Direct observation of nanoscale dynamics of ferroelectric degradation

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Failure of polarization reversal, i.e., ferroelectric degradation, induced by cyclic electric loadings in ferroelectric materials, has been a long-standing challenge that negatively impacts the application of ferroelectrics in devices where reliability is critical. It is generally believed that space charges or injected charges dominate the ferroelectric degradation. However, the physics behind the phenomenon remains unclear. Here, using in-situ biasing transmission electron microscopy, we discover change of charge distribution in thin ferroelectrics during cyclic electric loadings. Charge accumulation at domain walls is the main reason of the formation of \( c \) domains, which are less responsive to the applied electric field. The rapid growth of the frozen \( c \) domains leads to the ferroelectric degradation. This finding gives insights into the nature of ferroelectric degradation in nanodevices, and reveals the role of the injected charges in polarization reversal.
Ferroelectric materials have been extensively used in electronic nanodevices because of their polarization reversal behavior under an applied electric field. However, the application of repeated electric fields has been shown to reduce the ferroelectric performance, leading to polarization reversal failure, i.e., ferroelectric degradation. Ferroelectric degradation results in short life cycles, which impacts the reliability and endurance of electronic nanodevices. Ferroelectric degradation changes the physical properties of ferroelectrics, including coercive field, remnant polarization, and resistivity under cyclic electric loadings. With the increasing usage of nanoscale electronic devices, a comprehensive understanding of the mechanisms and evolution of ferroelectric degradation is essential.

Ferroelectric degradation is often linked to numerous mechanisms, including domain wall pinning, domain nucleation suppression, and microcracks. The domain wall pinning mechanism claims that the charge carriers and/or defect dipoles accumulate at the domain walls during electric cycling, leading to domain locking. Some studies proposed a competitive process between domain wall pinning and unpinning, where the detrapping of charge carriers also occurred during ferroelectric degradation to unpin the domain walls. Ferroelectric degradation occurs once the pinning rate dominates. The domain nucleation suppression mechanism suggests that charge carriers injected from the electrode prohibit the nucleation and growth of domains near the sample surface, degrading the ferroelectric performance. The microcrack mechanism states that long-term electric cycling could cause the formation of microcracks initiated from the grain boundaries or domain walls.

Ferroelectric degradation is usually attributed to the activity of excess charges from the space or injection, which is generally accumulated at the domain wall under cyclic electric field and accounts for the degraded polarization. However, it is not clear how these charges lead to the ferroelectric degradation. Direct observation of charge accumulation and real-time evolution of domain structure with cyclic electric field is critical to understand the impact of charge activities on ferroelectric degradation. Owing to the advancements of in-situ transmission electron microscopy (TEM), real-time nanoscale observation of ferroelectric domain switching behavior under electric fields has become possible. In addition, the recently developed microelectromechanical system (MEMS)-based nano-chip technique for TEM have improved the stability and reliability of the experiment under repeated electric fields, and therefore experiments revealing the mechanism of ferroelectric degradation have become technically feasible.

In this study, the domain switching behavior of Pb(Mg1/3Nb2/3)O3-0.38PbTiO3 (PMN-0.38PT) single crystals was investigated using in-situ biasing TEM with MEMS-based nano-chips, where an in-plane electric field was repeatedly applied to the sample. Scanning transmission electron microscopy-differential phase contrast (STEM-DPC) imaging was used to explore the charge distribution at domain walls during cyclic electric loading. With the increase of the electric loading cycles, domains with out-of-plane polarization (c domains) were initiated from the original domain walls, during which the charge accumulation was responsible for the nucleation and growth of the c domains. Of particular interest is that the c domains were less responsive to the applied electric field, showing a frozen state under electric field, which is a critical factor in ferroelectric degradation. The discovery of this ferroelectric degradation mechanism not only strengthens the understanding of ferroelectric degradation at nanoscale, but also provides guidance on the design of ferroelectric nanodevices.

