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Reversible oxygen migration and phase transitions in hafnia-based ferroelectric devices

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Unconventional ferroelectricity exhibited by hafnia-based thin films, robust at nanoscale sizes, presents tremendous opportunities in nanoelectronics. However, the exact nature of polarization switching remains controversial. We investigated $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3/\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ capacitor interfaced with various top electrodes while in situ electrical biasing using atomic resolution microscopy with direct oxygen imaging, as well as synchrotron nanobeam diffraction. When the top electrode is oxygen reactive, we clearly show reversible oxygen vacancy migration with electrodes being the source and sink of oxygen, and the dielectric layer acting as a fast conduit at millisecond timescales. With non-reactive top electrodes and at longer time scales (seconds), the dielectric layer also acts as an oxygen source/sink. Our results show that ferroelectricity in hafnia-based thin films is unmistakably intertwined to oxygen voltammetry.

The discovery of silicon compatible nano-ferroelectricity in hafnia-based thin films (1) has triggered a vast amount of fundamental research and rejuvenated interest in ferroelectric materials in microelectronics, for low-power non-volatile memory and logic devices. This ferroelectricity is robust even at film thicknesses as low as 1 nm (2–4), a situation that was believed impossible based on the classical understanding of ferroelectricity. The spontaneous polarization observed in these films is ascribed generally to a metastable polar orthorhombic phase ($Pca2_1$, o-phase) (5). A higher energy rhombohedral phase ($R3m/R3$, r-phase) has been reported for epitaxial growth of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO) on $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO) buffered perovskite and on trigonal substrates (6). Remnant polarization (P_r) values as high as 35 $\mu\text{C}/\text{cm}^2$ were measured (7) on HZO. The pronounced effects of particle size reduction, surface effects, dopants, oxygen vacancies ($\ddot{\text{V}}_{\text{O}}$), epitaxial strain and residual stresses at nanoscale have been investigated as possible reasons to stabilize these otherwise metastable phases in thin films (5, 8, 9). On the other end of the size range, films as thick as 1 μm (10) and bulk samples (11) are ferroelectric, with the stabilization due to dopant and defect chemistry (10, 12).

Armed with an understanding of the virgin state polarization, vibrant research is being conducted on the mechanism

of polarization switching. The dynamics of this process, through the lens of a nucleation-limited switching model and pointing out the negligible role of domain growth (or domain wall motion), have been studied for doped hafnia films grown in the o-phase (13–19). Flat phonon bands and localized dipoles in half unit cells in the o-phase have been postulated as an intrinsic reason for switching without forming domain walls in these systems (20).

Hafnia-based and zirconia-based materials are also an important class of resistive memory devices and oxygen conductors that exhibit memristive hysteresis driven by $\ddot{\text{V}}_{\text{O}}$ conduction and redox reactions (21, 22). More generally, in devices of thin-film ferroelectric oxides such as tunnel junctions, both $\ddot{\text{V}}_{\text{O}}$ migration and polarization switching lead to hysteresis (23–28). Understanding whether these effects are synergetic or independent is crucial to achieve device control (29–33). In tunnel junctions of HZO thin-films on LSMO buffered SrTiO_3 (STO), Wei *et al.* (23) observed a divergence of the tunnel electro-resistance (TER), from 100% to $10^{6\%}$ upon device cycling, which the authors explained as a possible transition from polarization switching to $\ddot{\text{V}}_{\text{O}}$ migration assisted switching. This observation suggested the two mechanisms are independent. Sulzbach *et al.* (24) also reported a similar divergence in the TER as a function of the applied

voltage in HZO layers before breakdown. However, the electric polarization in hafnia has been theoretically proposed to originate from oxygen vacancies through electrostrictive effects, strongly suggesting the extrinsic nature of the polarization switching (29). Direct structural observations during polarization switching can potentially resolve these controversies (34).

