

Bulklike Costless Domain Walls Driven by Phonon Pair Condensation in HfO_2

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Ferroelectric domain walls are described as interfacial regions between oppositely polarized domains, where the original bulk distortions are suppressed or reconstructed at energetic cost. Here, we demonstrate that Pca_2 HfO_2 exhibits a distinct ferroelectric domain wall where the polarization-reversal boundaries remain structurally bulk compatible and exceptionally low in energy. The central mechanism is a pair-condensation—the simultaneous condensation of the two trilinearly coupled phonon modes located at opposite termini of a single phonon branch. We show that this pair condensation not only establishes the microscopic origin of layer-selective ferroelectricity in bulk but also governs the exceptionally low energy of the 180° domain walls. Specifically, the simultaneous reversal and complementary energetic responses of the paired condensed modes compensate the domain-wall energy cost and facilitates a wall-centered structure where bulk motifs are locally recovered rather than suppressed. This bulklike domain wall is corroborated by the agreement between density-functional-theory calculations and annular-bright-field-STEM measurements of oxygen displacements. This logic extends to suboptimal and higher-energy domain walls which emerge as accessible structural bridges via the selective, energy-minimizing reversal of individual condensed phonon modes. By unifying these structural and energetic observations under the principle of pair condensation, this work provides a generalized predictive framework for engineering domain-wall physics in multimode functional materials.

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I. INTRODUCTION

Ferroelectricity provides a typical example of a switchable order parameter in solids: A material develops a spontaneous polarization and can adopt multiple symmetry-related polarization states. In real crystals, these states are accommodated by the formation of domains [1–4], and the polarization reversal between neighboring domains is realized over a finite spatial region—the domain wall. Domain walls are therefore not simply geometric

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boundaries; they are nanoscale transition regions where the polarization and the accompanying lattice distortions vary in space to connect two stable bulklike states. The energetic cost of this spatial variation, together with lattice-level constraints, sets both the formation energy and the characteristic structures of a wall [5–7], and ultimately shapes which domain patterns are favored in a given microstructure.

Because the wall region can host a local structural motif that differs from that of the domains [8–10], domain walls have been recognized as fertile ground for interface-enabled phenomena, ranging from altered electronic transport [11–16] to unusual polarization textures [17,18] and topology-driven stability [19–21] of otherwise unfavorable configurations. Beyond such wall-specific responses, domain walls are also fundamental to ferroelectric functionality in a more general sense: Polarization reversal under an applied field is commonly described in terms of the nucleation of reversed regions and the subsequent creation, motion, and interaction of domain walls [22,23]. Accordingly, understanding how a crystal accommodates polarization reversal at the atomic scale, i.e., which lattice distortions participate and how they redistribute across a wall, provides a structural and energetic basis for interpreting the domain patterns observed in equilibrium microstructures and the polarization-reversal boundaries.

Recent experimental studies have shown that domain walls in HfO₂-based ferroelectrics often exhibit structural complexity beyond the idealized picture of polarization boundaries. In particular, atomically resolved investigations have reported local phase distortions and multiphase regions in the vicinity of domain walls, including monocliniclike structures, mixed tetragonal and orthorhombic symmetry [24], and other high-symmetry intermediate states [25,26]. These features have been observed in conjunction with interphase boundaries, transition regions, and domain evolution processes [24–26], suggesting that experimentally observed domain walls may involve additional structural complexity beyond idealized polarization boundaries. To provide a structural basis for understanding such complexity, it is essential to identify the intrinsic principles governing polarization reversal at the atomic scale, which define the energetically favorable mode-level interactions underlying domain-wall formation under practical conditions.

Orthorhombic HfO₂ presents a compelling model system for this purpose, as its ferroelectric distortion involves multiple, linearly coupled lattice modes [27]. In this work, we address this fundamental question by developing a structural-energetic framework based on “pair condensation” defined here as the coordinated condensation of two lattice distortions located at the termini of the same phonon-dispersion branch and linked by symmetry-allowed trilinear couplings. We demonstrate that this pair-condensation mechanism not only identifies the microscopic origin of

layer-selective ferroelectricity but also provides an energy-compensation channel that governs the formation and energetics of 180° domain walls [28,29]. This framework facilitates a wall-centered structure that locally recovers bulk distortion motifs, as confirmed by the quantitative agreement between density-functional-theory (DFT) calculations and annular-bright-field- (ABF) STEM measurements. Furthermore, we show that even suboptimal, higher-energy interfaces can emerge as accessible structural bridges governed by the selective, energy-minimizing reversal of individual condensed-distortion modes. Ultimately, these findings establish a generalized predictive logic for interfacial formation in complex ferroelectric systems, providing a critical foundation for engineering domain-wall physics in multimode functional materials.

II. RESULTS AND DISCUSSION

A. Definition of pair condensation as a unifying principle for HfO₂ interfacial physics

Multimode condensation via trilinear couplings, which drives the transition from the cubic to the ferroelectric orthorhombic phase in HfO₂, has been extensively established [27,30]. Our study demonstrates that among these condensed modes, the satisfaction of specific criteria leads to a unique structural phenomenon during 180° ferroelectric domain-wall (DW) formation. The present analysis focuses on a specific subset of multimode condensation defined here as pair condensation to characterize this distinct domain-wall behavior. Here, we define pair condensation as the simultaneous condensation of two lattice-distortion modes linked by trilinear symmetry and tied to opposite termini (e.g., at Γ and Y) of a single y -directed phonon branch. At a qualitative level, the two modes do not act independently but instead form a coupled entity that appears and evolves together. Within each identified pair, one mode carries an additional momentum of π along the y direction relative to the other. This relation places the two modes at opposite ends of the same phonon branch and gives rise to closely correlated spatial displacement patterns.

This π offset ensures that the two modes occupy opposite ends of the same dispersion branch (Fig. S1 [31]), as exemplified by the Γ_{15}^z - Y_5^z and X_5^y - Z_5^y connections. While couplings at the W point may split the band connecting X_2^x and Z_5^x , this splitting does not alter the fundamental pair relation that governs the domain-wall energetics (Fig. S2 [31]).

This pair condensation establishes the structural basis for (i) layer-selective ferroelectricity in the orthorhombic phase, where the combined displacement patterns of the paired modes naturally produce alternating ferroelectric and spacer layers (Sec. II B). Furthermore, when these paired modes undergo a coordinated sign reversal across a boundary, their complementary dispersion curvatures enable an energy-compensation channel. This mechanism

facilitates (ii) 180° reversal of the z polarization via domain walls that incur minimal energetic penalties and locally recover bulk distortion motifs (Secs. II C and II D). Crucially, this perspective also accounts for (iii) the formation of relatively higher-energy interfaces observed in thin films (Sec. II E): Even in the absence of a coordinated reversal, the system may favor configurations where at least one mode in the pair reverses in a relatively energy-lowering direction. Such interfaces, while less stable than the fully compensated motifs, remain energetically accessible and can be identified through local structural signatures. (For clarity on the terminology and phonon-mode concepts used throughout this work, see Supplemental Material Note 1 [31].)