![Fig. 1 In-situ biasing TEM setup and determination of initial a1/a2 90° domains.](image-url)

- **a** A schematic diagram of the experimental setup. A focused ion-beam fabricated PMN-0.38PT lamella was fixed between two Pt electrodes. A cyclic electric field was applied to the lamella along ±[100] crystallographic direction of the lamella. The yellow, purple, and blue arrows denote the polarizations of a1/a2, a1/a2, and c/c, respectively.
- **b** Schematic diagrams showing [001] projected lattices of a1/a2 domains and their corresponding schematic of electron diffraction pattern showing the split spots.
- **d** A TEM image showing 90° stripe domains in PMN-0.38PT, and **e** the corresponding electron diffraction pattern showing the split spots of the 90° domains.
Results

Determination of initial $a_0/a_2$ 90° domains. Figure 1 shows a schematic of the in-situ TEM experiment setup (Fig. 1a) and the initial domain structure of a PMN-0.38PT single crystal before cyclic electric loading (Fig. 1b–e). As PMN-0.38PT is a ferroelectric material with a tetragonal structure at room temperature, there are six possible polarization directions in PMN-0.38PT along $\pm[100]$, $\pm[010]$, and $\pm[001]$ orientations, which are defined as $a_1$ ($a_1^+/a_1^-$), $a_2$ ($a_2^+/a_2^-$), and $c$ ($c^+/c^-$) domains, respectively, as indicated in Fig. 1a. A PMN-0.38PT lamella with stripe domains prepared by focused ion-beam was fixed between the two Pt electrodes with a distance of 4 µm apart. A cyclic electric field was applied to the lamella along the $\pm[100]$ crystallographic direction. The stripe domains with domain walls along the [110] direction indicate that they are $a_1$ and $a_2$ domains with 90° ferroelastic domain walls. To minimize the system energy, the 90° stripe domains follow the head-to-tail configuration, in which the polarizations of the domains in Fig. 1a are either $a_1^+/a_2^-$ (−/+) or $a_1^-/a_2^+$ (+/−) (Fig. 1b). Figure 1b, c presents schematic diagrams of [001] projected lattices of $a_1/a_2$ domains and the corresponding schematic of electron diffraction pattern, respectively. The electron diffraction pattern shows the spots splitting caused by the 90° polarization rotation of $a_1$ domains and $a_2$ domains. The yellow and purple spots are contributed by the yellow ($a_1$ domains) and purple ($a_2$ domains) lattices, respectively.

Formation of c domains under cyclic electric field. Figure 2 shows the evolution of domain structure in PMN-0.38PT under cyclic electric loading. The parameter set for the repeated electric biasing test was a bipolar triangle wave with a peak voltage of ±4.7 V and a frequency of 1/30 Hz. The electric field $E$ applied to the lamella can be calculated using the equation: $E = \frac{V}{d}$, where $V$ and $d$ are the applied voltage and the distance between the electrodes, respectively. Since the electric field between the two electrodes is homogeneously distributed and the distance between the two electrodes is 4 µm, the peak applied electric field is ±1.175 MV/m. The pristine domain structure is presented in Fig. 2a (0 cycle), with $a_1^+/a_2^-$ domain configuration before the application of a cyclic electric field. After 130 cycles, some domains nucleated from the original domain walls (blue domains in the schematic). As the number of electric cycles was increased, additional domains nucleated from regions of the domain wall while earlier formed domains propagated along the [010] direction in the $a_1$ domains and the [001] direction in the $a_2$ domains. Electron diffraction was used to determine the polarization direction of these domains. Figure 2b, c presents electron diffraction patterns obtained from areas marked with the green and red circles in Fig. 2a, respectively. The diffraction spots acquired from the selected area of the green circle split along the [100] direction (Fig. 2b), and those acquired from the red circle split along the [001] direction (Fig. 2c). The lattice parameter of PMN-0.38PT along the [100] direction is a little larger than that along the [010] direction for the $a_1^+$ domains, while for $c$ domains, the lattice parameters along the [100] and [010] are equal. This leads to the split diffraction spots along the [100] direction (Fig. 2d), which is consistent with the highlight in the green square of Fig. 2b, implying the coexistence of $a_1^+$ and $c$ domains in the green circle in Fig. 2a. Meanwhile, the coexistence of $a_1^+/c$ domains also follows a similar scenario (Fig. 2e), represented by the highlight in the red square of Fig. 2c. Figure 2f shows the curve of the area of the projected $c$ domains vs. the number of cycles. The growth rate of the $c$ domains increased exponentially with the number of electric cycles.

