

Dynamic Ferroelectricity in Antiferroelectric Hafnia-Zirconia Thin Films at Cryogenic Temperatures

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Abstract

We report a novel, dynamic, ferroelectric response in ultrathin tetragonal-phase-rich antiferroelectric (AFE) $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO) films at cryogenic temperatures. At room temperature, AFE switching in these films arises from a field-induced tetragonal-to-orthorhombic (t-to-o) transformation followed by rapid o-to-t back-switching during each switching cycle, retaining little-to-no polar o-phase after applied electric field removal. However, upon cooling, the o-to-t back-switching during each bipolar voltage cycle becomes kinetically suppressed, allowing the field-induced polar o-phase to persist over the measurement timescale and at zero bias, resulting in dynamic ferroelectricity. At 12.5 K, the switchable polarization exceeds $20 \mu\text{C}/\text{cm}^2$, despite quasi-static tetragonal phase structure of the films at this temperature, verified by capacitance–voltage measurements. In-situ cryogenic grazing incidence X-ray diffraction confirms no structural transformation at cryogenic temperatures. Unlike conventional polarization “wake-up”, this high-polarization state is reversible upon thermal cycling and remains stable after 10^{10} polarization reversals at 12.5 K. Temperature- and frequency-dependent measurements link the enhanced polarization to the kinetics of o-to-t back-switching rather than an irreversible structural transformation. These results establish a novel mode of dynamic ferroelectricity achieved in nominally antiferroelectric hafnium zirconium thin films and tunable by temperature and operating frequency.

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Introduction

Ferroelectric hafnium oxide (HfO_2)-based thin films have emerged as promising materials for next-generation non-volatile memories because of their CMOS compatibility, scalability, and potential for compute-in-memory architectures.^{1–4} The functional behavior of HfO_2 -based thin films arises from an intricate competition among polymorphs (multiple metastable phases), whose relative stability is highly sensitive to processing conditions, dimensional scale, interfaces and mechanical boundary conditions. While the non-centrosymmetric orthorhombic (o-phase, space group $Pca2_1$) is responsible for the

ferroelectric response, it is only one of several energetically competing phases, including the non-ferroelectric monoclinic (m-phase, space group $P2_1/c$), anti-ferroelectric tetragonal (t-phase, space group $P4_2/nmc$), cubic (c-phase, space group $Fm\bar{3}m$), and non-polar orthorhombic polymorphs (space groups $Pbcm$ and $Pbca$). In bulk HfO_2 at low pressures, the m-phase is thermodynamically stable at room temperature, whereas the t- and c-phases are stable at much higher temperatures,⁵ and other non-polar orthorhombic polymorphs occur under extreme conditions.⁶ The emergence of ferroelectricity in nanoscale HfO_2 therefore reflects a delicate balance among phases that are not the equilibrium bulk structure.

In thin films, reduced dimensionality and interfacial effects substantially modify the free-energy landscape, enabling these metastable phases to coexist over a broad range of processing conditions.⁷ This phase competition becomes particularly pronounced in $Hf_xZr_{1-x}O_2$ (HZO), where HfO_2 - ZrO_2 alloying promotes stabilization of the ferroelectric orthorhombic phase and produces a maximum remanent polarization near the equimolar (Hf:Zr 1:1) composition.⁸ The final phase assembly and, therefore, the macroscopic polarization of HZO thin films depends sensitively on myriad factors, such as the synthesis thermal pathway,^{9–11} strain,^{12–15} applied electric field,^{8,16} thermal annealing method,^{17–19} etc. Understanding the relationships among these structural transformations and the electrical polarization is therefore central to controlling the switching behavior of HZO. Although the m-phase is thermodynamically stable at room temperature, its formation in HZO thin films that are initially crystallized into the t-phase during thermal processing is suppressed by the mechanical boundary condition imposed by a stiff top electrode layer, which hinders the shear deformation required for the t-to-m phase transformation.²⁰ Instead, after post-electrode annealing, the t-phase may readily transform into the ferroelectric orthorhombic o-phase upon cooling. As a result, a key competition arises between the ferroelectric o-phase and the non-ferroelectric t-phase in HZO thin films.^{1,21,22}

In our previous work, we developed a synthesis approach to obtain otherwise identical HZO thin films composed predominantly of either antiferroelectric t-phase or ferroelectric o-phase by varying the plasma-enhanced atomic layer deposition (PEALD) temperature from 200°C to 250°C, followed by a rapid thermal anneal.¹⁰ The deposition temperature influences the formation of nano-crystallites in the as-deposited, quasi-amorphous HZO films, thereby governing the phase evolution during post-electrode annealing. Using these t-phase- and o-phase-rich films, the polarization wake-up - an increase in switchable polarization (P_{sw}) during voltage-driven cyclic polarization switching - was shown to originate from an electric-field-induced irreversible transformation from the t-phase to the ferroelectric o-phase.¹⁶ Conventional wake-up represents a progressive evolution of the structural phase with field cycling, in which repeated electric-field application increases the population of the polar orthorhombic phase.

Cryogenic electronics, including low-temperature computing, quantum–classical interfaces and space-based electronics, motivate the development of non-volatile memories capable of stable operation at low temperatures. HfO_2 -based ferroelectrics are attractive for such applications because of their CMOS

compatibility and the potential for integration of high density FeRAM and FeFET memory devices in cryogenic circuits. Several studies have investigated the low-temperature behavior of HfO_2 -based ferroelectric capacitors, reporting enhanced endurance, increased coercive field (E_c), and enhanced switchable polarization (P_{sw}) compared to room temperature, but with varying interpretations.^{23–28} Hur et al. demonstrated $> 10^{10}$ -cycle endurance at 4 K, with negligible wake-up and fatigue (loss of P_{sw} during cyclic polarization switching), while Zhou et al. reported an increase in E_c with decreasing temperature.^{23,24} Xing et al. attributed the enhanced P_{sw} at 77 K relative to room temperature to the temperature-dependent changes in the relative stabilities of different HZO phases.²⁶ These prior studies focused on films that are ferroelectric at room temperature, rather than the AFE-like thin films investigated in the present work. Recent work by wang et al. on ultrathin 4-nm HZO films reported a reversible transition from antiferroelectric-like to ferroelectric-like switching upon cooling, attributed to interfacial charge pinning and polarization-switching kinetics rather than a structural phase transition. However, the role of field-induced structural transformation kinetics in the cryogenic polarization response of tetragonal-phase-rich HZO remains unclear.²⁹