We report operando atomic scale electron microscopy investigations of LSMO/HZO/LSMO capacitor stacks grown on conducting (Nb-doped) STO substrate under electric field (35). LSMO is a standard choice of bottom electrode in complex oxide devices (23–26, 31) and so our conclusions are relevant for understanding a wider class of devices. We performed in situ biasing measurements while employing two scanning transmission electron microscopy (STEM) imaging modes, high-angle annular dark-field (HAADF) STEM and integrated differential phase contrast (iDPC) STEM. With iDPC STEM, we recently imaged hydrogen atoms next to Ti metal atoms (36), demonstrating this robust atomic resolution imaging technique for simultaneously measuring heavy and light elements. By directly imaging oxygen, we provide evidence of the reversible and hysteretic migration of $\ddot{V}_o$ from the bottom to the top electrode through the HZO layer. Associated with such migration, we show $\ddot{V}_o$ induced phase transitions in LSMO (bottom electrode) and HZO layers. Additionally, through operando x-ray diffraction, ex situ microscopy, and transport measurements on devices with both noble (Au) and oxygen reactive top electrodes (LSMO, TiN), we show that oxygen voltammetry is also found at short time-scales (millisecond and less). We believe these observations clearly show that polarization switching and oxygen voltammetry are not independent. The long-term effects include redox-based and topotactic phase transitions in both HZO and LSMO layers.

We begin by showing the evolution of the epitaxial LSMO layer (bottom electrode) with bias, with the voltage applied to the top electrode, and keeping the bottom electrode at 0 V (fig. S1) (22). Our iDPC-STEM image of the virgin state (Fig. 1A and fig. S2A) shows the antiphase octahedral δ tilts present in the LSMO perovskite structure (22). Mn-O-Mn bond angles, as we measured in various s regions, are between 165° - 176° (37). Upon increasing the bias to 2 V, a noticeable displacement of Mn columns away from the center of oxygen octahedra (Fig. 1B) appears throughout the film (barring the first three monolayers at the interface with Nb:STO). These displacements are randomly oriented with a mean value of 18.6 pm and std. deviation of 10.2 pm (fig. S3), indicating a transformation from an MnO_6 octahedral toward an MnO_5 square pyramidal coordination (35). Thus, at 2 V the LSMO film contains a combination of MnO_5 and MnO_6 polyhedra. While this structural feature was not previously observed for LSMO, Brownmillerite (BM, oxygen deficient perovskite)

phases are reported to exhibit MnO_5 square pyramids in the parent compound, SrMnO_3 (38). We refer to this MnO_5 - MnO_6 combination as a BM-precursor phase (39). As for the first 3 monolayers, an important feature is the exaggerated antiphase δ tilts, with Mn-O-Mn bond angles of 143 - 146° that are not typical of perovskite structures (fig. S2, B to D).

Upon increasing the biasing voltage to 4 V, LSMO converts into a well-studied BM phase (40, 41) except for the first few monolayers near the interface with the substrate, which transform to the BM-precursor phase (fig. S4A). Transformation from perovskite to BM phase occurs via $\ddot{V}_o$ ordering in every alternate Mn-O plane along the c' -axis (Fig. 1C), transforming the Mn coordination from octahedral or square pyramidal to tetrahedral. Back-to-back MnO_4 tetrahedra along $[1-10]$ alternate with MnO_6 octahedra along c' , indicating the BM phase (Fig. 1C). This transformation is hysteretic and non-volatile, with LSMO remaining in the BM phase even when the external bias is removed (fig. S4) (35).