B. Pair condensation of phonon modes and layer-selective ferroelectricity in HfO_2

The fundamental mechanism established in Sec. II A is identified through the microscopic origin of layer-selective ferroelectricity, which is enforced by Y'_3 -mediated trilinear couplings (Fig. S3 [31]). (The energy variation arising from trilinear coupling is provided in Supplemental Material

Fig. S4 [31]). The Y'_3 mode, characterized by antiphase Hf displacements along the y direction (Fig. 1, dotted box), couples trilinearly to the pair composed of the polar Γ_{15}^z mode and antipolar Y_5^z mode (Fig. 1, top).

A recent study proposed a hybrid-triggered mechanism in which polarization emerges through trilinear couplings between polar and nonpolar modes, without requiring an unstable polar phonon [30]. This perspective is consistent with the presence of symmetry-allowed mode couplings in HfO_2 , while the present work further relates these couplings to the layer-selective lattice distortions governing the ferroelectric structure. Condensation of the Γ_{15}^z - Y_5^z pair *suppresses* the z displacement of oxygen atoms in closely spaced layers (spacer layers, shaded region) and amplifies oxygen displacements in more widely spaced layers (ferroelectric layers, unshaded region). Oxygen atoms in ferroelectric layers therefore contribute disproportionately to the macroscopic polarization, whereas oxygen atoms in spacer layers remain comparatively inert, yielding an inherently patterned ferroelectric structure in orthorhombic HfO_2 . Additionally, the Y'_3 mode couples trilinearly with the pair of X'_2 - Z_5^x modes (Fig. 1, middle), and the pair of X_5^y - Z_5^y

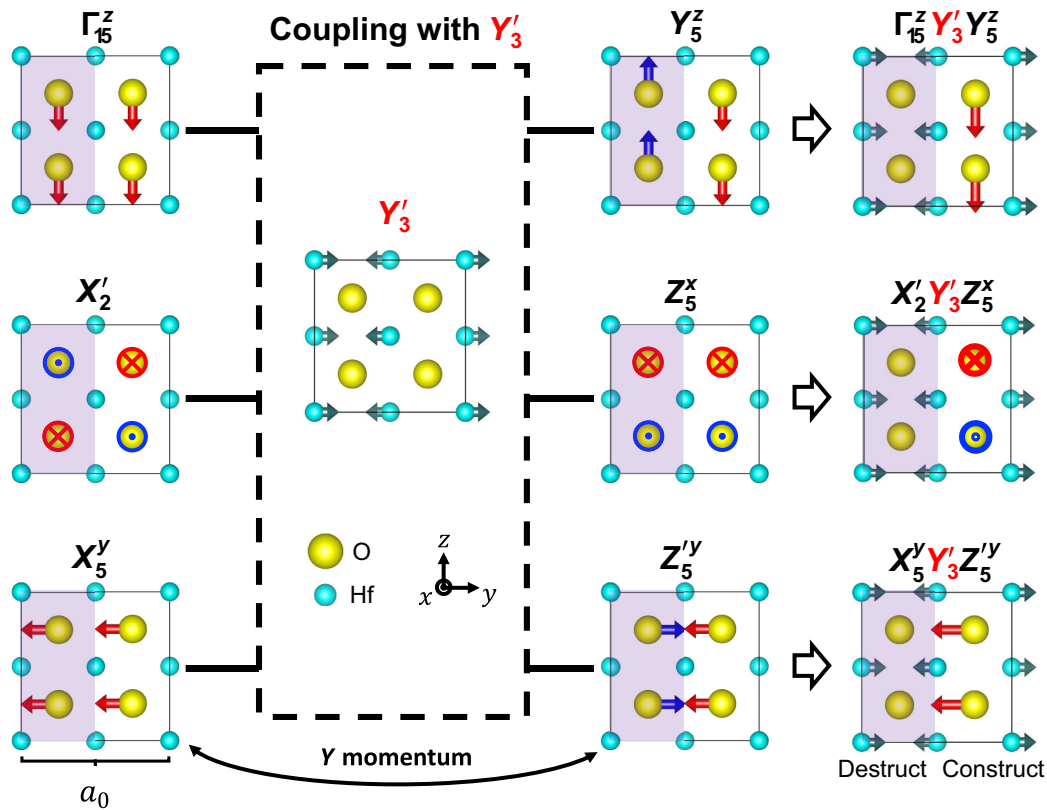


FIG. 1. Phonon pair formation via trilinear coupling in HfO_2 . The Y'_3 mode (dotted box) mediates the simultaneous condensation of three phonon pairs via trilinear couplings. Top, z -displacing pair (Γ_{15}^z - Y_5^z); middle, x -displacing pair (X'_2 - Z_5^x); bottom, y -displacing pair (X_5^y - Z_5^y). Their collective condensation concentrates oxygen displacements within the narrow Hf-spacing (shaded) regions, establishing the basis for layer-selective ferroelectricity. Red and blue arrows indicate atomic displacements along the positive and negative directions, respectively, for each Cartesian component.

modes (Fig. 1, bottom) and condensation of these pairs leads to the reduction of the x and y displacement of oxygen atoms in the spacer layers while enhancement in the ferroelectric layers. Independent theoretical and experimental studies support the layer-selective mechanism [24,28].

This pair condensation is found in the phase-transition pathway, such as the strain-induced transition from the cubic to the Pbcn phase [61]. In this process, the prior condensation of specific lattice modes (X'_2 , Y_5^z , and $Z_5^{y'}$) renders their partner modes (Z_5^x , Γ_{15}^z , and X_5^y) thermodynamically unstable, effectively inducing a cooperative condensation to reach the global energy minimum (Fig. S5 [31]). Rather than resolving the specific origin of the phase transition, our framework focuses on defining these rigorous pairing relationships as the essential structural condition established after the transition to ensure energetic and functional stability.

Collectively, Y_3' -mediated trilinear couplings enforce pair condensation and generate an intrinsic layer-selective ferroelectric pattern by suppressing oxygen displacements in spacer layers while enhancing them in ferroelectric layers. Moreover, this pair condensation provides the structural background for the domain-wall behavior associated with the 180° reversal of the z polarization between y -adjacent ferroelectric domains, which is discussed in the subsequent section.

C. Energy-compensated and structure-recovered polarization-reversal center in HfO₂

Following the layer-selective ferroelectric motif established in Sec. II B, the 180° reversal of the z polarization between ferroelectric domains adjacent along the y direction is examined through pair condensations in orthorhombic HfO₂. The discussion focuses on an energy-compensation mechanism enabled by simultaneous reversal of lattice-distortion modes in pair condensation, together with a wall-centered structure in which bulk distortion motifs are locally recovered rather than strongly suppressed.

A useful contrast is provided by a conventional perovskite ferroelectric such as BaTiO₃, where spontaneous polarization is predominantly associated with the condensation of a single polar mode. In such a single-mode setting, a 180° ferroelectric domain wall disrupts translational symmetry and requires finite-wave-vector components along the polar phonon branch [Fig. 2(a)]. The positive curvature of this branch implies a substantial energetic penalty for these finite- q distortions. To minimize this cost, the system is forced to strongly suppress the amplitude of the polar distortion at the wall center, leading to a structural state that deviates significantly from the stable bulk motifs [Fig. 2(b)]. Consequently, a wall separating domains of opposite polarization incurs a non-negligible formation energy due to this unavoidable suppression of the order parameter.