Herein, we show that cooling t-phase-rich HZO reveals a distinct regime of reversible, kinetically controlled phase dynamics that produces a large polar response without any irreversible phase transition of the underlying tetragonal structure (see Fig. 1). In the pristine state at room temperature, the AFE switching response is consistent with a field-induced t-to-o transformation followed by rapid o-to-t back-switching, resulting in little retained polar phase after removal of the electric field for single switching cycle observed as pinched P-V loop in Fig. 1. Repeated cycling at room temperature additionally activates an irreversible transformation to the orthorhombic phase, giving rise to conventional polarization wake-up. Upon cooling, however, the kinetics of the reverse o-to-t transformation become significantly suppressed. The field-induced orthorhombic phase can consequently persist over the timescale of electrical measurement, producing a pronounced polar response even though the quasi-static structural state of the HZO remains predominantly tetragonal. We refer to this kinetically enabled polar response as *dynamic ferroelectricity*. In contrast to conventional ferroelectricity, in which the polar phase constitutes the persistent structural state, dynamic ferroelectricity arises from the transient generation and kinetic retention of the polar orthorhombic phase during each cycle of field programming. Unlike wake-up, this process is reversible: the enhanced polarization can be recovered or removed through thermal cycling without the progressive structural evolution characteristic of irreversible wake-up. By combining temperature- and frequency-dependent electrical measurements with in-situ synchrotron cryogenic X-ray diffraction, we investigate the relationship between field-driven t-to-o phase transformations, their kinetics and the resulting polarization from 12.5 to 296 K. We find that suppression of o-to-t back-switching at cryogenic temperatures enables switchable polarization exceeding $20 \mu\text{C}/\text{cm}^2$, while largely suppressing the irreversible wake-up observed at higher temperatures. These findings establish reversible dynamic phase transformation as a distinct pathway to high-polarization, cycling-stable operation in tetragonal-phase-rich HZO and provide a framework for understanding its potential in long-endurance cryogenic memory applications.

Results

Structural and electrical characteristics of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ capacitors

Prior work establishes that controlling the PEALD temperature can be used to engineer the number density of nano-crystallites formed in as-deposited, quasi-amorphous HZO films, thereby dictating the phase evolution during subsequent annealing.¹⁰ HZO films deposited at 200°C have pinched P - V hysteresis loops characteristic of the t-phase, exhibiting antiferroelectric behavior, whereas films deposited at 250°C display conventional ferroelectric hysteresis indicative of predominantly o-phase structure.^{10,16} This deposition strategy was employed herein to reproducibly synthesize predominantly t-phase, AFE HZO films, as shown in Fig. 2(b). The synchrotron (XRD experimental setup shown in Fig. 2(a)) XRD patterns exhibit characteristic diffraction peak shifts for the two HZO PEALD temperatures, consistent with our previous findings (see Fig. 2(c)).¹⁶ These 200°C-deposited films are used to investigate the temperature-dependent polarization switching behavior of t-phase HZO.

Temperature-dependent electrical response and cycling stability of t-phase rich antiferroelectric HZO capacitors

Figure 3(a) and 3(b) presents the initial (“pristine-state”) P - V hysteresis loops and the evolution of the switchable polarization with the number of switching cycles for MFM capacitors containing the HZO films deposited by PEALD at 200°C and measured over a range of temperatures. For measurements at 296 K, the pristine switchable polarization is near-zero, consistent with the expected behavior of t-phase HZO films. A remarkable > 10-fold increase in the pristine switching polarization P_{sw} is observed as the temperature is reduced to 12.5 K (Path-1). This increase in P_{sw} at low temperatures is a *reversible* process as confirmed by re-measuring capacitors. For example, Device 1 was initially measured and cycled (10^8 polarization reversal) at 12.5 K and subsequently remeasured at 296 K, Fig. 3(c). Re-measurement at 296 K for Device 1 shows a pinched antiferroelectric P - V hysteresis loop with low P_{sw} comparable to the pristine state measurement of an otherwise identical Device 2 that had not undergone cryogenic cycling.

In contrast, electrical cycling at 296 K produces the pronounced polarization wake-up characteristic of t-phase-rich HZO (Path 2).¹⁹ The magnitude of this wake-up decreases strongly with decreasing temperature, from an approximately ~12-fold increase in P_{sw} upon cycling at 296 K to only a ~ 1.07-fold increase at 12.5 K. Prior results indicate that the wakeup (Path-2) in t-phase rich HZO thin films is an apparently *irreversible* t-to-o phase transformation.¹⁹

Capacitance-voltage (C-V) measurements of t-phase rich HZO thin films at different measurement temperatures exhibit similar antiferroelectric C-V loops as the temperature changes from 296 K to 12.5

K, Fig. 3 (d). No significant change in the C-V loop is observed as the capacitor is cycled at 12.5 K, (Fig. 3(e)). However, at 296 K, the post-cycling C-V loop resembles a butterfly-like ferroelectric loop coinciding with the field-driven irreversible phase transformation of t-phase to o-phase HZO following polarization wake-up after extensive voltage cycling, as noted in previous reports.¹⁶ Together, these results demonstrate a striking distinction between the *reversible* enhancement of polarization upon cooling and the *irreversible* evolution of the HZO electrical state during room-temperature wake-up.

Temperature-dependent structural evolution of t-phase rich antiferroelectric HZO capacitors

In-situ synchrotron XRD measurements were performed on the t-phase rich HZO thin film capacitors schematic shown in Fig. 4(a), cooling from room temperature to 50 K, to test whether cooling itself may be responsible for noteworthy structural changes in the HZO films. Figure 4(b) shows representative synchrotron X-ray diffraction patterns over a broad measured Q range for HZO capacitors at room and cryogenic temperatures. The Pt(111) reflection from the top metal contact also shifts systematically toward higher Q upon cooling (Fig. 4(c)), consistent with thermal contraction of the Pt electrode reported in the literature.¹⁷ Fig. 4(d) shows that upon cooling, the HZO diffraction peaks shift systematically to higher Q values, consistent with expected lattice parameter contraction due to thermal strains arising from the mismatch between the coefficient of thermal expansion of the HZO and the underlying silicon substrate. However, no new diffraction peaks, peak splitting, or changes in texture are observed, indicating the absence of any detectable structural phase transformation during cooling. These results indicate that the temperature-dependent t-to-o phase transformation is not responsible for ~ 12-fold reversible increase in polarization P_{sw} [Fig. 3(b)]. This conclusion is further supported by the persistence of antiferroelectric C-V characteristics over the entire temperature range as shown in Fig. 3(d).