It should be noted that nanodomains formed in some of the original $a_2$ domains during electric cycling and extended along the [110] direction (denoted by the red arrow in Fig. 2a). Literature reports suggest that mechanical stress could introduce these kinds of nanodomains in PMN-0.38PT. In the current research, the two ends of the lamella were fixed onto the electrodes, which constrained the deformation from domain switching and induced the local stress that was the driving force for the formation of the nanodomains.

Charge accumulation at domain walls under cyclic electric loadings. It has been reported that ferroelectric domain walls are preferred regions for the accumulation of oxygen vacancies and other structural defects. With increasing the number of cyclic electric loadings, an increasing number of mobile charges will accumulate at domain walls due to the electrostatic effect. The accumulation of the space charges or injected charges changes the local electric field in the ferroelectric materials. The STEM-DPC technique can image local electric field with high accuracy, which makes it possible to monitor the evolution of local electric fields in ferroelectrics under external stimuli. Our experimental results suggest that the repeated electric loading processes did not change the focus and tilt (Supplementary Fig. 1) and that defocus condition did not change the electron field maps observed from STEM-DPC images within a certain defocus range (Supplementary Fig. 2). Figure 3a, b shows the local electric field maps, which were acquired using the STEM-DPC technique, of an area in a sample before and after the application of a cyclic electric field. The direction and amplitude of local electric fields are presented by colors, see the color wheel at the lower-left corner of Fig. 3a, and image intensity, respectively. After cyclic electric loadings, the direction of local electric fields (the colors in the image) remained the same. However, the amplitude of local electric fields (or local image intensity) at areas denoted by the white hollow arrows (mainly domain walls) increased. Figure 3c presents the result of Fig. 3a subtracted from Fig. 3b in the grayscale to show clearly the change of local image intensity. Significant contrast variation in areas marked by the white hollow arrows indicates the amplitude variation of local electric field, which was caused by the difference in local charge density before and after the application of cyclic electric field (the electron beam was blocked during the application of electric field to avoid any potential effect from electron beam illumination). Because there are few free charges before the application of electric field for as-grown PMN-0.38PT, the change of local charge density can only be an increase after the application of repeated electric field. Hence, the contrast variation in Fig. 3c is a result of charge accumulation. TEM images of the same area captured before (Fig. 3d) and after (Fig. 3e) cyclic electric loadings show no apparent difference, indicating that the change in local charge density did not change the local structure. To further validate the stability and reliability of STEM-DPC imaging, we provide additional data in Supplementary Figs. 3 and 4. With extra data from electron energy loss spectroscopy (EELS), a powerful technique to evaluate the electronic state of materials, we confirm the charge accumulation at domain walls. EELS was used to measure the plasma peak shift at domain walls before and after cyclic electric loadings (Supplementary Fig. 5). The energy shift is 1.2 eV, corresponding to the change in charge density of 3.76 electrons/nm² at the domain walls (see the calculation in Supplementary note 1).
**Fig. 2** c domain formation during cyclic electric loading. **a** A series of TEM images showing the evolution of domain structure in PMN-0.38PT under a cyclic electric field. The schematics of the domains were presented at the bottom of each image. The pink double arrow denotes the directions of the applied electric field. The red arrow denotes nanodomains formed in an original $a_2^+$ domain. **b, c** Electron diffraction patterns obtained from the areas marked with green and red circles in **a** after 280 electric cycles, respectively. The green and red squares denote the splitting of diffraction spots along the [100]* and [010]* directions, respectively (*represents reciprocal space). **d, e** Schematic diagrams of [001] projected lattices of $a_1^+/c$ and $a_2^+/c$ domains and their corresponding schematics of electron diffraction patterns. **f** The area of projected c domain vs. the number of cycles showing the rate of the c domain growth in **a** from 0 to 280 cycles.