The multiple-step transformations (Fig. 1D) from MnO_6 octahedra (virgin state) toward square pyramids plus octahedra (2 V), to alternating octahedra and tetrahedra (4 V) also correlate to the variation of the pseudo-cubic lattice parameter along the electric-field direction (called c'). We determined the c' values at various bias voltages for the first 20 monolayers in LSMO starting from the Nb:STO interface (Fig. 1E). In the virgin state, we measured c' to be $384 (\pm 5)$ pm with $\ddot{V}_o$ disorder induced expansion in some planes (35). At 2 V, c' oscillates with values between 335 and 425 pm, without resulting in any particular superstructure. At 4 V, except for the first few monolayers, c' alternates between 375 and 445 pm, doubling the lattice periodicity. Energy dispersive spectroscopy (35) reveals a clear gradient of oxygen concentration in the bottom electrode, compared to the virgin state, even at a low bias of 1.5 V, with more $\ddot{V}_o$ occurring closer to the Nb:STO interface (Fig. 1, F and G).

Importantly, the BM phase can be reoxygenated when negative voltages are applied to the top electrode. We show this takes place for biases as low as -1 V (fig. S5A). The hysteretic BM phase clearly begins to reoxygenate in iDPC-STEM images of the same field view at 0 V and -1.3 V (Fig. 2, A and B), with the appearance of extra oxygen columns at -1.3 V in the Mn-O planes that were oxygen deficient at 0 V (fig. S5A). Upon ramping the bias to -3 V, the entire layer converts to the BM-precursor phase (Fig. 2C) and was retained also when the bias is removed (Fig. 2D), as we confirmed by the corresponding 'disorderly' c' variation (fig. S5B).

In order to address the timescales of the processes associated with de- and re-oxygenation of LSMO layers, we followed the dynamics through HAADF-STEM image acquisition, after poling at -4 V (transforming LSMO completely back to the starting perovskite phase). In the HAADF-STEM image evolution that occurs within 2 min of one region having a bias

increase to 3V (Fig. 2E), the initial perovskite phase changes to the BM-precursor phase in 60 s, and then to the BM phase within 120 s. These changes were indicated by the variations we observed in the c' parameter. By applying -3 V, we observed a complete transformation from a BM phase back to perovskite phase within 90 s in the region (Fig. 2F; FFT in fig. S5C). We then followed the same region for 10 s using a faster HAADF-STEM image series (1.2 s/frame). From the c' parameter variations, we concluded that the BM-precursor phase transformed to the perovskite phase (Fig. 2F, center panel). Thus, while the complete transformation from perovskite to BM and back takes about a couple of minutes at 3 and -3 V, $\ddot{V}_o$ migration and partial phase-transitions already started occurring in time scales of seconds at these voltages. At 2 V, however, the partial transition to the BM-precursor phase itself takes 3-4 hours. The change in kinetics with voltage is consistent with the ultra non-linear “voltage-time dilemma” typically observed in oxide resistive memories (42). Thus, we expect that at higher voltages these mechanisms will occur at very short time scales.

We also monitored the structural evolution in the HZO (6 nm) layer under the application of bias. From the multislice iDPC-STEM image simulations for HZO [see also (43)] in the r-phase ($R3m$) with [111] out-of-plane (Fig. 3A, inset), we recognized the (001) planes (at $\sim 55^\circ$ with respect to the [111] direction) by cationic (Hf/Zr) columns surrounded by two oxygen columns on either side of them. In the virgin state, our experimental images perfectly match the r-phase simulations. We followed the evolution of a supercell (Fig. 3A) in this grain upon application of bias along the out of plane [111] direction. We show how the displacement of $\ddot{V}_o$ for this supercell occurs (35) (fig. S6A) with respect to the 0 V configuration (Fig. 3B). While $\ddot{V}_o$ migrate toward the bottom electrode with increasing bias (Fig. 3B), they also gather some in-plane displacement (Fig. 3B, inset).

