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Hf_{0.5}Zr_{0.5}O₂/La_{0.67}Sr_{0.33}MnO₃ heterostructures**

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In situ heating studies on temperature-induced phase transitions in epitaxial $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ heterostructures

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ABSTRACT

Hafnia-based thin films exhibit unconventional ferroelectricity. These materials also show rich polymorphism, and thus temperature and field-driven phase transitions, as well as oxygen migration. In a bigger context of exploring the synergy between ferroelectricity and diffusion-based structural phenomena, here we study temperature-dependent phase transitions in epitaxial $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2(\text{HZO})/\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (LSMO, bottom electrode) heterostructures. We report topotactic phase transitions and their clear pathways in both LSMO and HZO layers upon heating under vacuum, using *in situ* scanning transmission electron microscopy (STEM). Specifically, we directly image oxygen and cationic columns using integrated differential phase contrast STEM and follow their evolution with temperature. We also perform *in situ* high temperature x-ray diffraction in air and show that the LSMO layer undergoes reversible thermal expansion and contraction when heated up to 850 °C, whereas HZO undergoes strain relaxation beyond 750 °C without any reversible phase transition. Our results provide a comprehensive and direct understanding of temperature-dependent structure, defect, and property correlations in these systems.

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Nanoscale ferroelectricity in hafnia-based thin films has been of significant interest from both fundamental and application points of view^{1,2} ever since its discovery.³ Doped-hafnia films as thin as 1 nm and as thick as 1 μm have exhibited ferroelectric (FE) behavior,^{4,5} and this is related to the existence and stabilization of a polar phase. While the orthorhombic (o-) phase ($\text{Pca}2_1$) is the least energetic polar phase and is commonly observed through various synthesis procedures, a higher energy rhombohedral phase ($R3m$, $R3$) was also shown to be stabilized under specific conditions in epitaxial $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ systems (HZO).^{6,7} Surface energy and size effects, epitaxial strain, thermal and inhomogeneous stress effects, oxygen vacancies, and dopants have all been explored as possible ways of stabilizing the polar phases.^{2,8}

The nature of these polar phases and the investigations of polarization switching continue to reveal intriguing details, confirming the unconventional nature of this ferroelectricity. First, experimentally the question of how polarization switching can be relatively immune to the depolarization fields is starting to be addressed.⁹ Second, hafnia

systems exhibit a plethora of stoichiometric and nonstoichiometric polymorphs, which automatically begs the question of what field- or temperature-induced structural phase transitions are relevant for FE behavior. Structural studies on orthorhombic epitaxial yttria-doped hafnia systems^{10,11} have revealed that the high temperature paraelectric phase is tetragonal. However, unlike in conventional FEs, neither soft-mode-driven nor order-disorder transitions have been observed in any of the doped hafnia systems near the Curie temperature. In polycrystalline TiN/doped-hafnia samples, there is no clear structural signature of a reversible ferroelectric to paraelectric phase transition obtained from comprehensive *in situ* high temperature x-ray diffraction (XRD) studies.¹² Third, domain wall motion and domain wall-assisted transitions¹³ have not been reported in these systems.^{14,15} Recently, there has been a theoretical breakthrough, which suggested that, indeed, ferroelectricity in o-phase hafnia is of a different type, associated with flat phonon bands and 2D polar planes in a nonpolar matrix.¹⁶ Such an intrinsic mechanism could provide some key answers to aforementioned puzzles in FE hafnia.¹⁷

Alternatively, oxygen voltammetry between the electrodes and the hafnia layer has been shown to be inherently coupled to polarization switching through direct *in situ* electron microscopy observations in epitaxial HZO thin films grown in the *r*-phase.¹⁸ An oxygen vacancy (V_o)-assisted extrinsic mechanism has also been proposed theoretically as a general phenomenon to explain nanoscopic ferroelectricity.¹⁹ Such an extrinsic mechanism means that V_o formation and redox processes in the electrode materials are as important to explain the nanoscale ferroelectricity as the field-induced phase transitions in HZO, as shown in Ref. 18. In this regard, investigations involving field-induced acceleration of switching kinetics suggest a nucleation-limited switching behavior,^{20–22} which cannot distinguish nucleation processes in topotactic phase transitions^{23,24} from FE phase transitions. Thermal acceleration of kinetics (by heating) in addition to field acceleration (by applying bias) can perhaps distinguish these processes or establish their coupling from a transport perspective. However, this would first require detailed understanding of thermally induced structural transitions and defect evolution in FE hafnia-based heterostructures. Here, we report direct observations of defect-induced thermal phase transitions in *r*-phase HZO/La_{0.67}Sr_{0.33}MnO₃ (LSMO, bottom electrode) epitaxial heterostructures:

- (1) in vacuum, at an atomic scale, using *in situ* scanning transmission electron microscopy (STEM) and
- (2) in air using *in situ* x-ray diffraction (XRD).