**Fig. 3** Charge accumulation at domain walls during cyclic electric loadings. **a, b** Electric field mapping before and after cyclic electric loadings, respectively. The direction and amplitude of local electric fields are represented by colors, see the color wheel at the lower-left corner of **a**, and image intensity, respectively. **c** A grayscale image obtained from the subtraction of the image in **a** from the image in **b**, showing the variation in local image intensity. The white hollow arrows in **b** and **c** mark the places with significant intensity variation after cyclic loading. **d, e** TEM images before and after cyclic loadings, respectively.
domains grew along the [010] direction in the (Fig. 2a). It was clearly observed in the TEM image series that (see Supplementary note 1).

The small white hollow arrow denotes the zipper-shaped domain wall formed during the switching process. The blue lines mark the contours of some domains. Accumulated charges is strong enough to stabilize the indicated by the calculations that the electric loading, but a consequence of the cyclic electric loading. It is also accomplished when the charges accumulate to a certain level. That is, dynamic process, while domain switching can only be accommodated when the charges accumulate to a certain level. That is, dynamic process, while domain switching can only be accommodated when the charges accumulate to a certain level. That is, dynamic process, while domain switching can only be accommodated when the charges accumulate to a certain level. That is, dynamic process, while domain switching can only be accommodated when the charges accumulate to a certain level. That is, dynamic process, while domain switching can only be accommodated when the charges accumulate to a certain level. 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cycles (Supplementary Fig. 6) show that the switchable area of domains decreased as the number of cycles increased. Besides, the growth rate of the unswitchable domains (Fig. 2f) was increasing, indicating a degradation of ferroelectric property. The frozen state of the \(a_2^+\) domains can sustain long times after the experiment, and remains even 18 months after the cyclic electric loading (Supplementary Fig. 7).

It is worth noting that most of the \(a_2^+\) domains, in which there were no stress-induced nanodomains, experienced 180° switching, while the switching process of the \(a_2^-\) domains with stress-induced nanodomains inside was complicated in that multi-switching steps occurred via the formation of the intermediate ferroelastic domains.\(^{29}\) The small red hollow arrows in Fig. 4c indicate the intermediate ferroelastic domains in an \(a_2^-\) domain. The zipper-shaped domain wall, which is denoted by the small white hollow arrow in Fig. 4c, was also formed during the switching process. These observations are consistent with the literature demonstrating the switching behavior of PMN-0.38PT both without and with constraint.\(^{29}\) However, despite the switching behaviors of the \(a_2^-\) domains during electric cycling, the \(c\) domains remain unchanged in the \(a_2^-\) domains during the poling cycle.

**Discussion**

Charge accumulation is commonly cited as the origin of ferroelectric degradation.\(^{7}\) However, the route from charge accumulation to ferroelectric degradation remains unclear. Our results provide direct evidence of charge accumulation at the domain walls and subsequently these charges promote the formation of frozen domains, leading to ferroelectric degradation. This picture of the dynamic process bridges the knowledge gap of how the space charges or injected charges contribute to ferroelectric degradation. As this study was performed on specimens with nanoscale dimensions, the physics of ferroelectric degradation demonstrated here might only be applicable to thin-film ferroelectrics and nanodevices. In spite of this, our work is thought-provoking as ferroelectric degradation in ferroelectric memories,\(^{3}\) MEMS and nanoelectromechanical system devices\(^{1}\) is still a major issue to be tackled with.

In this work, we illustrate that frozen domains initiated from the typical polarization transition zones-domain walls. More completely, any polarization transition zones, including phase boundaries, interfaces and surfaces of ferroelectrics, could be potential sites for the formation of frozen domains during cyclic electric loadings. This is because the phase boundaries, interfaces and surfaces of ferroelectrics are not only the preferred sites where extra charges accumulate but also polarization transition regions.\(^{22}\) It can be corroborated by the formation of some frozen domains near the lower edge of the sample in our experiment (Fig. 2a) as the sample edge is a reconstructed surface where the polarizations are randomly distributed.\(^{43}\) We can make a reasonable conjecture that multi-phase coexisted regions, film/substrate interfaces, ferroelectric/electrode interfaces, and grain boundaries could be the regions where frozen domains frequently appear under cyclic electric loadings.