Antiferroelectric switching mechanism and temperature-dependent switching response

In HZO thin films, the free-energy landscape is governed by several factors, including $\text{HfO}_2\text{:ZrO}_2$ molar ratio, film thickness, temperature, elastic strain and the applied electric field. In the t-phase rich HZO thin films synthesized and fabricated into capacitors in this study, the t-phase is observed at zero bias for all temperatures investigated, as confirmed by diffraction measurements. At room temperature, application of a sufficiently large electric field modifies the free-energy landscape such that crystallites of the non-polar t-phase transiently distort to form the polar o-phase, producing the observed AFE-like, pinched-loop, response at 296 K [Fig. 3(a)].^{30,31} This behavior is consistent with the applied field altering the relative free energies of the t- and o-phases to favor the o-phase, for example at a “forward” switching field of -3×10^8 V/m, consistent with application of a +3V (+ P_{sat}) switching pulse to the capacitors, as shown in Fig. 5(a).

The corresponding switching-current response measured at 296 K is shown in Fig. 5(b). During the positive voltage sweep (0 to +3 V), the field-induced t-to-o transition generates the first switching-current peak (Peak 1). As the voltage returns to zero, the reverse o-to-t transition produces the second switching-current peak (Peak 2). During the negative voltage sweep (0 to -3 V), the same sequence occurs with reversed polarization, giving rise to the third (t-to-o) and fourth (o-to-t) switching-current peaks. The resulting t-o-t phase transition sequence provides a microscopic picture for the AFE polarization switching response, i.e the polar o-phase is generated during each switching cycle by the applied field but largely disappears when the field is removed.

This interpretation is consistent with previous theoretical and time-resolved experimental studies of HZO. Vishnumurthy et al. used sixth-order Landau–Ginzburg–Devonshire (LGD) model to analyze the free energy of a thin 12 nm ZrO₂ thin film as a function of polarization. Their results showed that the applied electric field continuously reshapes the free-energy landscape, leading to a first-order t-to-o transition at the forward switching field and a reverse o-to-t transition as the field is removed.⁷ As the applied electric field is reduced, the o-phase becomes energetically unfavorable and transforms back to the t-phase, resulting in a reversible o-to-t phase transition within the timeframe of single switching cycle. Time-resolved measurements have likewise demonstrated transient and field induced reversible t-o transformations in antiferroelectric Hf_{0.2}Zr_{0.8}O₂ capacitors and showed that substantial reversibility is achieved in the films containing a high fraction of the antiferroelectric t-phase.³⁰ However, these measurements were limited to room temperature, and the effect of cooling on the reversible t-to-o transition was not explored.

In addition to the applied electric field, these transient t-to-o and o-to-t phase transitions are also dependent on temperature, as is apparent from the changing position of current peaks (1–4) shown in Fig. 5(c). This can be explained by a change in the relative free energies of the two phases as the temperature is varied. Previous theoretical studies proposed that cooling increases the relative free energy of the tetragonal phase and lowers the energy barrier for t-to-o transformation.^{26,27,31} Reduced thermal energy at low temperature may kinetically suppress the transformations between them, requiring higher electric fields. Thus, a combination of thermodynamic and kinetic effects makes the reversible distortion from t- to o-phase easier (current peaks 1 and 3 occur at a lower voltage bias) while the back-switching from o- to t-phase requires a larger (and opposite polarity) field as the temperature is decreased. Quantification of the current peak positions in the Gaussian fitting of the differential polarization response (Supplementary Fig. S1), and their temperature dependence is summarized in Fig. 5(d). Peak 4 is excluded from the peak-shift analysis because its discontinuous shape results from the voltage sweep beginning at 0 V. Over temperature range of 12.5–296 K, the forward t-to-o transitions (peaks 1 and 3) exhibit relatively weak and approximately linear temperature dependences of 1.2 ± 0.3 and 1.4 ± 0.1 mV/K, respectively. whereas the reverse o-to-t transition represented by peak 2 exhibits a substantially larger slope of 4.4 ± 0.4 mV/K. The larger slope for peak 2 indicates that the voltage required for o-to-t back-switching is considerably more temperature sensitive than that of the forward t-

to-o transformation. This asymmetry provides a basis for understanding the enhanced polarization observed at cryogenic temperatures (Fig. 3).

At room temperature, the field-induced o-phase rapidly back-switches toward the t-phase as the applied field is removed, resulting in the low remanent polarization characteristic of the pristine AFE state. Upon cooling, the o-to-t back-switching becomes progressively slower. Consequently, the field-induced polar o-phase can persist over the timescale of the electrical measurement, producing a substantial polar response at nominally zero bias even though the quasi-static structural state remains predominantly tetragonal. We refer specifically to this regime as *dynamic ferroelectricity*: a polar response generated by reversible field-induced t-to-o transformation in a nominally tetragonal HZO film, enabled by kinetically suppressed o-to-t back-switching.

The distinction from conventional polarization wake-up is important. The t-to-o transformation described above is reversible within an individual switching cycle, whereas repeated cycling at room temperature additionally activates an irreversible process that progressively stabilizes the o-phase and produces wake-up. At cryogenic temperature, this irreversible evolution is strongly suppressed, while the reversible field-induced transformation remains active. Thus, dynamic ferroelectricity does not represent a permanent conversion of the film from the tetragonal to the orthorhombic phase; instead, it reflects a temperature-dependent imbalance in the timescales of the forward and reverse field-induced lattice distortions.

Frequency-dependent switching and cycling endurance of tetragonal-phase-rich HZO at room and cryogenic temperatures

To further probe the origins of the dynamic ferroelectricity observed at low-temperatures in t-phase-rich HZO film, the frequency dependence of polarization switching at room and cryogenic temperatures was measured. Figure 6(a) shows P–V hysteresis loops measured at 296 and 12.5 K at cycling frequencies of 10, 50 and 100 kHz. At 296 K, the hysteresis response is essentially frequency independent over the investigated range. At 12.5 K, however, a weak but reproducible frequency dependence emerges, indicating that the switching response becomes sensitive to the measurement timescales studied at cryogenic temperatures. We observe that P_{sw} also varies with the measurement frequency as shown in Fig. 6(a). At 100 kHz, there is less time for the o-phase to back-switch before the voltage crosses zero. Therefore, more polar o-phase survives through zero bias, resulting in larger measured P_{sw} . At 10 kHz, there is more time for the o-phase to back-switch, resulting in lower P_{sw} .