Pulsed laser deposition was used to grow epitaxial films of HZO (6 nm)/LSMO (30 nm) on SrTiO₃ (STO), with the deposition parameters described elsewhere.⁷ A cross-sectional TEM lamella was transferred to a MEMS-based resistive heater (HennyZ) on a SiN_x membrane [Fig. 1(a)], through focused ion beam-based protocols,

developed in house. One such protocol is shown in Figs. 1(b)–1(d). First, a cross-sectional chunk of the heterostructure (protected by e-beam and ion-beam deposited carbon and Pt) is lifted onto a micromanipulator, where it is thinned down to an ~ 150 nm thickness using a 30 kV Ga⁺ ion beam. A hole patterned in between the electrodes of the heater coil on the SiN_x membrane defines the electron transparent region, to which the lamella is transferred and welded. Final thinning (up to ~ 60 nm) and cleaning is performed at lower voltages (16, 5, and 2 kV) on the membrane itself. This heater is then hosted in an *in situ* TEM heating/biasing holder (HennyZ), and the local membrane temperature is calibrated and controlled through an external software.

In situ atomic resolution studies were performed using a Themis Z microscope at 300 kV, by simultaneously using two scanning transmission electron microscopy (STEM) imaging modes: high angle annular dark field (HAADF) STEM and integrated differential phase contrast (iDPC) STEM. With the latter technique, even hydrogen (lightest element) atomic columns were successfully imaged recently.²⁵ *In situ* electrical biasing studies on this ferroelectric system using similar techniques are reported elsewhere.¹⁸ *In situ* high temperature XRD studies were done on a Panalytical diffractometer, attached with an Anton Paar DHS1100 hot stage in air.

We begin with discussing the evolution of the LSMO (bottom electrode) layer upon heating inside the TEM. Figure 1(e) shows a schematic of the perovskite phase of LSMO viewed along the [110]_{pseudocubic} (pc) direction (or zone axis, ZA: [110]_{pc}). La(Sr)O and MnO₂ planes alternate along the *c*-axis, which is the out-of-plane (growth) direction. Along the in-plane [1–10], antiphase ($a^-a^-a^-$) tilts of oxygen octahedra manifest as antiphase δ tilts with a zigzag arrangement of Mn–O–Mn bonds.²⁶ Figure 1(f) shows an iDPC-STEM image of the LSMO layer in the virgin state. The antiphase δ

FIG. 1. *In situ* TEM sample preparation and virgin state: (a) SEM image of the resistive heating coil on the SiN_x membrane of a MEMS heating chip. (b) Cross-sectional chunk, protected by Pt and C (deposited through gas injection system) lifted off onto a micromanipulator in the FIB. (c) Thinned cross section lamella using 30 kV Ga⁺ ions. (d) Lamella transferred to the MEMS chip after defining an electron-transparent hole in it and subsequently cleaned. (e) Schematic of LSMO in the perovskite phase. La/Sr: green, Mn: violet, and O: red. (f) iDPC-STEM image of the LSMO layer in the virgin state. Select oxygen columns are shown in red as a guide to the eye to identify the octahedral δ tilts.

tilts can be clearly seen, with Mn–O–Mn bond angle being 166° – 176° throughout the layer.

Upon heating to 150°C and stabilizing for ~ 1 h, we observed an irreversible transformation of MnO_6 octahedra to MnO_5 square pyramids [Fig. 2(a), inset], triggered by loss of oxygen. This is detectable through displacement of Mn away from the center of the octahedron (mid-point of the line connecting adjacent oxygens) in various directions in different locations. Square pyramidal Mn coordination is common in Brownmillerite (BM) phases of a related compound of strontium manganite. A mixture of square pyramidal and octahedral coordination, referred to as the BM-precursor phase, has been recently reported during electric field-induced deoxygenation studies in LSMO in Ref. 18.

iDPC-STEM images acquired after stabilization at 300°C reveal a further deoxygenation-assisted transformation into a BM phase of LSMO [Fig. 2(b)]. This is characterized by alternating planes of Mn in tetrahedral and octahedral coordination separated by La(Sr)O planes along the c -axis. These topotactic phase transformations are also reflected as changes in the c' parameter (distance between LaO planes). In the perovskite phase, c' measured across 20 consecutive unit cells of LSMO is uniform ($3.86 \text{ \AA} \pm 0.05 \text{ \AA}$), with perturbations most likely arising from growth-induced V_O .⁶ In the BM-precursor phase (at 150°C), c' varies in a disorderly fashion between 3.55 and $4.27 \text{ \AA}$. In a

BM phase, at 300°C , there is an alternating oscillation of the c' parameter between 3.79 and $4.43 \text{ \AA}$ ($\pm 0.05 \text{ \AA}$), resulting in a doubling of the original perovskite unit cell along the c' -axis [Fig. 2(c)].

