR patterns, identified by deep neural network analysis, in the same regions as in (c) and (g), respectively. The color indicates the probability of each OOR pattern. (e) and (i) present the polarization vectors for each unit cell of the same regions as in (c) and (g), respectively. The arrows denote the polarization direction; the stronger the polarization, the darker the arrow color. The strength of polarization is also expressed as a color map, ranging from white (weak) to red (strong). (f) illustrates a schematic free energy landscape, showing the relaxation of R3c state (a–a–a–) into Pnma state (a–b+a–).](https://www.scitation.org/doi/fig/10.1063/5.0035958)
technique\textsuperscript{97,98} can be used to locate the positions of the required lighter elements for polarization direction determination.\textsuperscript{96} The technique iDPC will be discussed in more detail later in Sec. III A 1. Once the position of the lighter elements relative to heavier elements for the polarization direction has been established, HAADF alone can measure the displacement of the heavier atoms, while the position of invisible lighter atoms can be assumed. For example, in the well characterized PbTiO\textsubscript{3}, O and Ti columns move in the same direction away from the neutral position at the center of the unit cell. However, O\textsuperscript{2\textendash} moves further than Ti\textsuperscript{4\textendash} so that the polarization, pointing negative to positive, forms exactly opposite to the direction of Ti\textsuperscript{4\textendash} displacement. This phenomenon allows the “reverse B-site displacement vector” method of using only HR-STEM HAADF images to place arrows denoting polarization vectors on each unit cell of PbTiO\textsubscript{3} or BiFeO\textsubscript{3}.\textsuperscript{100–104}

C. Alternative methods of imaging light element shifts

1. Integrated differential phase contrast imaging

While iDPC was proposed by Rose,\textsuperscript{105} its commercialization with a segmented annular detector has led to widespread adoption.\textsuperscript{106} iDPC has a contrast transfer function closely proportional to Z\textsuperscript{1}, as opposed to Z\textsuperscript{1.7} for HAADF. Thus, iDPC allows light elements to be efficiently imaged alongside heavier elements. Atomic resolution CoM-DPC derived from annular quadrants or 4DSTEM data\textsuperscript{74} requires a large convergence angle $\alpha$ of $\sim$ 30 mrad. In contrast to the deflection described for nanoscale E fields above, the effect of (atomic) potentials smaller than the probe size is a redistribution of intensity in the $\sim$ 30 mrad BF disk. CoM represents the expectation value of the electron beam’s quantum mechanical probability current flow through the sample (Fig. 5).\textsuperscript{109,110}

2. Ptychography

Ptychography is a well established technique in light\textsuperscript{112} and x-ray\textsuperscript{113–116} based characterization; however, it is only recently the technique has been exploited in STEM research.\textsuperscript{117–120} The main benefit of potentially using pytchography for atomic resolution polarization mapping at ferroelectric DWs and polar vortices would be the ability to image clearly the lighter elements within even complex unit cells. The main benefit of using pytchography over segmented detector iDPC imaging is that much lower doses can be used,
achieving the same potential atomic column resolution. Additionally, as described by Yang et al., the phase information extracted from a 4DSTEM dataset collected on a direct electron detector while simultaneously collecting a z-contrast image on a HAADF detector. The main drawback of ptychography currently is the time taken to process the data, whereas iDPC can be done live via commercial software from most microscope vendors.

D. Post-processing techniques to quantitatively measure polarizations

In order to maximize the information that can be extracted from atomic resolution TEM and STEM images, there are a number of steps that can be taken during and after acquisition. Live drift corrected frame integration helps signal-to-noise while allowing a lower dose through a smaller beam current and thus a smaller electron probe and better resolution. Furthermore, summing images with orthogonal scan directions can correct for scanning distortions, especially with the use of non-rigid registration software. Post-acquisition, Fourier space filters such as double Gaussian can be used to further reduce noise, and statistical reconstruction can be used to further clean up noisy data. This approach has been used, in particular, for samples like hexagonal rare-earth manganites where spacing between atomic columns is smaller within the unit cell compared to PbTiO$_3$, and a more complex atomic displacement corresponding to their polarization, and beam sensitive ferroelectric materials like LiNbO$_3$.

Following image filtering, mapping the atomic displacements and thus assigning polarization per unit cell can typically be automated using 2D Gaussian fitting python based programs such as Atomap and TEMUL toolkit, Pycroscopy, and Matlab based scripts (Fig. 6).