In orthorhombic HfO₂, pair condensation enables an energy-compensated response during ferroelectric domain-wall formation because the two simultaneously condensed modes participating in a given pair condensation are tied to opposite termini of a single y -dispersing phonon branch [Fig. 2(c)]. The branch curvature at the two termini has opposite sign, implying complementary energetic contributions under wall-associated deviations: An energy increase associated with one terminus is accompanied by an energy-lowering contribution associated with the other, reducing the net energetic penalty of the wall-forming distortion. Trilinear couplings link the two modes participating in each pair condensation, enforcing their simultaneous participation and thereby enabling the dispersion-related complementarity to operate as an energy-compensation channel. This mechanism is exemplified by the Γ_{15}^z - Y_5^z case and extends to the X'_2 - Z_5^x and X_5^y - $Z_5^{y'}$ cases, consistent with the reduced gradient-energy coefficient (Fig. S3 [31]).

Pair condensation also constrains the wall-centered atomic structure such that the distortion patterns characteristic of the bulk are not extinguished at the interface but are redistributed locally within a unit-cell-scale region. For the Γ_{15}^z - Y_5^z case, the z -directed displacement patterns associated with both modes reverse sign across a wall normal to the y direction ($-\Gamma_{15}^z, -Y_5^z \rightarrow (\Gamma_{15}^z, Y_5^z)$) [Fig. 2(d), top]. Importantly, the wall-centered configuration does not require a strong suppression of the bulk lattice-distortion amplitude. Instead, the local structure within approximately one unit-cell width from the wall center is described by a continuous reallocation between the two displacement patterns participating in the pair condensation: The wall-adjacent region on the Γ_{15}^z side acquires a displacement motif closer to that of Y_5^z , while the wall-adjacent region on the Y_5^z side acquires a motif closer to that of Γ_{15}^z . This mutual replacement yields a wall profile in which key symmetry features of the bulk distortions are locally recovered, while still accommodating the sign reversal required by the 180° polarization reversal.

A similar local redistribution occurs for the X'_2 - Z_5^x [Fig. 2(d), middle] and X_5^y - $Z_5^{y'}$ [Fig. 2(d), bottom] cases. The wall-centered region is again characterized by an interchange between the two displacement motifs participating in the pair condensation, allowing the interface to maintain distortion patterns compatible with the bulk on the unit-cell scale rather than forming a sharply distinct structural core (Fig. S6 [31]).

In summary, 180° ferroelectric domain walls in orthorhombic HfO₂ are accommodated with a significantly reduced energetic penalty compared to conventional single-mode ferroelectrics. This efficiency stems from the pair-condensation mechanism, which enforces the simultaneous participation of two lattice-distortion modes whose complementary phonon-dispersion curvatures provide an intrinsic energy-compensation channel. Rather than necessitating the suppression of the order parameter at the interface, this

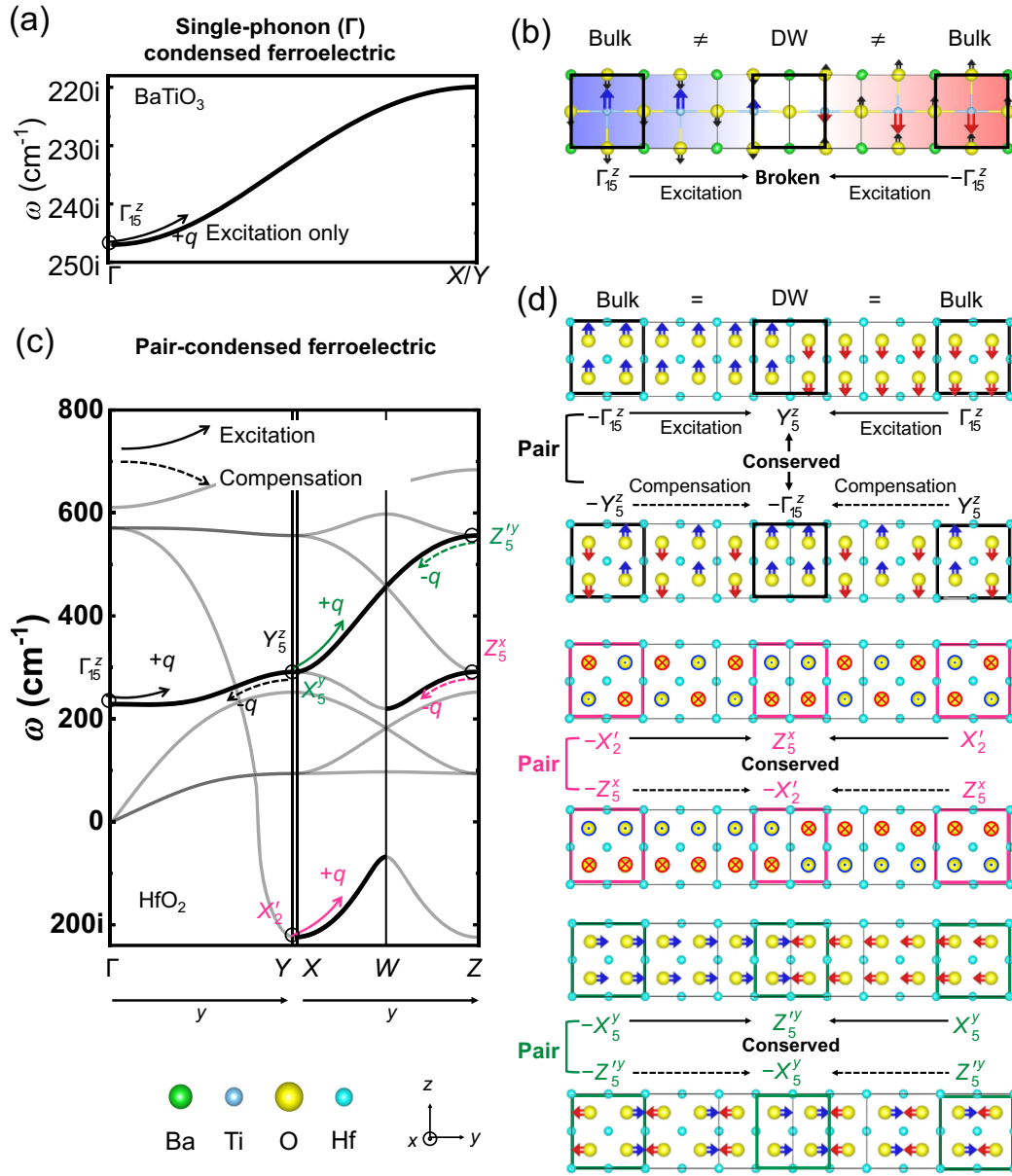


FIG. 2. Comparison of domain-wall formation in single-mode and pair-phonon ferroelectrics. (a),(b) Single-phonon condensed system BaTiO_3 : (a) phonon dispersion showing the energetic excitation (solid curved arrow) required for a momentum change $+q$ at the Γ point. (b) Atomic displacement profile showing the suppression of the order parameter at the domain-wall center (dashed line). (c),(d) Pair-condensed system (HfO_2): (c) complementary dispersion curves of paired modes (Γ and Y), where the excitation of one mode is compensated by its counterpart. (d) Atomic displacement profile showing the conservation and local recovery of bulklike motifs across the interface, with the wall-centered unit cells remaining structurally consistent with the adjacent domains. Imaginary phonon frequencies are denoted by using “i” indicating dynamically unstable modes. The symbol “ $\neq$ ” indicates that the interfacial region is structurally distinct from the bulk.

coordinated participation allows the wall-centered region to maintain the structural integrity of the bulk motifs. The resulting interface is characterized by a continuous, unit-cell-scale redistribution of the paired displacement patterns, yielding a sharply defined yet structurally bulk-compatible boundary. By bypassing the energetic costs typically associated with order-parameter suppression, pair condensation establishes a microscopic basis for the exceptionally low

domain-wall energies and high-fidelity structural recovery observed in HfO_2 -based ferroelectric systems.