More deoxygenation upon heating up to 400°C results in transformation to a multiple domain BM phase. In Fig. 2(c), the domains D1 and D2 correspond to viewing the BM structure along the $[1-10]_\text{pc}$ and $[110]_\text{pc}$ zone axes, respectively. In D1, back-to-back tetrahedra in the ZA: $[110]_\text{pc}$ can be clearly visualized as Mn doubling in the tetrahedral Mn planes [Fig. 2(d), inset]. To understand the effect of time on oxygen loss, the lamella was kept at 400°C for ~ 12 h inside the microscope before imaging again. Figure 2(e) shows the iDPC-STEM and corresponding HAADF-STEM image of a particular region in LSMO, where Ruddlesden–Popper (RP) defects start to form in the BM phase (another region is shown in the inset). RP defects are characterized by the absence of MnO_2 planes, arising out of not just the loss of oxygen but also the loss of B-site cations, Mn. Further heating to 450°C results in frequent occurrence of these faults [Fig. 2(f)], and at 500°C , the LSMO layer develops cracks and voids owing to huge loss of material [Fig. 2(g)]. It is worth noting that the HZO layer remains mechanically intact even after the failure of the bottom LSMO layer [Fig. 2(g)].

The topotactic transitions involving loss of oxygen in bare LSMO layers have been studied also through *in situ* XRD heating experiments

FIG. 2. Evolution of the LSMO layer upon heating in the TEM: (a) iDPC-STEM image of the LSMO layer stabilized at 150°C for ~ 1 h. It is in a BM-precursor phase with the general displacement of Mn from the centers of octahedron marked in two locations. The inset shows a zoomed view of the region in red box. Mn displacements in select unit cells are clearly marked. (b) iDPC-STEM image of the LSMO layer stabilized at 300°C for ~ 1 h. It is in a BM phase with ZA: $[1-10]_\text{pc}$. The inset shows the schematic of the BM phase with ZA: $[1-10]_\text{pc}$ green: La, green: Mn, red: O: brown (c) c' parameter variation in 18 pseudocubic unit cells of LSMO at various temperatures. (d) iDPC-STEM image of the LSMO layer stabilized at 400°C for ~ 1 h. Domains with ZA $[110]_\text{pc}$ (D1) and $[1-10]_\text{pc}$ (D2) are imaged. The inset shows the schematic of D1. In this orientation, back-to-back tetrahedra along the $[1-10]_\text{pc}$ in alternate tetrahedral Mn layers can be clearly visualized. (e) iDPC and corresponding HAADF-STEM images of the LSMO layer retained at 400°C for ~ 12 h. RP faults (indicated in red rectangles) appear. The inset shows the iDPC-STEM image of another region with more RP faults. (f) iDPC-STEM image of the LSMO layer stabilized at 450°C showing frequent RP faults (red rectangles). (g) HAADF-STEM image of the entire lamella at 500°C . The LSMO layer forms cracks and voids. The HZO layer is more mechanically stable.

under vacuum by Cao *et al.* in Ref. 23. Interestingly, the authors also observe an “intermediate” noncentrosymmetric phase between the perovskite and the BM phase in LSMO, which we suggest is the same as our BM-precursor phase. Our work provides direct structural insight into the disorder (c' parameter) and nature (coordination) of this phase. Incidentally, unlike the suggestion of Cao *et al.*,²³ we find this phase to be also stable at room temperature (RT).

Next, we describe the evolution of the r -phase virgin HZO layer with heating. Figure 3(a) (inset) shows a multislice simulation of the iDPC-STEM image of HZO in the r -phase, with ZA: $[1-10]_{\text{HZO}}$, and out-of-plane: $[111]$ (also shown in Refs. 6 and 27). An immediately recognizable and unique feature of the r -phase is the arrangement of O–Hf(Zr)–O at an angle of 38° from the horizontal (100) planes, with every intense cationic column neighbored by two less intense anionic (O) columns. Figure 3(a) shows an iDPC-STEM image collation from three different domains of the HZO layer at 150°C , named D_{h1} – D_{h3} . D_{h1} and D_{h3} share the same ZA, $[1-10]_{\text{HZO}}$, and are 180° rotated about $[111]$ and exactly match the $R3m$ symmetry shown by simulations [Fig. 3(a), inset]. Thus, no significant changes occur to HZO upon heating up to 150°C despite phase transitions in the LSMO layer.