In summary, we investigated the ferroelectric domain evolution of PMN-0.38PT single crystals using in-situ biasing TEM. The observed domain switching behavior under cyclic in-plane electric biasing showed that ferroelectric degradation could be induced by the formation of frozen \(c\) domains. The \(c\) domains formed from the original domain walls as the number of electric cycles increased. STEM-DPC results indicate that charges accumulated at the domain walls with the increase of the number of cyclic electric loadings. These accumulated charges served as compensation charges to stabilize the \(c\) domains. The \(c\) domains did not reverse in response to in-plane cyclic electric loading, leading to the ferroelectric degradation of the material. This finding illustrates a dynamic process of ferroelectric degradation caused by the formation of frozen domains.

**Methods**

**In-situ biasing TEM.** The PMN-0.38PT single crystal was grown by a modified Bridgman method.\(^{77}\) It was selected as a model material for this work due to its simple and stable structure. PMN-0.38PT lamellae with dimensions of \(8 \mu m \times 4 \mu m \times 1 \mu m\) (length \(\times\) width \(\times\) thickness) were produced using mechanical grinding followed by focused ion-beam processing. The PMN-0.38PT lamellae were fixed at a gap length of 4 \(\mu m\) between the inner two electric contacts of MEMS-based nanochips by platinum deposition. The lamellae were thinned down by focused ion-beam to a thickness of about 100 nm. In-situ biasing TEM experiments were conducted with a Lightning holder produced by DENSolutions in a JEM-2100 electron microscope operated at 200 kV. A bipolar bias in a triangular waveform (peak voltage of 4.7 V and frequency of 1/30 Hz) was applied along the \(\pm [100]\) crystallographic direction of the specimen.

**STEM-DPC.** When a focused electron beam passes through a ferroelectric sample, the local electrostatic potential field causes a phase shift of the electron beam, which changes the intensity distribution of the corresponding convergent beam electron diffraction (CBED) pattern. The differential of this phase shift is linearly related to the position of the center of mass of the CBED pattern.\(^{46}\) For a TEM sample, the phase shift of the transfer function of the sample is approximately proportional to its projected electrostatic potential. Accordingly, the differential of the phase shift is proportional to the projected electrostatic field of the sample.\(^{47}\) The STEM-DPC technique relates the differential of the phase shift and the electrostatic potential field of the sample.\(^{48}\) In this work, STEM-DPC was performed in an aberration-corrected FEI-Temis Z STEM operated at 300 kV. The configuration of the detector segments is illustrated in Supplementary Fig. 8. The images were obtained with a semi-convergence angle of 17.9 mrad and collection angle range of 9–51 mrad. A beam current of 50 pA, a dwell time of 10 µs per pixel and an image size of 1024 × 1024 pixel were utilized. Because STEM-DPC imaging is very sensitive to crystallographic orientation, domain switching is not desired during the application of the cyclic electric field. STEM-DPC images were taken before and after the application of 100 cycles of electric loadings in another PMN-0.38PT sample. In order not to induce domain switching (Supplementary Fig. 9), a bipolar bias in a triangular waveform with a frequency of 1/8 Hz and a peak voltage of 3.0 V, which is smaller than the switching voltage in this sample, was applied along the \(\pm [100]\) crystallographic direction of the specimen.

**Data availability**

The authors declare that the data supporting the findings of this study are available within this paper and its supplementary information files.

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Author contributions
Q.H., Z.C., and X.L. designed and directed the study. Q.H. conducted the in-situ TEM experiments and performed data analysis. Z.C. and M.J.C. assisted in the experiment. F.W. and H.L. provided the samples. Q.H., Z.C., M.J.C., S.Z., F.L, Y.L., S.P.R., Y-W. M., and X.L. wrote the paper. All authors discussed the results and contributed to the paper.

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The authors declare no competing interests.

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