D. Locally recovered wall-center structures and low-energy domain wall enabled by pair condensation

A combined DFT and ABF-STEM analysis is employed to identify the lowest-energy 180° polarization-reversal

configuration in orthorhombic HfO_2 and to test whether pair condensation enables a locally recovered wall center that avoids strong suppression of the condensed lattice distortions discussed in Sec. II C. The analysis identifies a specific reversal configuration ($D_{XY}|U$, discussed below) whose formation energy is exceptionally small—slightly negative—and whose wall center retains condensed distortion amplitudes in a locally recovered manner.

DFT-based structural optimizations confirm that trilinear-coupling constraints among the condensed lattice distortions remain satisfied and generate eight symmetry-equivalent ferroelectric structures distinguished by mode-sign combinations [62–64], as denoted in Table I. Four structures are up-polarized (U , U_Y , U_X , and U_{XY}) and four are down-polarized (D_{XY} , D_X , D_Y , and D), consistent with their polarization-switching paths (Fig. S7 [31]). For notational clarity, all condensed lattice distortions in U are assigned positive sign. Four distinct 180° ferroelectric domain-wall configurations are constructed between U and the down-polarized structures, namely, $D_{XY}|U$, $D_X|U$, $D_Y|U$, and $D|U$ (Fig. S8 [31]). Among these, the $D_{XY}|U$ configuration exhibits the domain-wall energy (DWE) with a slightly negative value (a detailed formulation of the DWE is provided in Supplemental Material Fig. S9 [31]). Such an extremely low cost is consistent with the wall-center structure accessing a locally stable, antipolarlike motif related to Pbca [25,64–66].

Importantly, the relatively low domain-wall energy of the $D_{XY}|U$ configuration is associated with coordinated sign reversal across the localized reversal region within two pair condensations: the Γ_{15}^z - Y_5^z pair condensation and the X_2' - Z_5^x pair condensation [Fig. 3(a)]. The absolute amplitudes of the corresponding condensed lattice distortions remain close to the bulk-structural values in both the adjacent regions and the unit cell defining the wall center [Fig. 3(a)]. Other lattice distortions associated with the Y_3' , X_5^y , and Z_5^y

modes do not exhibit sign reversal across the localized reversal region and display only minor amplitude change. The mode-sign pattern in the wall-center unit cell matches the D_X structure (Table II), indicating that the local sign configuration required by the 180° polarization reversal is realized without strong suppression of condensed lattice distortions. In contrast, the $D_X|U$, $D_Y|U$, and $D|U$ configurations do not satisfy the same coordinated sign-reversal condition across the relevant pair condensations and exhibit substantially higher formation energies (Fig. S8 [31]). This wall-centered D_X motif is fundamentally consistent with descriptions of the boundary as a two-unit-cell-wide antipolar Pbca-like motif [25,64–66]. These differences in the structural labelings represent complementary classifications of the same symmetry-equivalent interface, depending on the choice of boundary or wall-center definition (Fig. S10 [31]).

ABF-STEM measurements quantitatively corroborate the DFT-derived $D_{XY}|U$ reversal motif by distinguishing its unique displacement signatures from other possible configurations. The y -direction oxygen-oxygen separation in spacer layers d_y reflects the combined contributions of the X_5^y and Z_5^y distortion modes. Experimental d_y values [black filled squares in Fig. 3(b)] agree closely with DFT predictions (open red squares), confirming that both X_5^y and Z_5^y distortion modes maintain their signs and amplitudes across the reversal region. This result is crucial as it experimentally rules out alternative motifs like $D_Y|U$, where d_y would be expected to significantly suppress or approach zero due to the reversal of one or both y -displacing modes. Furthermore, the z -direction off-centering displacements d_z in both spacer and ferroelectric layers [black filled circles and red open circles in Fig. 3(b)] also show a high degree of agreement with DFT (Fig. S11 [31]). This confirms the simultaneous sign reversal of the Γ_{15}^z and Y_5^z distortion modes across the boundary. Together, these metrics provide direct structural evidence for the $D_{XY}|U$ motif, where pair-condensation logic dictates a selective participation: While the z -polarization-carrying modes Γ_{15}^z and Y_5^z reverse to accommodate the 180° wall, the in-plane modes (X_5^y and Z_5^y) remain rigid, preserving the bulk-compatible integrity of the interface.

The DFT-identified low-energy wall-center motif is consistent with sharply localized polarization reversal observed experimentally. ABF-STEM images display alternating up and down polarization with polarization-reversal regions confined to a very narrow spatial extent, including cases where a down-polarized region between up-polarized regions approaches one-half unit cell in width [Fig. 3(c)]. Additional configurations exhibit clear alternation with distinct reversal regions [Fig. 3(d)] as well as more disordered arrangements [Fig. 3(e)]. These observations are consistent with the prevalence of locally recovered polarization-reversal regions exhibiting minimal energetic

TABLE I. Eight equivalent ferroelectric structures of HfO_2 according to signs of lattice-distortion modes. The structures are labeled by the signs of selected condensed lattice-distortion modes: U and D denote the positive and negative sign of Γ_{15}^z , subscript X denotes the negative sign of X_2' , and subscript Y denotes the negative sign of Y_5^z .

Structure	Γ_{15}^z	Y_5^z	X_2'	Z_5^x	X_5^y	Z_5^y	Z_5^x	Y_3'
U	+	+	+	+	+	+	+	+
U_Y	+	−	+	−	+	−	−	−
U_X	+	+	−	−	−	−	−	+
U_{XY}	+	−	−	+	−	+	+	−
D_{XY}	−	−	−	−	+	+	+	+
D_X	−	+	−	+	+	−	−	−
D_Y	−	−	+	+	−	−	−	+
D	−	+	+	−	−	+	+	−