To more clearly resolve individual switching events, the differential polarization response, dP/dV , is plotted as a function of voltage in Fig. 6(d) and 6(e). Peaks 1 and 3 correspond to the forward t-to-o phase transition, while Peaks 2 and 4 correspond to the reverse o-to-t phase transition. To further examine the frequency dependence of the t-to-o and o-to-t transformations, the switching peak positions are obtained from the Gaussian fits (see Fig. S2) and are compared between 296 and 12.5 K. The

difference between switching peak positions at 296 K and 12.5 K is denoted as $\Delta V(V_{296K}-V_{12.5K})$. The corresponding shifts in switching peak voltage ΔV_{Peak1} , ΔV_{Peak2} and ΔV_{Peak3} are plotted as a function of frequency in Fig. 6(b). Both ΔV_{Peak1} and ΔV_{Peak2} exhibit a systematic frequency dependence, indicating that the kinetics of both the forward (t-to-o) and reverse (o-to-t) transformations are sensitive to the measurement timescale. Notably, the frequency dependence is asymmetric: ΔV_{Peak2} corresponding to the o-to-t back-switching transition, exhibits a stronger variation with frequency than ΔV_{Peak1} , indicating a greater sensitivity of the reverse transformation to the available switching timescale. The asymmetric frequency response evident in Fig. 6 provides additional evidence of a kinetic slowing of the o-to-t back-switching at low temperature, consistent with persistence of the field-induced polar o-phase over the timescale of the P-V measurement.

Discussion

Combined electrical and structural measurements reveal that an enhanced polar response measured in nominally AFE HZO films at cryogenic temperature does not arise from a temperature-dependent transformation of the tetragonal HZO into the ferroelectric orthorhombic phase. Instead, the results point to a dynamic process in which the applied electric field repeatedly drives dynamic and reversible t-to-o structural distortions, in which the kinetics of the reverse o-to-t transition are more strongly temperature dependent. This distinction provides a framework for understanding both the cryogenic polarization enhancement and its contrasting behavior with conventional polarization wake-up.

The reversible t-to-o transformation observed within individual switching cycles is consistent with a predominantly field-driven, displacive transformation involving cooperative atomic displacements rather than longer-range atomic diffusion or nucleation and growth.^{7,32,33} The persistence of the characteristic switching sequence down to 12.5 K (Fig. 5c) further indicates that substantial thermal activation is not required to initiate this reversible field-induced transformation.^{34–36} Importantly, the kinetics of the o-to-t transformation exhibits a somewhat stronger temperature dependence than the forward, t-to-o process. The enhancement of P_{sw} upon cooling further indicates that temperature modifies the kinetics of the reversible transformation occurring in each polarization switching cycle.²⁶ The different coefficients of thermal expansion (CTE) of the TiN electrodes, HZO layer, and Si substrate generate temperature-dependent mechanical constraints within the TiN/HZO/TiN/Si stack.^{12,20} During cooling, the CTE mismatch with the Si substrate can produce in-plane tensile strain in the HZO layer, accompanied by an out-of-plane compressive strain component. The latter is probed by the GIXRD measurements along the scattering vector of the T(101) reflection, which is oriented approximately 14.5° from the surface normal under our measurement geometry. Thermally induced stresses can modify the relative free energies and transformation barriers of the competing t- and o-phases.^{22,37–39} Consistent with this idea, Fig. 5(c) shows that the field required for the o-to-t back-switching increases with decreasing temperature, indicating that cooling preferentially suppresses the o-to-t transformation. Such a kinetic asymmetry

allows a larger fraction of the field-induced o-phase to persist during the polarization measurement, contributing to the enhanced cryogenic P_{sw} .

In contrast, conventional polarization wake-up exhibits a much more pronounced temperature dependence. As shown in Fig. 3(b), the magnitude and rate of wake-up decrease substantially with decreasing temperature and become almost negligible at 12.5 K, even after 10^{10} polarization reversals. This behavior contrasts with the persistence of reversible t-to-o switching at cryogenic temperatures and indicates that the irreversible phase evolution associated with wake-up involves other, thermally activated, processes. Previous studies have proposed that wake-up in t-phase-rich HZO involves field-assisted nucleation and growth of o-phase regions.^{10,16} Such processes would progressively increase the fraction of stabilized o-phase during field cycling at room temperature, whereas their kinetics are strongly suppressed at cryogenic temperatures.

The frequency-dependent measurements provide independent evidence for a pronounced kinetic asymmetry between the forward and reverse transformations at cryogenic temperature. The characteristic timescale of the reverse transformation becomes comparable to the timescale of the electrical measurement at the lowest temperatures investigated herein. The contrasting P-V and C-V responses further indicate a finite timescale for relaxation of the field-induced polar o-phase. At 12.5 K, the polar state persists over the microsecond-to-tens-of-microseconds timescale of the P-V measurement, whereas the much slower C-V sweep (0.2 V/s) yields a predominantly AFE response, consistent with substantial o-to-t relaxation on longer timescales. Thus, the present measurements constrain the persistence of the polar o-phase between the fast P-V and slow C-V regimes.

The high P_{sw} state established at 12.5 K remains remarkably stable during prolonged electrical cycling, showing negligible wake-up and fatigue even after 10^{10} polarization reversals (see Fig. 6(c)). The combination of high polarization ($\sim 20 \mu\text{C}/\text{cm}^2$), reversible field-induced t-to-o switching and nearly wake-up- and fatigue-free endurance over 10^{10} cycles highlights the strong potential of dynamic ferroelectricity in t-phase HZO thin films for application in reliable memories for cryogenic electronics.

Declarations

Competing Interests

The authors declare no competing financial interest.

Author Contributions

R.R. and B.S. contributed equally to device fabrication, electrical characterization, data analysis, and manuscript preparation. C.E.R.A. helped with in-situ cryogenic XRD experiments and data analysis. V.T. contributed to the in-situ cryogenic XRD measurements. J.D.B., W.T., and P.C.M. provided guidance and

feedback throughout the study. All authors contributed to the discussion and interpretation of the results and to the preparation of the manuscript. All authors reviewed and approved the final version of the manuscript.

Data Availability

The data supporting the findings of this study are available within the Article and its Supplementary Information. Additional data is available from the corresponding author upon request.