At 4 V, the same grain transforms into a combination of multiple grains (Fig. 3C). Upon inspecting various regions in the film, we found that the majority of the grains have changed their structure from r-phase toward the more thermodynamically stable orthorhombic (o-) and monoclinic (m-) phases (Fig. 3D and fig. S6C). The o-phase is commonly observed in ferroelectric HZO layers grown by various methods (5), while the r-phase is only observed under specific growth procedures and conditions (6). Our observations on HZO point to the r-phase being stabilized under slight oxygen deficient conditions. Replenishment of oxygen in the HZO layer under bias (originating from the bottom LSMO layer), transforms it into more stoichiometric m- or o-phases. The $\ddot{V}_o$ in the HZO layer, and thus the r-phase, is restored (by reverse migration) upon applying a bias of -3 V, as can be seen from the perfect match of the experimental iDPC-STEM of two representative domains (180° rotated from each other) (Fig. 3E),

with the multislice image simulations (Fig. 3A, inset). The m/o-phases can be reversibly obtained again in subsequent cycles of positive bias (fig. S6D).

To elucidate the effects of device cycling with sub-millisecond pulses (35), we present results on tunnel junction Co/HZO (2 nm)/LSMO//STO devices switched between low-resistance state (LRS) and high-resistance state (HRS) at large voltages of ± 6 V. The devices showed an increasing TER (35) from 100% (stage A) to $10^{6\%}$ (stage B) upon cycling ~ 100 times (23, 44). An iDPC-STEM image from a selected region in the LSMO (bottom electrode) layer in the LRS (stage A) (Fig. 4A) shows a clear perovskite structure. In the HRS (stage B), however (Fig. 4B), Co inhomogeneously oxidizes exhibiting co-existing Co rich and CoO_x rich regions as revealed from the EDS analysis (fig. S7). This leaves oxygen deficient LSMO in the BM precursor-phase. Thus, progression from stage A to stage B results in gradual increase of CoO_x regions, an accumulated effect of oxygen voltammetry, which is reflected electrically in diverging resistance values.

To disentangle the short-term field effects on our devices from accumulated effects (35), we report ex situ structure-property correlation results on ferroelectric capacitor stacks of LSMO (or TiN)/HZO (7 nm)/LSMO//STO cycled at 1 kHz for < 10 times at 5.5 V. The intrinsic P_r of our virgin devices in r-phase obtained from atomic displacements (35) (fig. S5B) is $< 9 \mu\text{C}/\text{cm}^2$, which is very small compared to the $35 \mu\text{C}/\text{cm}^2$ that were measured from P-V loops at room temperature (7). This discrepancy is already an indication that most of the switching charge is intertwined with extrinsic factors. From the P-V hysteresis loops at various temperatures (Fig. 4C), we observed that, contrary to what it is expected in classical ferroelectrics, the P_r increases with increasing temperature in the range from 150 K to 300 K (22). This observation is in line with the polarization switching being correlated to the thermally activated oxygen migration mechanism. These devices were prepared in a “down polarized” configuration (5.5 V, 1 kHz) and imaged. The iDPC-STEM images clearly reveal the oxygen deficient BM-precursor phase in the bottom LSMO layer close to the HZO interface (Fig. 4D) as also confirmed by corresponding disorderly oscillations in the c' parameter (Fig. 4D, inset). Close to the STO interface, we found exaggerated oxygen octahedral tilts with Mn-O-Mn bond angles $< 146^\circ$ (marked in fig. S8A), which is the same interfacial feature observed during in situ DC testing at 2 V (fig. S2B). These observations also suggest that such extreme tilts initiate the transformation from perovskite to BM-precursor phase. These incipient oxygen-migration induced topotactic structural transitions result from the discharge of $\ddot{V}_o$ in the electrodes. This thermally activated process leads to a built-in field at lower temperature, which decreases as the temperature rises (fig. S8, B and C). The HZO layer, however, remains in an r-phase (Fig. 4E), revealing that it just acts as a conduit

of oxygen between the source and sink (both reactive) electrodes in the short-term.