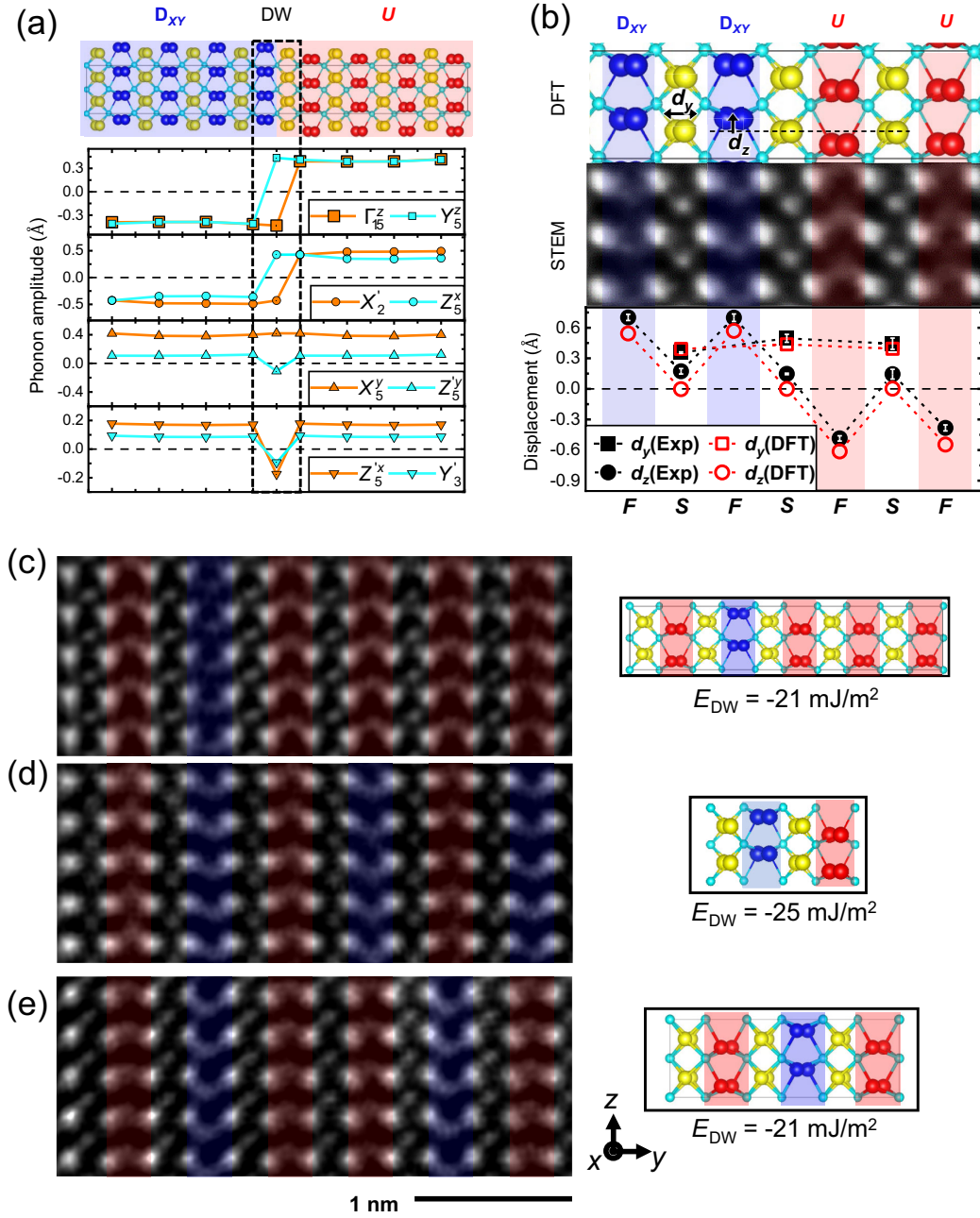


FIG. 3. Experimental and theoretical validation of the $D_{XY}|U$ reversal motif. (a) Atomic model and local distortion mode amplitudes across the $D_{XY}|U$ boundary (dashed line). Red and blue columns denote up- and down-polarization, respectively. Red and blue atoms denote oxygen atoms in these up- and down-polarization regions. (b) Comparison between experimental (filled) and DFT-calculated (open) oxygen displacements: d_y (squares) in the spacer layers and d_z (circles) in the ferroelectric (F) and spacer (S) layers. (c)–(e) Inverted ABF-STEM images and calculated domain-wall energies (insets) for various configurations: (c) a single reversed unit cell, (d) sharp alternating domains, and (e) randomly mixed domain regions.

penalty, in contrast to higher-energy alternatives; calculated energetics for the observed configurations are provided in the insets of Figs. 3(c)–3(e).

Our identification of low DWE and the associated D_X motif (or Pbc-like motif [25,64–66]) might appear to follow existing reports. However, the significance of this work lies in providing a framework based on rigorous

physical principles for the interpretation of such structures and energetics. This approach serves as a versatile tool for analyzing other interfacial systems (Figs. S12 and S13 [31]), invariance of dielectric constants (Fig. S14 [31]), and offers a systematic strategy for designing new materials and phases characterized by inherently low DWE.

TABLE II. Structural comparison of the interfacial motif between U and D_{XY} structure with the bulk D_X configuration. Dashed boxes indicate the pairs of modes that mutually induced each other at the domain wall.

Structure	Γ_{15}^z	Y_5^z	X_2'	Z_3^x	X_5^y	$Z_5^{y'}$	$Z_5^{x'}$	Y_3'
U	0.38	0.38	0.48	0.34	0.38	0.11	0.17	0.08
D_{XY}	-0.38	-0.38	-0.48	-0.34	0.38	0.11	0.17	0.08
DW ($\sim D_X$)	-0.41	0.41	-0.43	0.43	0.42	-0.11	-0.18	-0.09

E. Formation of higher-energy interfaces between energetically favored domain configurations in HfO_2

Sections II C and II D established that a recovered, low-energy polarization-reversal boundary is achieved in orthorhombic HfO_2 when the paired lattice distortions undergo a coordinated sign reversal. In realistic thin-film microstructures, however, the system is rarely defined by a single, isolated boundary; instead, complex junctions emerge where different energetically preferred domain configurations

meet. These geometric constraints often prevent a coordinated reversal of the condensed modes, necessitating the formation of alternative interfacial structures. Accordingly, this section elucidates the formation principles of accessible interfaces that, while not energetically optimal, emerge as necessary structural connections under such constraints. We demonstrate that these nonoptimal junctions are not arbitrary but follow the energetic hierarchy dictated by pair condensation: When a coordinated reversal is hindered, the system favors interfaces that minimize the energetic penalty by selectively reversing only one lattice-distortion mode within a pair that offers a relatively lower energy state.

The $U_Y|U$ interface serves as a primary example of this selective reversal mechanism [Fig. 4(a) and Supplemental Material Fig. S15 [31]]. Unlike the energetically preferred $U|D_{XY}$ interface, the $U_Y|U$ configuration does not satisfy the coordinated reversal condition because the two condensed lattice distortions participating in the pair condensation (Γ_{15}^z and Y_5^z) do not reverse sign together. In this motif, only the Y_5^z distortion mode undergoes a sign change