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Figures

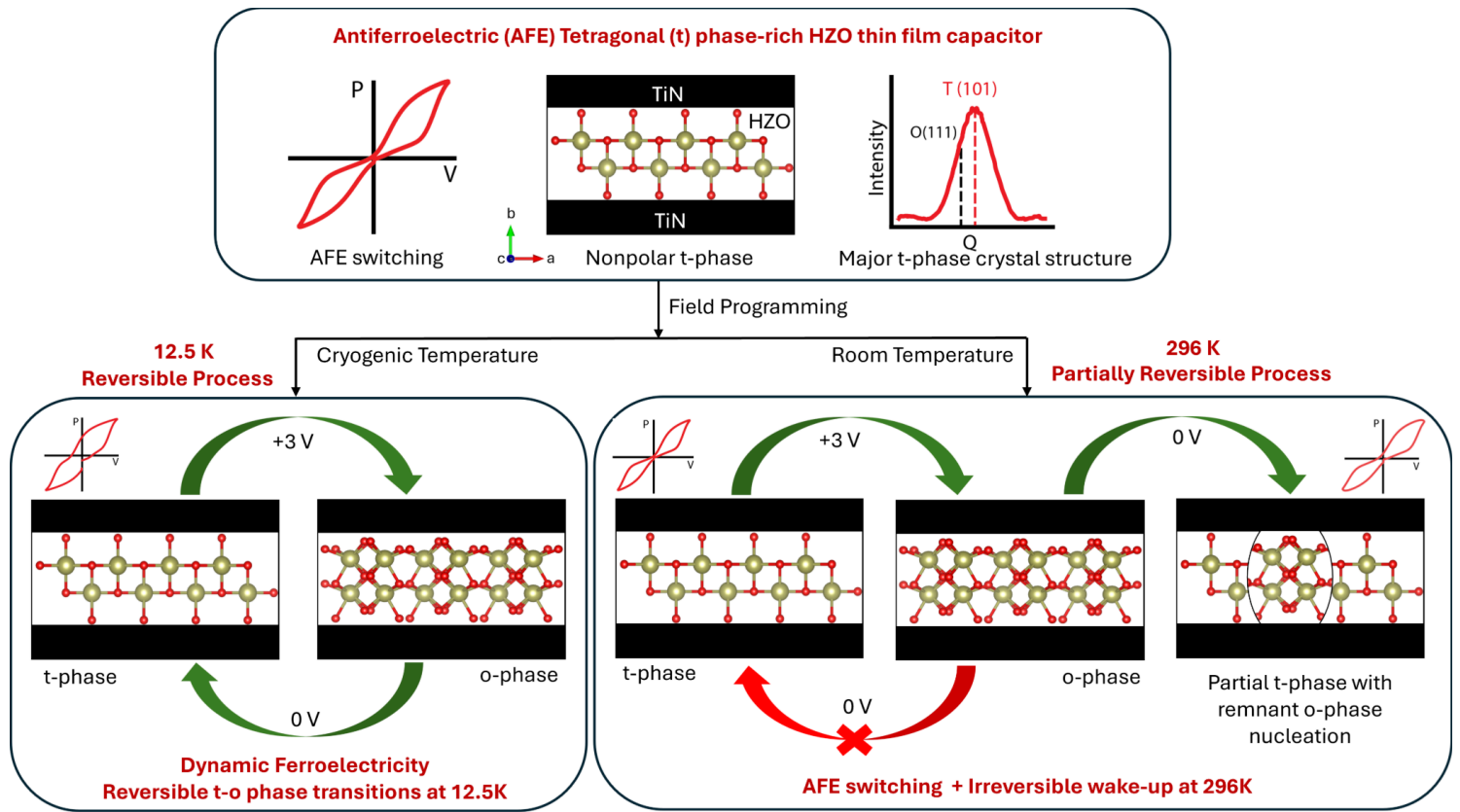


Figure 1

Dynamic ferroelectricity in antiferroelectric tetragonal-phase-rich HZO capacitors. Top: Schematic of the TiN/Hf_{0.5}Zr_{0.5}O₂/TiN metal-ferroelectric-metal (MFM) capacitor, showing the antiferroelectric polarization response associated with field-induced transient t-o-t phase transformations, while the zero-bias structure remains predominantly tetragonal. Bottom left: At 12.5 K, field cycling produces reversible t-o phase transformations, with the field-induced polar o-phase persisting over the measurement timescale, giving rise to dynamic ferroelectricity. Bottom right: At 296 K, the field-induced t-o-t process is accompanied by an additional, gradual and irreversible transformation to the o-phase generally termed polarization "wake-up".

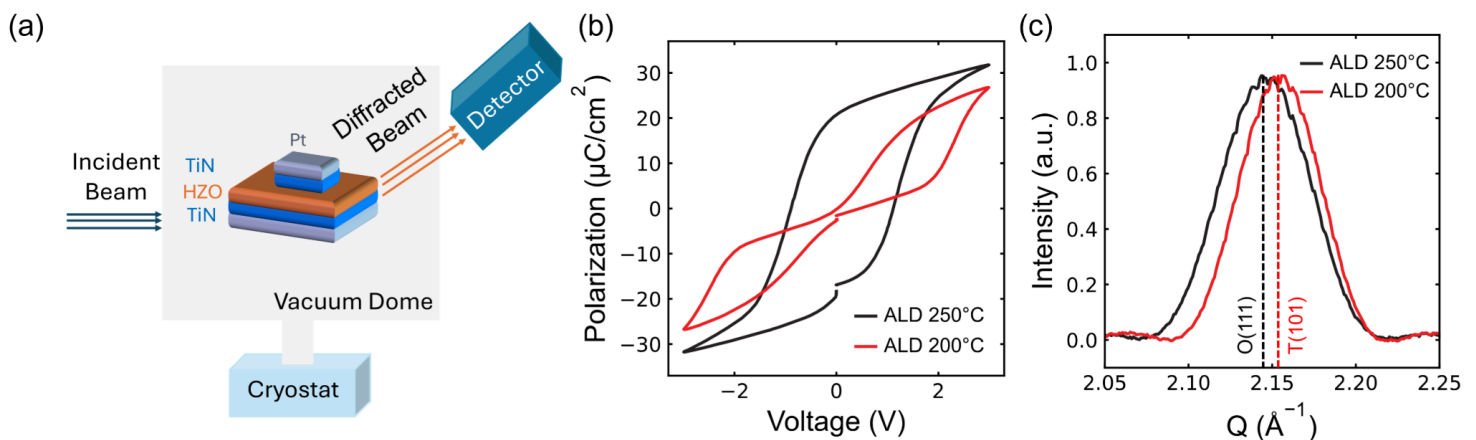


Figure 2

Structural and electrical characteristics of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ capacitors. (a) Schematic of the temperature-dependent grazing-incidence XRD measurement setup at Beamline 17-2 SSRL. (b) Pristine-state polarization–voltage (P-V) hysteresis loops of MFM capacitors fabricated from HZO films deposited by PEALD at 200 and 250 °C. (c) Room-temperature diffraction patterns showing the characteristic tetragonal (101) and orthorhombic (111) reflections of the HZO films deposited at 200 and 250 °C, respectively. Plots (b) and (c) are reproduced from reference 16.