At 300°C , although the r -phase can be identified in some domains [red box in Fig. 3(b)], most of the domains exhibit a different oxygen arrangement [right grain in Fig. 3(b)]. At this stage, we cannot fit the exact symmetry, based on the oxygen and cationic arrangement,

to any known phase in HZO. However, we suspect that these are one (or more) of the V_o' ordered phases of HZO theoretically proposed by Rushchanskii *et al.*,²⁸ formed by loss of oxygen from HZO. The iDPC-STEM image of a HZO domain at 400°C shown in Fig. 3(c) gives more credence to this hypothesis. While O–Hf–O arrangements in the (100) planes resemble that of an $R3m$ phase in terms of atomic positions, it is defined by asymmetric intensity profiles of the intensities of O columns (alternating high and low) next to Hf(Zr) columns (as revealed by the line scan on the right). Such a contrast can result from V_o' ordering along certain oxygen columns.

Another feature of the r -phase is the nonequivalence of the d-spacings of (111) and (11-1) planes. From here on, irrespective of the material symmetry, we refer to this nonequivalence as rhombohedral distortion. Figure 3(d) shows $d_{(111)}$ and $d_{(11-1)}$ of various domains as a function of temperature. In addition to thermal expansion, it can be noted that the rhombohedral distortion reduces with temperature. In typical ferroelectrics, such a distortion can be considered as an order parameter, which goes to zero upon a ferro-to-paraelectric phase transition. However, irreversible changes in oxygen stoichiometry and associated V_o' ordering phase transitions preclude us from defining an order parameter through *in situ* TEM heating experiments.

In the case of the *in situ* biasing experiments presented in Ref. 18, we note that under bias, when LSMO loses oxygen, HZO (and the top electrode) gains it, and vice versa upon bias reversal. Thus, electric

FIG. 3. Evolution of the HZO layer upon heating in the TEM: (a) collated iDPC-STEM images of three domains D_{h1} – D_{h3} at 150°C . D_{h1} and D_{h2} and D_{h2} and D_{h3} are 90° rotated about $[111]$. D_{h1} and D_{h3} (rotated about $[111]$ by 180°) share the same ZA: $[110]_{\text{HZO}}$ and match the $R3m$ symmetry of the r -phase simulated through multislice simulations [inset, Reprinted with permission from Lours *et al.*, Phys. Rev. Mater. 4, 043041 (2020). Copyright 2020 American Institute of Physics]. Select oxygen positions are marked in red in D_{h1} as a guide to eye. The O–Hf–O bonds are at 35° – 38° with respect to the horizontal, signifying the r -phase. (b) Collated iDPC-STEM image of different domains at 300°C . While the domain on the left resembles $R3m$ symmetry, domain on the right exhibits a different oxygen arrangement (some select oxygen positions are marked). (c) iDPC-STEM image of HZO domain at 400°C . (right) Line scan of intensities along the long axis of the marked box on the image (left). The alternating intensities of oxygen columns most likely suggest V_o' ordering. (d) $d_{(111)}$ and $d_{(11-1)}$ of various grains at different temperatures showing trends in rhombohedral distortion.

field-driven migration plays a dominant role in oxygen exchange across the interface. Ambient temperature plays only a minor role in accelerating the diffusion kinetics. Here however, we show that under vacuum, both LSMO and HZO lose oxygen together (albeit at different rates) irreversibly. Such an irreversible oxygen loss also occurs for individual layers (as also shown by Cao *et al.*, in Ref. 23) and does not require a heterostructure geometry. However, a comparative heating study between the heterostructures and individual layers would be needed in order to clearly assess the role of the interface in oxygen loss.