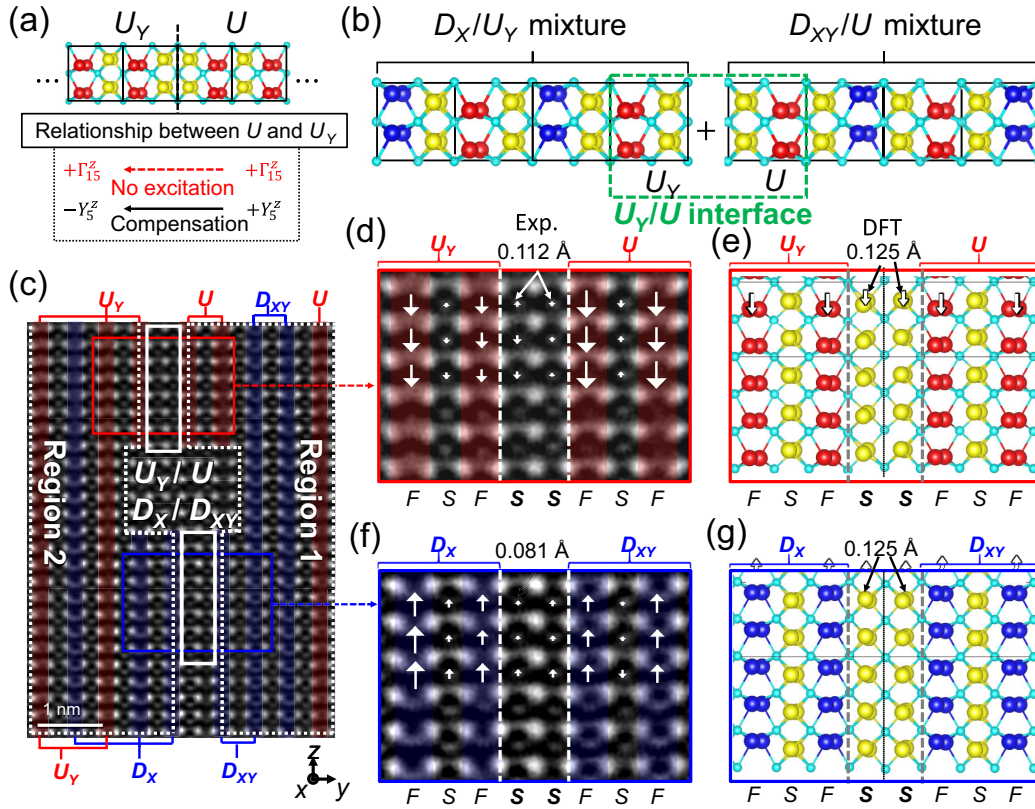


FIG. 4. Direct observation of unconventional, energy-accessible interfaces in HfO_2 thin films. (a) Schematic of the selective reversal mechanism in the $U_Y|U$ interface, where only the Y_5^z mode (lower energy cost) reverses while the Γ_{15}^z mode remains fixed. (b) Schematic representation of a junction between $U|D_{XY}$ and $U_Y|D_X$ mixtures, necessitating transitional bridges. (c) ABF-STEM image of a complex domain landscape. Red and blue boxes indicate the analyzed junctions. (d) Enlarged ABF-STEM image of the red box region with oxygen-displacement mapping. White dashed lines mark the reversal boundaries. (e) DFT-relaxed atomic model identifying the boundary in (d) as a $U_Y|U$ interface. (f) Enlarged ABF-STEM image of the blue box region. (g) DFT-relaxed atomic model identifying the boundary in (f) as a $D_X|D_{XY}$ interface. The identification of these motifs confirms that selective reversals of distortion modes act as essential structural connections between preferred domain configurations.

while its paired Γ_{15}^z distortion mode remains fixed. This incomplete reversal is driven by the energetic asymmetry between the two lattice-distortion modes. As discussed in Sec. II C, the negative curvature of the phonon dispersion at the Y_5^z mode implies that a sign reversal of the Y_5^z distortion mode can provide an energy-lowering contribution that partially offsets the cost of interface formation. In contrast, a standalone reversal of the Γ_{15}^z condensed mode would incur a prohibitive energy penalty due to its positive dispersion curvature. By selectively toggling the Y_5^z distortion mode—the energetically accessible component of the pair—the system minimizes the net formation energy at junctions where geometric constraints prevent a full coordinated reversal. Consequently, $U_Y|U$ emerges as a structurally accessible connection between predominantly preferred mixed-domain configurations such as the $U|D_{XY}$ mixture and $U_Y|D_X$ mixture [Fig. 4(b)]. This interpretation extends conventional energetic assessments [67] by identifying these single-mode reversals as localized geometric compromises at the junctions of stable domains. Beyond ideal symmetry, such deviations are often necessitated by practical boundary conditions, including interfacial pinning or incomplete charge screening that can freeze specific lattice distortions. By linking interfacial stability to phonon band curvature and these environmental constraints, our framework provides a microscopic justification for single-mode reversals as essential structural bridges within complex domain networks.

ABF-STEM measurements provide direct structural evidence for these partially compensated interfaces. Figure 4(c) presents an overview of two spatially separated polarization regions denoted as region 1 and region 2. To facilitate the analysis of the intervening junctions, we modeled region 1 as a $U|D_{XY}$ mixture and region 2 as a $U_Y|D_X$ mixture, consistent with the configuration proposed in Fig. 4(b). To test the robustness of our framework, we analyzed the junctions between these regions by identifying local displacement signatures. Detailed oxygen-displacement measurements at the red boxed junction [Fig. 4(d)] exhibit a displacement pattern that is best reproduced by the DFT-relaxed $U_Y|U$ -type interface model [Fig. 4(e)]. The quantitative agreement between the experimentally extracted oxygen-displacement metrics and the DFT-calculated values supports the $U_Y|U$ assignment, confirming that only the Y_5^z distortion mode reverses across this segment, while the Γ_{15}^z distortion mode maintains its sign. Similarly, the displacement pattern at the blue boxed junction [Fig. 4(f)] closely matches the structural parameters of the DFT-relaxed $D_X|D_{XY}$ model, validating the $D_X|D_{XY}$ assignment for this lower junction segment [Fig. 4(g)]. The identification of $U_Y|U$ and $D_X|D_{XY}$ segments confirms that thin-film microstructures are not limited to the energetically preferred interfacial building block. Instead, as evidenced in Figs. 4(d) and 4(f), while these interfaces are energetically suboptimal compared to the $U|D_{XY}$ motif, they persist as necessary

structural bridges at the intersections of competing domain configurations.

To sum up, the presence of higher-energy interfaces does not overturn the fundamental preference for pair condensation; rather, it illustrates the robustness of the mechanism. Even under complex constraints, the system remains governed by the selective, energy-minimizing reversal of condensed lattice distortions, which act as the essential structural glue maintaining the continuity of the ferroelectric lattice.

III. CONCLUSIONS

In summary, we have demonstrated that trilinear couplings in orthorhombic HfO_2 enforce the pair condensation of specific condensed lattice distortions, establishing the microscopic origin of its intrinsic-layer-selective ferroelectricity. Our analysis reveals that a 180° reversal of the z polarization can remain atomically sharp with an exceptionally low formation energy when the two condensed modes participating in a given pair condensation undergo a coordinated sign reversal. This mechanism allows the reversal center to locally recover bulk distortion motifs, as corroborated by the quantitative agreement between DFT calculations and ABF-STEM measurements. Furthermore, we show that thin-film microstructures are not exclusively limited to these energetically optimal motifs. While interfaces that do not satisfy the coordinated reversal condition are higher in energy, they emerge as structurally accessible connections at junctions between preferred domain configurations. The selective reversal of condensed lattice distortions that provide energy-lowering contributions enables the system to bridge competing regions with a minimized energetic penalty. This localized, interface-resolved understanding of both preferred and competing interfaces provides a fundamental materials-level basis for relating domain-wall populations to the switching microstructures in hafnia-based ferroelectric devices.

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DATA AVAILABILITY

The data are not publicly available. The data are available from the authors upon reasonable request.