E. Atomic resolution DPC/CoM

While mapping the domain polarity provides important information about the likely macroscopic properties and behavior of a DW, the true power of aberration corrected STEM lies in probing the interior of the DW itself. Using specific alignment conditions, 4DSTEM datasets can also be used to measure the internal electric fields and electrostatic potentials of ferroelectric topological features. Particularly, effective studies embracing this approach include the studies of Yadav et al. and Gao et al. Both studies measured the polarization vectors from atomic imaging and the electric field/charge density from 4DSTEM. Yadav et al. used the independent measurements to estimate the free energy gradient near polar vortexes and thus confirmed the existence of local areas of negative capacitance. Gao et al. demonstrated a spatial difference between the polarization and the charge density and persuasive evidence that the 4DSTEM-derived electric field/charge density was an independent measurement to that of the atomic structure. When the samples are thinner than 7 nm and beam broadening cannot be neglected, atomic resolution CoM maps should not be interpreted as the gradient of the atomic potential, but the gradient of the probe (Fig. 7). As extremely thin samples are required, the ideal samples would be 2D ferroelectric materials such as CuInP$_2$S$_6$.

Yadav et al. took a different approach to mapping out the polar skyrmions, more akin to the description above for electric field mapping in domains. Polar skyrmions are effectively merged/continuous ferroelectric domains with a more gradual potential gradient than atomic fields. Thus, Yadav et al. used a...
smaller convergence angle to separate the diffraction disks and measured exclusively the shift of the BF disk on the pixelated detector. In this way, the longer range electric fields are effectively decoupled from atomic potential gradients and can be compared to the polarization vectors.

V. COMPLEMENTARY TECHNIQUES

A. In situ biasing TEM holder based DW dynamics

By combining aberration corrected TEM imaging and fast cameras with in situ biasing holders, experimentation not possible by any other method at the same spatial and time resolution is now accessible to the ferroelectric research community. Understanding the relationship between the DW and vortex formation during phase changes within ferroelectric materials is essential for future nanoelectronics based on these polar entities. In 2019, Linze et al.146 published a thorough review on the progress of in situ biasing TEM holder based microscopic processes of ferroelectric domain switching. There has been extensive work to date on live imaging during the in situ biasing via lower magnification TEM to investigate domain nucleation, domain switching, relaxation, and interplay between different types of domains (Fig. 8).28,111,147-155 These in situ biasing experiments have improved our understanding of the underlying physics governing ferroelectric domain dynamics. However, to date, real-time biasing quantifiable sub-atomic imaging has not been achieved. With improvements in TEM cameras and in situ biasing holders, this is the next hurdle to overcome for the TEM ferroelectric community.

B. DW dynamics induced by the electron beam

As described earlier, the electron beam of an SEM can be used to induce and move DWs while imaging. Hart et al.156 was the first to show that the TEM beam could be used to induce ferroelectric domain nucleation in PbTiO₃ (Fig. 9), and Barzilay157 used atomic resolution TEM to form 2 nm domain periodicity in BaTiO₃. Recently, there has been a surge in interest in atomic scale manipulation of 2D materials using an aberration controlled STEM probe.158-162 Conroy et al.55 showed that ferroelectric DWs can also be controllably moved via the STEM probe for the boracite material while monitoring sub-atomic shifts and thus polarization changes during movement. Using the STEM probe as an applied electric field allows one to study the dynamics of ferroelectric domain walls under vast different experimental conditions such as probe scan direction, speed of scan, dose, and probe size without complicated in situ experimental preparation. However, this may not be possible for all ferroelectric materials and most likely is restricted to materials with low coercive fields.