We conducted comparative operando synchrotron nano-beam diffraction on Au/HZO/LSMO and LSMO/HZO/LSMO capacitors in order to answer the question whether oxygen voltammetry can still occur if HZO is interfaced with a non-reactive electrode in the short-term (35) (fig. S9). Both devices showed ferroelectric switching peaks (Fig. 4E and fig. S10) and we cycled them at 100 Hz in a modest voltage range between -3.5 and 3.5 V for tens of thousands of cycles (fig. S10C). In LSMO/HZO/LSMO devices the virgin state and cycled state do not show any substantial differences of the HZO lattice parameter, indicating the persistence of the r-phase during cycling (fig. S10D). However, in the case of Au/HZO/LSMO, we see evidence that a monoclinic phase (with a Bragg peak at $2\theta=24.9^\circ$) appears after cycling, and coexists with the r-phase (fig. S10, E and F). This reveals that the HZO layer itself is forced to act as source/sink of oxygen vacancies in the short-term (35), when Au is used as a top electrode, resulting in reversible structural phase transitions between r and m phases. Further DC biasing, results in increase of m-phase fraction increasing positive bias, in agreement with the long-term in situ TEM observations (fig. S11).

Using the model system of epitaxial HZO/LSMO/STO, we demonstrated that oxygen voltammetry and ferroelectric switching are intertwined (Fig. 4F) (35). With reactive top electrodes such as TiN (45), Co, and LSMO, the HZO layer acts as a mere conduit for reversible oxygen migration between the electrodes, with incipient topotactic transformations taking place in them. With a noble top electrode (Au), HZO instead itself acts as a sink/source of $\bar{V}_o$. In the longer-term, redox-based phase-transition effects that follow oxygen migration in both HZO and LSMO become more dramatic. We clearly show that oxygen voltammetry is intertwined with ferroelectric switching of HZO. While we remain agnostic about the nature of this coupling, recent predictions of electrochemical origin of ferroelectricity in hafnia-based compounds (29), as well as demonstrations of giant electrostriction in the sister compound $\text{Gd}:\text{CeO}_2$, (46) can provide important clues.

In the context of tunnel junction devices, perovskite manganites (47) are routinely used as a back electrodes (24–27, 48). Their crucial role as oxygen conducting memristive layers (41) actively participating in charge transport is being recognized (35), with recent seminal demonstrations in ferroelectric tunnel junctions (28). Thus, our results have deep implications not just to hafnia-based ferroelectrics, but also to the wider field of oxide electronics.

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SUPPLEMENTARY MATERIALS

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Materials and Methods

Supplementary Text

Figs. S1 to S11

References (50–53)

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Fig. 1. Deoxygenation of bottom electrode LSMO layer with increasing positive bias. (A) iDPC-STEM image of a representative region of the bottom LSMO layer in the virgin state, viewed along the [110] zone axis, exactly matching the perovskite structure. Schematic in the inset showing MnO₆ octahedra and their antiphase tilts, clearly imaged in (A). (inset) La/Sr: green, Mn: red, O: brown). (B) iDPC-STEM image at V = 2 V. Panels on the right show various unit cells, illustrating Mn columns (circled in white) and their displacements (marked by green arrows) away from the center of an octahedron. Oxygen columns are marked in red circles. (C) iDPC-STEM at 4 V. BM LSMO (zone axis: *a*, schematic in inset) denoted by alternating MnO₄ tetrahedra and MnO₆ octahedra along *c'*. (D) Schematic showing the evolution of an MnO₆ octahedra in the virgin state (enclosed in black box) toward MnO₅ square pyramids at 2 V (enclosed in red box) to alternating MnO₄ tetrahedra and MnO₆ octahedra at 4 V (enclosed in blue). (E) Plot of variation of *c'* (La-La distance) parameter from the STO interface in perovskite (black), BM-precursor (red) and BM phases (blue). (F) Overview image of LSMO/HZO/LSMO capacitor with regions marked where oxygen content was quantified from EDS (G) at 0 V and 1.5 V. Scale bars, 1 nm in (A-C), and 5 nm in (F).