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- [1] C. H. Ahn, K. M. Rabe, and J. M. Triscone, *Ferroelectricity at the nanoscale: Local polarization in oxide thin films and heterostructures*, *Science* **303**, 488 (2004).
 - [2] M. W. Chu, I. Szafraniak, R. Scholz, C. Harnagea, D. Hesse, M. Alexe, and U. Gösele, *Impact of misfit dislocations on the polarization instability of epitaxial nanostructured ferroelectric perovskites*, *Nat. Mater.* **3**, 87 (2004).
 - [3] J. F. Ihlefeld, D. T. Harris, R. Keech, J. L. Jones, J. P. Maria, and S. Trolier-McKinstry, *Scaling effects in perovskite ferroelectrics: Fundamental limits and process-structure-property relations*, *J. Am. Ceram. Soc.* **99**, 2537 (2016).
 - [4] Y. G. Wang, W. L. Zhong, and P. L. Zhang, *Lateral size effects on cells in ferroelectric-films*, *Phys. Rev. B* **51**, 17235 (1995).
 - [5] V. Ginzburg, *Some remarks on second order phase transitions and microscopic theory of ferroelectrics*, *Fiz. Tverd. Tela* **2**, 2031 (1960).
 - [6] F. Bloch and F. Bloch, *Zur theorie des austauschproblems und der remanenzerscheinung der ferromagnetika* (Springer, New York, 1932).
 - [7] L. Néel, *Energie des parois de Bloch dans les couches minces*, *C. R. Hebd. Sean. L Acad. Sci.* **241**, 533 (1955), <https://hal.science/hal-02878458/document>.
 - [8] J. Wang *et al.*, *Ferroelectric domain-wall logic units*, *Nat. Commun.* **13**, 3255 (2022).
 - [9] I. Stolichnov *et al.*, *Bent ferroelectric domain walls as reconfigurable metallic-like channels*, *Nano Lett.* **15**, 8049 (2015).
 - [10] Z. Y. An *et al.*, *Tuning of polar domain boundaries in nonpolar perovskite*, *Adv. Mater.* **35**, e2207665 (2023).
 - [11] R. Palai, R. S. Katiyar, H. Schmid, P. Tissot, S. J. Clark, J. Robertson, S. A. T. Redfern, G. Catalan, and J. F. Scott, *β phase and $\gamma - \beta$ metal-insulator transition in multiferroic BiFeO₃*, *Phys. Rev. B* **77**, 014110 (2008).
 - [12] P. Maksymovych, J. Seidel, Y. H. Chu, P. P. Wu, A. P. Baddorf, L. Q. Chen, S. V. Kalinin, and R. Ramesh, *Dynamic conductivity of ferroelectric domain walls in BiFeO₃*, *Nano Lett.* **11**, 1906 (2011).
 - [13] J. Seidel *et al.*, *Conduction at domain walls in oxide multiferroics*, *Nat. Mater.* **8**, 229 (2009).
 - [14] H. Béa and P. Paruch, *A way forward along domain walls (vol 8, pg 168, 2009)*, *Nat. Mater.* **8**, 255 (2009).
 - [15] R. Scherwitzl, P. Zubko, C. Lichtensteiger, and J. M. Triscone, *Electric-field tuning of the metal-insulator transition in ultrathin films of LaNiO₃*, *Appl. Phys. Lett.* **95**, 222114 (2009).
 - [16] A. Q. Jiang, C. Wang, K. J. Jin, X. B. Liu, J. F. Scott, C. S. Hwang, T. A. Tang, H. Bin Lu, and G. Z. Yang, *A resistive memory in semiconducting BiFeO₃ thin-film capacitors*, *Adv. Mater.* **23**, 1277 (2011).
 - [17] Y. L. Wang, Y. C. Su, and J. G. Hu, *Approach to writing-induced different types of spin vortex structure into ferromagnetic nanostripes*, *J. Magn. Magn. Mater.* **328**, 21 (2013).
 - [18] I. I. Naumov, L. Bellaiche, and H. X. Fu, *Unusual phase transitions in ferroelectric nanodisks and nanorods*, *Nature (London)* **432**, 737 (2004).
 - [19] T. Choi, Y. Horibe, H. T. Yi, Y. J. Choi, W. D. Wu, and S. W. Cheong, *Insulating interlocked ferroelectric and structural antiphase domain walls in multiferroic YMnO₃*, *Nat. Mater.* **9**, 253 (2010).
 - [20] T. Jungk, A. Hoffmann, M. Fiebig, and E. Soergel, *Electrostatic topology of ferroelectric domains in YMnO₃*, *Appl. Phys. Lett.* **97**, 012904 (2010).
 - [21] D. Meier, J. Seidel, A. Cano, K. Delaney, Y. Kumagai, M. Mostovoy, N. A. Spaldin, R. Ramesh, and M. Fiebig, *Anisotropic conductance at improper ferroelectric domain walls*, *Nat. Mater.* **11**, 284 (2012).
 - [22] W. J. Merz, *Domain formation and domain wall motions in ferroelectric BaTiO₃ single crystals*, *Phys. Rev.* **95**, 690 (1954).
 - [23] W. J. Merz, *Switching time in ferroelectric BaTiO₃ and its dependence on crystal thickness*, *J. Appl. Phys.* **27**, 938 (1956).
 - [24] E. D. Grimley, T. Schenk, T. Mikolajick, U. Schroeder, and J. M. LeBeau, *Atomic structure of domain and interphase boundaries in ferroelectric HfO₂*, *Adv. Mater. Interfaces* **5**, 1701258 (2018).
 - [25] Y. Cheng *et al.*, *Reversible transition between the polar and antipolar phases and its implications for wake-up and fatigue in HfO₂-based ferroelectric thin film*, *Nat. Commun.* **13**, 645 (2022).
 - [26] Y. Z. Zheng *et al.*, *Dynamic structure evolution under invariant lattice framework in fluorite-type ferroelectrics*, *Nano Lett.* **25**, 14913 (2025).
 - [27] F. Delodovici, P. Barone, and S. Picozzi, *Trilinear-coupling-driven ferroelectricity in HfO₂*, *Phys. Rev. Mater.* **5**, 064405 (2021).
 - [28] H. J. Lee, M. Lee, K. Lee, J. Jo, H. Yang, Y. Kim, S. C. Chae, U. Waghmare, and J. H. Lee, *Scale-free ferroelectricity induced by flat phonon bands in HfO*, *Science* **369**, 1343 (2020).
 - [29] S. S. Cheema *et al.*, *Emergent ferroelectricity in subnanometer binary oxide films on silicon*, *Science* **376**, 648 (2022).