C. Electron spectroscopy

Atomic scale core loss EELS has been used extensively in ferroelectric oxide thin film hetero-interfaces, relating changes in

FIG. 8. (a) Schematic and TEM image of the experimental setup: A thin cross-sectional Pb(Zr₀.₂Ti₀.₈)O₃ film with a concentration of ferroelastic 90° domains (a-domains) was grown on SrRuO₃/DyScO₃ and SrRuO₃/SrTiO₃. A mobile tungsten tip acts as one electrode for electrical switching with the SRO layer being grounded, whereas a diamond indenter is used for mechanical switching. (b) High-resolution HAADF STEM image of a/b/c-domains overlaid with vectors describing the head-to-tail polarization arrangement. Scale bar: 1 nm. (c) Image sequence showing a clamped 90° domain is stable at applied negative voltages from 0 \(\rightarrow\) (-18) V. At -19 V, the domain is eventually erased and, simultaneously, damage to the film occurs due to the high strength of the electric field. Scale bar: 100 nm.150
polarization to chemical bonding and oxidation states. More recently, with improved STEM and spectrometer designs, the energy resolution now possible has allowed researchers to measure the core loss fine structure changes within the DWs of homogeneous materials. Mundy et al. showed the clear Mn valence change at charged DWs in manganites, and Rojac et al. measured Fe cations and bismuth vacancies at DWs, revealing p-type conduction at domain walls caused by the presence of electron holes associated with Fe.

Monochromated high-energy resolution low loss EELS has been used to probe changes in the electronic structure at quantum wells and 2DEGs for other material systems. More recently, Zhang et al. has shown the clear change in bandgap at conducting domain walls in BiFeO$_3$, and Conroy et al. has shown the change in bandgap and also the signal enhancement of the energy loss intensity in the 2 eV–3.5 eV regime in conducting LiNbO$_3$ DWs. With advances in spectrometer design, low loss EELS can now also be used to map out changes in phonon modes at the atomic scale in 2D materials. We propose this technique would be ideal to map out the phonon modes in ferroelectric DWs at the spatial resolution needed to understand the fundamental physics governing the ferroelastic ferroelectric coupling.

VI. CONCLUSION

Aberration corrected STEM is the only experimental technique that allows one to probe the internal physical and electronic structure of ferroelectric DWs and polar vortices at the picoscale. Advances in our knowledge of the fundamental physics that govern the formation of 3D polar topological features such as room temperature skyrmions have only been made possible by pushing the limits of STEM techniques. We can now directly relate theoretical density functional theory (DFT) studies with experimental results, hence increasing the speed of material research and development design. With the end goal of using these polar topological entities for devices based on their dynamics, in situ STEM allows the research community to investigate exactly how the atomic displacements occur during movement. Thus, informing us of how to improve our materials to lower the energy required to move these ferroelectric polar entities. In this Review, we have laid out how to identify ferroelectric regions of interest via electron microscopy from the bulk sample scale and then step by step details of what types of electron microscopy characterization techniques can be used with increasing magnification finalizing in aberration corrected picoscale STEM, as shown in Table II.

A. Future developments

There are various ways in which phase effects and 4DSTEM datasets promise to improve atomic scale electric field measurements. Recently, there has been work on re-shaping or even splitting the STEM beam to use the electron dose more efficiently, thus obtaining the same polarization data more efficiently. These methods can also make use of interference effects generated by multi-beam scanning to gain further phase sensitivity. There has been a major focus on controlled beam sculpting into vortex patterns, thus opening up further types of available characterization techniques for 3D polar ferroelectric topologies, as seen in ferromagnetic materials. Multi-beam electron diffraction is another fascinating development, which may enable efficient phase sensitivity. Time resolution at the attosecond timescale is also possible via microscopes with laser pumped sources. As described in the STEM perspective by Idrobo, there has been a renaissance of using cryogenic temperatures (liquid nitrogen or helium) for physical materials. El Baggari et al. have shown how aberration corrected cryogenic STEM can be used to quantify the atomic displacement within the unit cell between phases and thus investigate the broken symmetry states. As certain ferroelectric materials have a ferromagnetic phase at lower temperatures, cryogenic STEM would also allow researchers to study the charge to spin...
relationship of these multiferroic phases. The STEM is a powerful one-stop laboratory to characterize ferroelectric topological defects and their dynamics by combining polarization mapping, oxidation mapping, and band structure changes all at DW or polar entity resolution via EELS and in situ biasing.

AUTHORS’ CONTRIBUTIONS

All authors contributed to the discussions and manuscript preparation.

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NOMENCLATURE

4DSTEM four-dimensional scanning transmission electron microscopy
CoM center of mass
DPC differential phase contrast
DW domain wall
EELS electron energy loss spectroscopy
FFT fast Fourier transform
FIB focused ion beam
GPA geometric phase analysis
SEM scanning electron microscopy
STEM scanning transmission electron microscopy
TEM transmission electron microscopy

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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