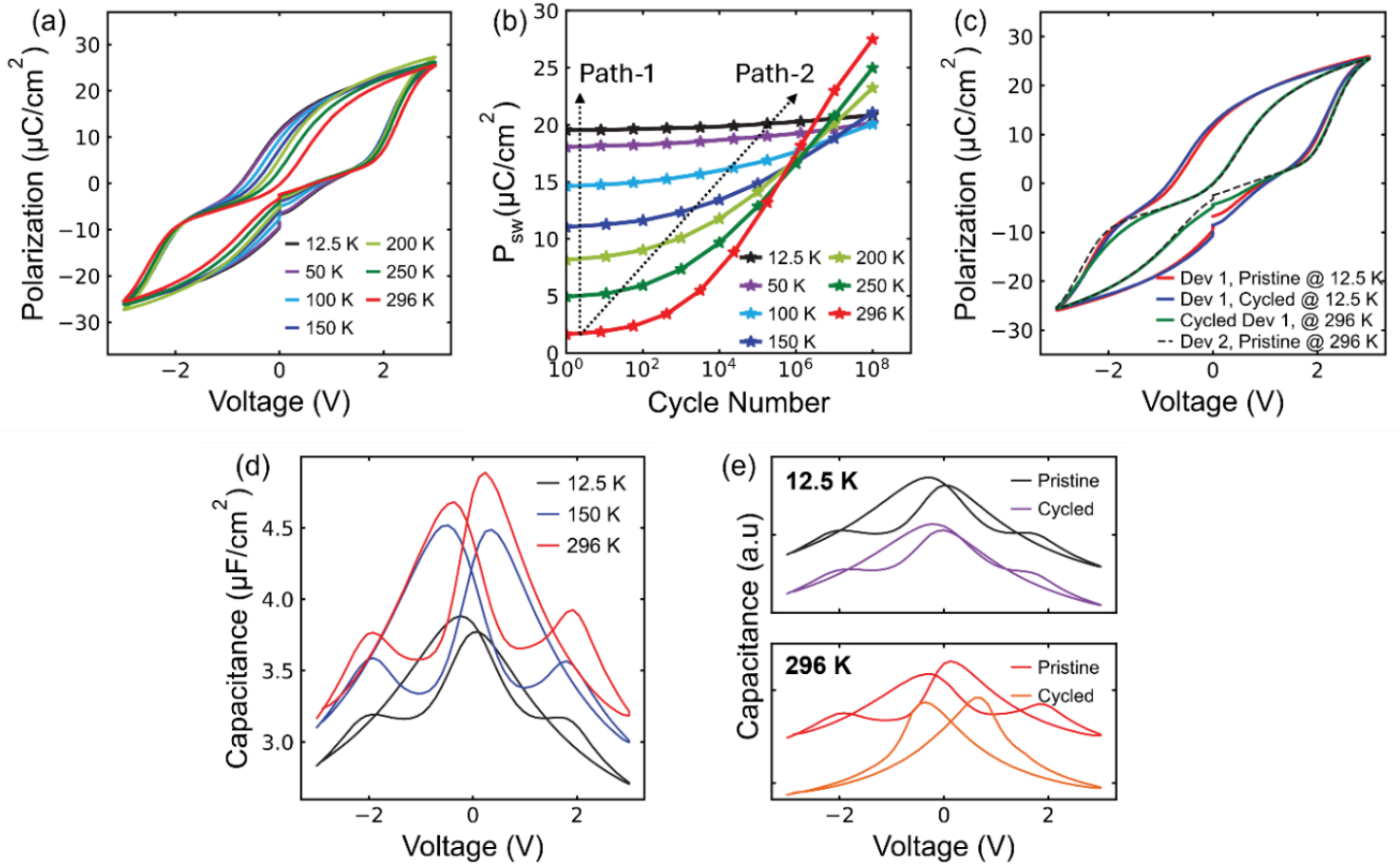


Figure 3

Temperature-dependent electrical response and cycling stability of t-phase rich antiferroelectric HZO capacitors. (a) Pristine-state P-V hysteresis loops measured at different temperatures. (b) Evolution of switchable polarization P_{sw} with field cycling at different temperatures. (c) Reversible enhancement of P_{sw} demonstrated for device 1 ("Dev 1") at 12.5 K by comparison of its pristine and post-cycling states, together with measurements of pristine device 1 and device 2 at 296 K. (d) Capacitance–voltage (C-V) characteristics of a pristine t-phase rich HZO capacitor measured at different temperatures, exhibiting AFE double-loop behavior across the investigated temperature range. (e) C-V characteristics before and after 10^8 polarization switching cycles at 12.5 and 296 K.