Fig. 2. Oxygenation of bottom electrode LSMO layer with increasing negative bias. iDPC-STEM images of a region in the same field of view at 0 (A) and -1.3 V (B). At -1.3 V oxygen columns start to appear (marked by red arrows) in positions where there were none in the BM phase at 0 V. (C) BM phase transforms to BM precursor phase at -3 V and is retained so at 0 V (D). (E) Dynamics is recorded via HAADF-STEM imaging within 120 s of ramping from 0 to 3 V from a starting perovskite phase. A BM-precursor phase is imaged at 60 s, BM phase is imaged at 120 s. (F) Upon changing the bias to -3 V, a BM phase is recorded at 30 s, changes to perovskite phase by 90 s (disappearance of the superstructure spots in FFT, fig. S4). The intermediate BM-precursor phase recorded at 60 s, converts to perovskite-like phase in about 6 s as can be seen by the variation in c' parameter, giving an idea about the time scales of $\bar{V}_o$ migration. Scale bars: 1 nm in (A-D) and 5 nm in (E-F).

Fig. 3. Oxygenation and deoxygenation of HZO and associated phase transitions. (A) Evolution of an r-phase HZO grain while oxygenating under positive bias followed through iDPC-STEM image, where both cations and oxygen columns are displayed. The image of the virgin state at 0V shows two red arrows pointing to two oxygen columns in the (100) planes neighboring a cationic column. Multislice iDPC-STEM image simulations of the r-phase ($R3m$ symmetry) in the inset shows the good match with the observations. (B) Out-of-plane displacement of $\vec{V}_o$ with external bias, in the marked supercell (red box) with respect to the positions in (A). Negative values indicate displacement toward bottom electrode. $\vec{V}_o$ shows both in-plane and out-of-plane (toward bottom electrode) components (inset). (C) A new grain nucleates in the same region at 4 V, giving rise to a polycrystalline nature (FFT in inset). (D) Another region in the HZO film back at 0 V showing o-phase and m-phase (with multislice simulations of both in the insets). Also note the change of orientation from [111] to [100]. (E) iDPC-STEM image of domains (mutually rotated by 180° about [111]) in the r-phase [to be compared with simulation in inset of figure 3a from (36)], which is retained when poled at -3 V (imaged at 0 V). Scale bars: 1 nm in (A, C, E) 2 nm in (D). Interfaces between HZO and top and bottom LSMO are marked in orange. In (D) only HZO/bottom electrode interface is shown.

Fig. 4. Cycled tunnel junctions and ferroelectric capacitors. (A) Co/HZO (2 nm)/LSMO tunnel junction in LRS (500 μ s, 100s of cycles poled at -6 V). HAADF-STEM image on the left (scale bar: 5 nm), and iDPC-STEM of a selected region in LSMO on the right (scale bar: 1 nm). (B) Ex-situ imaging of tunnel junction in HRS (500 μ s, 100s of cycles, poled at 6 V). (right) HAADF-STEM (and corresponding information from EDS) shows CoO_x/HZO/LSMO stack (scale bar: 5 nm). (left) iDPC-STEM of a region in LSMO shows BM-precursor phase (scale bar: 1 nm). Selected Mn column displacements toward a square pyramidal geometry are marked by green arrows. (C) Temperature dependent P-V loops obtained from dynamic hysteresis measurements at 1 kHz in LSMO/HZO (7 nm)/LSMO (30 nm) capacitors. Inset shows the corresponding 2P_r vs T curve (see also fig. S8). (D) iDPC-STEM image of LSMO close to HZO interface (marked in orange) in TiN/HZO (7 nm)/LSMO capacitors, prepared in "down polarized" state (at 5.5 V). BM-precursor phase is formed, confirmed by disorder in c' parameter (inset). (E) iDPC-STEM image of a "down" polarized HZO layer, which is structurally still in r-phase (inset left, HAADF-STEM image with the iDPC-STEM image presented for the region in the blue box; inset right, multislice simulation of R3m phase). Scale bar in (D) and (E): 1 nm. (F) Schematic of the polarity dependent oxygen voltammetry process in the Metal-Insulator-Metal device structure. Oxygen deficient phases in various layers are represented with lighter colors.