Next, we performed *in situ* high temperature XRD measurements to understand the temperature-dependent structural evolution in these heterostructures in air (in contrast to the STEM experiments previously described, which are performed under vacuum). Specular scans were obtained with 2θ from 20° to 32° at various temperatures while heating and cooling in every thermal cycle (after stabilization at every temperature for 20 min). Three such cycles were performed: (i) heating from room temperature (RT) to 550°C and cooling back to RT, (ii) RT to 750°C and back, and (iii) RT to 850°C and back. Specular scans at room temperature corresponding to the virgin state and after cycles 2 and 3 are shown in Fig. 4(a). The $(001)_{\text{pc}}$ peak of LSMO of all these scans appears at the same position, and LSMO undergoes a reversible thermal expansion and contraction (and no structural changes) all the way up to 850°C [Fig. 4(b)]. The linear coefficient of thermal

expansion of the LSMO layer can be estimated as $11.94(\pm 0.05) \times 10^{-6} \text{ K}^{-1}$. We note from the work of Park *et al.*¹² that TiN, a commonly used electrode in doped-hafnia devices, starts to degrade via intermixing and formation of rutile TiO_2 between 800 and 950°C . Contrastingly, our LSMO electrodes (complex oxide electrodes) are very stable under these conditions at least until 850°C .

The HZO layer also undergoes a completely reversible thermal expansion and contraction in thermal cycle 1 [max temperature: 550°C , Fig. 4(c)]. However, in cycles 2 and 3 (max temperatures: 750 and 850°C), hysteretic behavior is observed with progressive reduction in $d_{(111)}$ at room temperature by 0.34% and 0.42% , respectively. In-plane compressive strain is one of the important reasons for the stabilization of the *r*-phase,^{6,7} and here we observe that the strain is partially relaxed upon thermal cycling for $T > 750^\circ\text{C}$. This, however, is unlikely to be a phase transition to one of the standard cubic, orthorhombic, or tetragonal phases, which requires a reduction in $d_{(111)}$ by at least 1.3% .⁸ It is worth noting that our films are grown in an oxygen pressure of 0.1 mbar at 800°C , which is roughly three orders of magnitude less than the partial pressure of atmospheric oxygen. This already renders the as-grown *r*-phase HZO slightly oxygen deficient.¹⁸ It is possible that strain relaxation is related to oxygenating the slightly oxygen-deficient as-grown *r*-phase HZO¹⁸ by high temperature annealing at atmospheric conditions, and this is different from phases

FIG. 4. *In situ* XRD heating measurements: (a) specular scans from $2\theta = 20^\circ$ to 32° at room temperature after various thermal cycles. Note that the LSMO peak is unchanged, whereas the HZO peak shifts to the right with cycling. (b) Lattice parameter [$d_{(001)}$] of LSMO as a function of temperature in various thermal cycles. Completely reversible expansion and contraction with thermal cycling can be seen. (c) Evolution of the HZO lattice parameter in various thermal cycles. Hysteretic reduction of lattice parameter begins from cycle 2 onwards ($T_{\text{max}} > 750^\circ\text{C}$).

obtained through deoxygenation in *in situ* TEM heating experiments. In comparison, the polycrystalline doped-hafnia (dopant: Al, Si, Sr, and Gd) samples studied by Park *et al.*¹² irreversibly transform to a stable monoclinic phase between 700 and 800 °C, testifying to the better thermal stability of our heterostructures. It is worth noting that there is no structural signature of a reversible ferroelectric-to-paraelectric phase transition from these experiments, similar to the observations on polycrystalline samples in Ref. 12.

In summary, we show various structural transitions that occur in LSMO/HZO ferroelectric heterostructures upon heating in vacuum using *in situ* TEM and complementarily in air using *in situ* XRD. Under vacuum, we directly show at an atomic resolution that the LSMO layer deoxygenates even at temperatures as low as 150 °C, resulting in a sequence of topotactic phase transformations. *r*-phase HZO, however, is robust until 300 °C, after which it exhibits V_0 ordered HZO phases with reduced rhombohedral distortions. The mass loss phenomena are also exaggerated owing to the very low thicknesses and thus more exposed surfaces in the TEM lamellae. In air, the LSMO layer is very robust all the way up to 850 °C. These results clearly elucidate the chemical stability of LSMO, a common electrode layer in oxide heterostructures upon heating under various atmospheres.

With regard to HZO, we systematically unravel the rich polymorphism of oxygen deficient and nonstoichiometric HZO. Furthermore, we show that there is no clear (reversible) ferro-to paraelectric phase transition temperature (T_c) in *r*-phase HZO. Rather, we observe an irreversible strain relaxation above 750 °C.

Our results show the crucial effect of the oxygen pressure in the thermal behavior of the HZO/LSMO devices and provide a comprehensive fundamental basis for understanding temperature-dependent structure–property relations in HZO devices. This is of much importance in this material that exhibits an unconventional nanoscopic ferroelectricity, where oxygen voltammetry and polarization switching are inherently coupled.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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