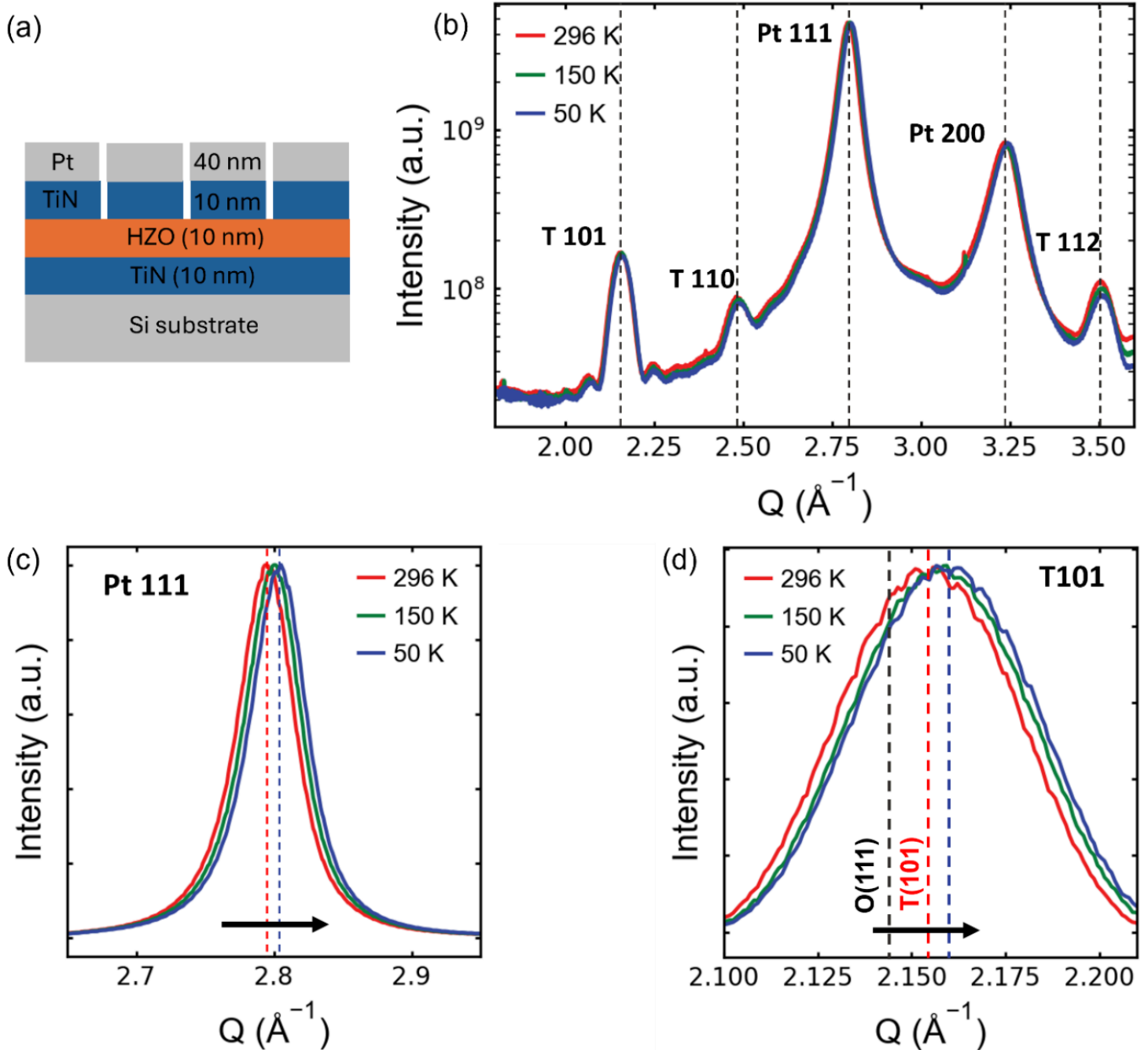


Figure 4

Temperature-dependent structural evolution of t-phase rich antiferroelectric HZO capacitors. (a) Schematic of HZO HFM capacitor structure used for measurements. (b) Full-range diffraction patterns showing the Pt (111) and (200) reflections and the t-phase HZO (101), (110) and (112) reflections. (c) Temperature-dependent evolution of the Pt (111) and, (d) HZO t(101) reflections, respectively, with arrows indicating the direction of peak shifts upon cooling. The black and red dotted lines indicate the expected positions of the orthorhombic o(111) and tetragonal t(101) reflections, respectively. The blue dotted line marks the temperature-induced shift of the t(101) reflection at 50 K.

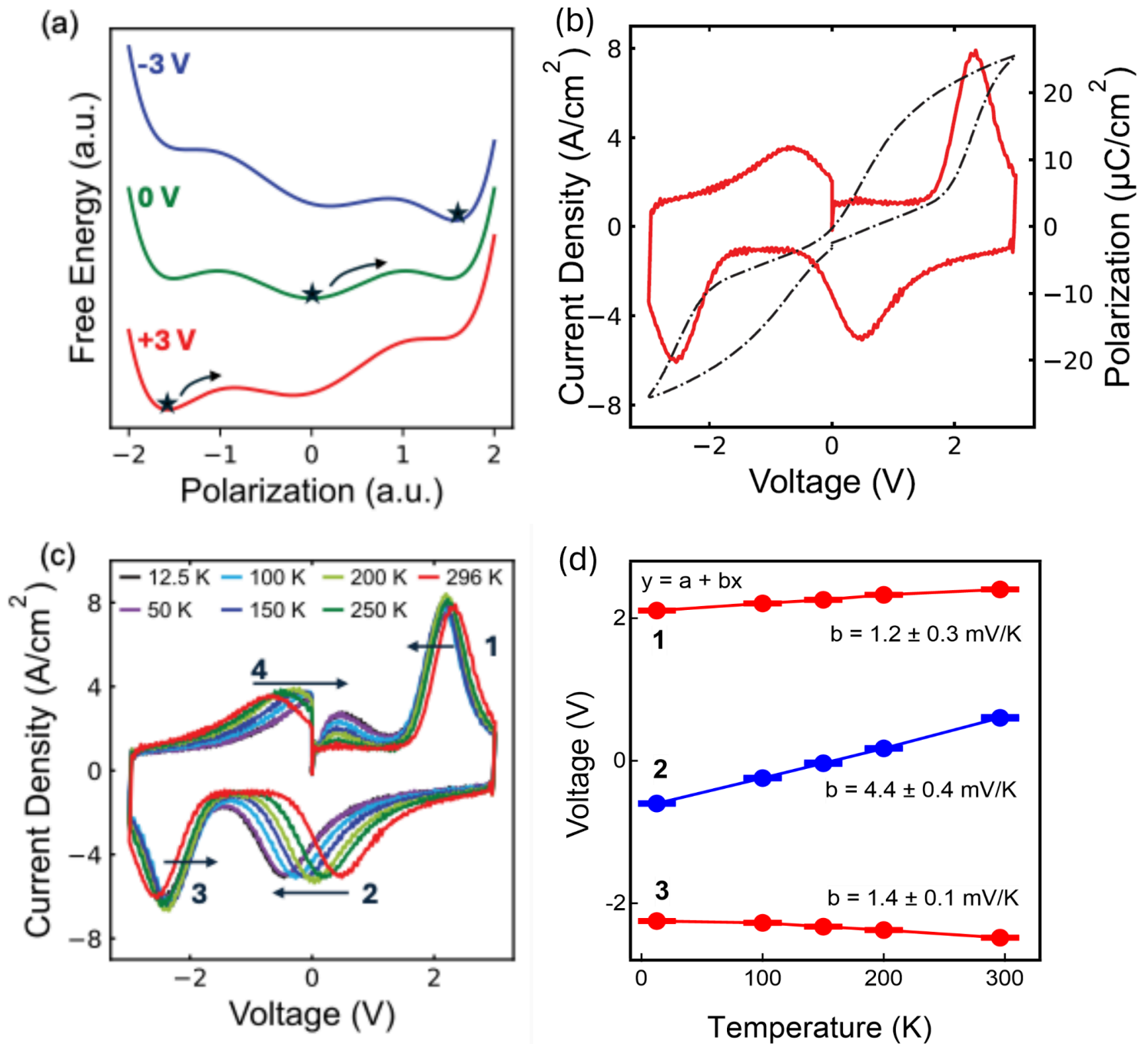


Figure 5

Antiferroelectric switching mechanism and temperature-dependent switching response. (a) Schematic illustration of the proposed two-step switching pathway between the tetragonal and orthorhombic phases during a bipolar voltage sweep from 0 to +3 to -3 V. The local minima associated with the polar o-phase are represented at $-P_{\text{sat}}$ and $+P_{\text{sat}}$ where P_{sat} denotes the saturation polarization. (b) Current-voltage (I-V) characteristics and corresponding polarization-voltage (P-V) hysteresis of a pristine t-phase rich antiferroelectric HZO capacitor at 296 K under a bipolar triangular voltage sweep. (c) Temperature-dependent I-V characteristics of pristine t-phase HZO capacitors, showing four distinct

switching-current peaks. (d) Temperature dependent shifts of the switching-current peaks extracted from the I-V characteristics.

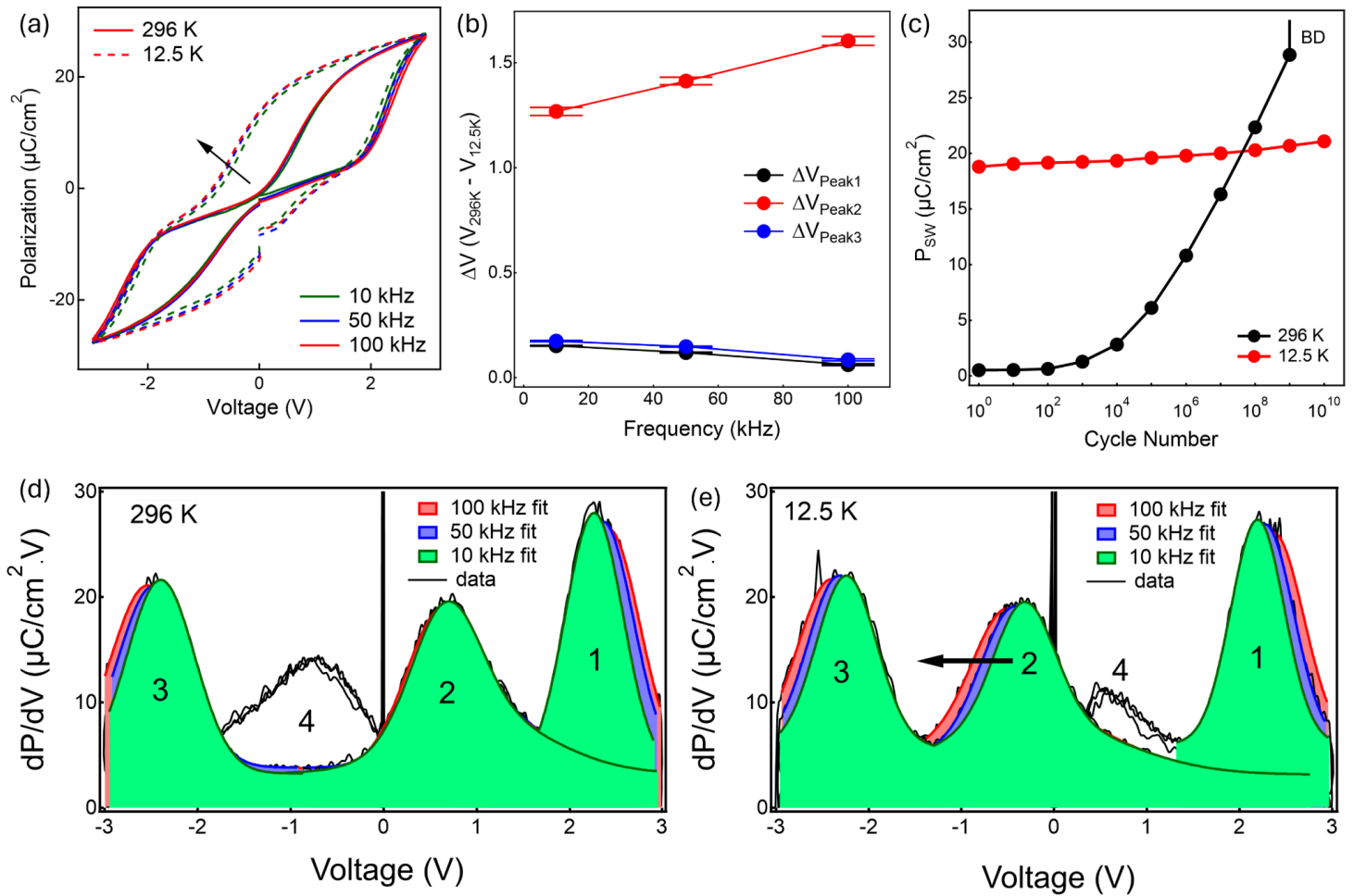


Figure 6

Frequency-dependent switching and cycling endurance of tetragonal-phase-rich HZO at room and cryogenic temperatures. (a) P-V hysteresis loops measured at 296 and 12.5 K at cycling frequencies of 10, 50 and 100 kHz. (b) Frequency dependence of the temperature-induced shifts in the switching voltages, ΔV_{Peak1} , ΔV_{Peak2} and ΔV_{Peak3} , obtained from Gaussian fitting of the (dP/dV) peaks in (d,e). (c) Cycling endurance of tetragonal-phase-rich HZO capacitors at 296 and 12.5 K, showing negligible polarization wake-up after 10^{10} cycles at 12.5 K. (d,e) Differential polarization response (dP/dV) as a function of applied voltage at 296 and 12.5 K, respectively, for the three cycling frequencies. The switching features are fitted using multiple Gaussian functions, with the individual fitted components shown as filled areas for visualization.

Supplementary Files

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