- [30] S. Jung and T. Birol, *Triggered ferroelectricity in HfO₂ from hybrid phonons and higher-order dynamical charges*, *Adv. Mater.* **38**, e21602 (2026).
- [31] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/631f-k7zs> for Fig. S1, the mode connection on phonon bands; Fig. S2, the phonon band splitting on the W point; Fig. S3, the lattice-distortion modes and trilinear couplings between them; Fig. S4, the energy change as functions of the lattice-distortion modes in the trilinear terms; Fig. S5, the phase-transition path from Pbcn to Pca2₁; Fig. S6, the corresponding zone-boundary relationships relevant to the local replacements; Fig. S7, the relation between eight structures and switching paths; Fig. S8, atomic structure and domain-wall energy for $D_{XY}|U$, $D_X|U$, $D_Y|U$, and $D|U$ domain walls; Fig. S9, the general formalism of domain-wall energy; Fig. S10, the contribution of pair condensation on antipolar Pbcn phase; Fig. S11, the comparison between experimental and calculational oxygen displacements in other types of domain walls; Fig. S12, the schematic lattice mode decomposition in a 90° DW in HfO₂; Fig. S13, the schematic mode decomposition in the monoclinic twin boundary in HfO₂; Fig. S14, the change in dielectric response according to domain-wall formation; Fig. S15, atomic structures and domain-wall energies for $U_{XY}|U$, $U_X|U$, and $U_Y|U$ domain walls; Note 1 Guide to Phonon-Mode Concepts; Methods. Supplemental Material includes Refs. [32–60].
- [32] G. Kresse and J. Furthmüller, *Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set*, *Comput. Mater. Sci.* **6**, 15 (1996).
- [33] S. Kambayashi and J. Chihara, *Ab initio molecular dynamics for simple liquid metals based on the hypernetted-chain approximation*, *Mol. Simul.* **16**, 31 (1996).
- [34] G. Kresse and J. Furthmüller, *Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set*, *Phys. Rev. B* **54**, 11169 (1996).
- [35] G. Kresse and D. Joubert, *From ultrasoft pseudopotentials to the projector augmented-wave method*, *Phys. Rev. B* **59**, 1758 (1999).
- [36] P. E. Blochl, *Projector augmented-wave method*, *Phys. Rev. B* **50**, 17953 (1994).
- [37] J. P. Perdew, K. Burke, and M. Ernzerhof, *Generalized gradient approximation made simple*, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [38] H. J. Monkhorst and J. D. Pack, *Special points for brillouin-zone integrations*, *Phys. Rev. B* **13**, 5188 (1976).
- [39] J. Müller, T. S. Börscke, U. Schröder, S. Mueller, D. Bräuhäus, U. Böttger, L. Frey, and T. Mikolajick, *Ferroelectricity in simple binary ZrO₂ and HfO₂*, *Nano Lett.* **12**, 4318 (2012).
- [40] A. S. Foster, F. L. Gejo, A. L. Shluger, and R. M. Nieminen, *Vacancy and interstitial defects in hafnia*, *Phys. Rev. B* **65** (2002).
- [41] J. Wang, H. P. Li, and R. Stevens, *Hafnia and Hafnia-toughened ceramics*, *J. Mater. Sci.* **27**, 5397 (1992).
- [42] T. S. Boescke, J. Müller, D. Bräuhäus, U. Schröder, and U. Böttger, *Ferroelectricity in hafnium oxide thin films*, *Appl. Phys. Lett.* **99**, 102903 (2011).
- [43] S. Mueller, C. Adelman, A. Singh, S. Van Elshocht, U. Schroeder, and T. Mikolajick, *Ferroelectricity in Gd-doped HfO₂ thin films*, *ECS J. Solid State Sci.* **1**, N123 (2012).
- [44] S. Mueller, J. Mueller, A. Singh, S. Riedel, J. Sundqvist, U. Schroeder, and T. Mikolajick, *Incipient ferroelectricity in Al-doped HfO₂ thin films*, *Adv. Funct. Mater.* **22**, 2412 (2012).
- [45] P. D. Lomenzo *et al.*, *Ferroelectric phenomena in Si-doped HfO₂ thin films with TiN and Ir electrodes*, *J. Vac. Sci. Technol. B* **32**, 03D123 (2014).
- [46] D. Sheppard, P. H. Xiao, W. Chemelewski, D. D. Johnson, and G. Henkelman, *A generalized solid-state nudged elastic band method*, *J. Chem. Phys.* **136**, 074103 (2012).
- [47] K. Momma and F. Izumi, *for three-dimensional visualization of crystal, volumetric and morphology data*, *J. Appl. Crystallogr.* **44**, 1272 (2011).
- [48] S. R. Bakaul *et al.*, *Single crystal functional oxides on silicon*, *Nat. Commun.* **7**, 10547 (2016).
- [49] L. Jones, H. Yang, T. J. Pennycook, M. S. Marshall, S. Van Aert, N. D. Browning, M. R. Castell, and P. D. Nellist, *Smart Align—a new tool for robust non-rigid registration of scanning microscope data*, *Adv. Struct. Chem. Imag.* **1**, 1 (2015).
- [50] J. Han, K. J. Go, J. Jang, S. Yang, and S. Y. Choi, *Materials property mapping from atomic scale imaging via machine learning based sub-pixel processing*, *npj Comput. Mater.* **8**, 196 (2022).
- [51] J. Barthel, *Dr. Probe: A software for high-resolution STEM image simulation*, *Ultramicroscopy* **193**, 1 (2018).
- [52] S. Kumar, K. P. S. S. Hembram, and U. V. Waghmare, *Intrinsic buckling strength of graphene: First-principles density functional theory calculations*, *Phys. Rev. B* **82**, 115411 (2010).
- [53] M. Sanati and A. Saxena, *Half-kink lattice solution of the φ model*, *J. Phys. A* **32**, 4311 (1999).
- [54] Y. H. Shin, I. Grinberg, I. W. Chen, and A. M. Rappe, *Nucleation and growth mechanism of ferroelectric domain-wall motion*, *Nature (London)* **449**, 881 (2007).
- [55] H. Aramberri and J. Íñiguez, *Theoretical approach to ferroelectricity in hafnia and related materials*, *Commun. Mater.* **4**, 95 (2023).
- [56] H. Du, C. Groh, C.-L. Jia, T. Ohlerth, R. E. Dunin-Borkowski, U. Simon, and J. Mayer, *Multiple polarization orders in individual twinned colloidal nanocrystals of centrosymmetric HfO₂*, *Matter Radiat. Extremes* **4**, 986 (2021).
- [57] P. Buragohain, C. Richter, T. Schenk, H. Lu, T. Mikolajick, U. Schroeder, and A. Gruverman, *Nanoscale studies of domain structure dynamics in ferroelectric La: HfO₂ capacitors*, *Appl. Phys. Lett.* **112**, 222901 (2018).
- [58] H. Mulaosmanovic *et al.*, *Switching kinetics in nanoscale hafnium oxide based ferroelectric field-effect transistors*, *ACS Appl. Mater. Interfaces* **9**, 3792 (2017).
- [59] C. Zhou *et al.*, *Fatigue-free ferroelectricity in Hf_{0.5}Zr_{0.5}O₂ ultrathin films via interfacial design*, *Nat. Commun.* **16**, 7593 (2025).
- [60] C. Zhou *et al.*, *Enhanced polarization switching characteristics of HfO₂ ultrathin films via acceptor-donor co-doping*, *Nat. Commun.* **15**, 2893 (2024).

- [61] A. Raeliarijaona and R. E. Cohen, *Hafnia HfO₂ is a proper ferroelectric*, *Phys. Rev. B* **108**, 094109 (2023); **110**, 139901 (2024).
- [62] G. D. Zhao, X. E. Liu, W. Ren, X. N. Zhu, and S. F. Yu, *Symmetry of ferroelectric switching and domain walls in hafnium dioxide*, *Phys. Rev. B* **106**, 064104 (2022).
- [63] Y. W. Chen, S. T. Fan, and C. W. Liu, *Energy preference of uniform polarization switching for HfO₂ by first-principle study*, *J. Phys. D* **54**, 085304 (2021).
- [64] Y. B. Qi, S. Singh, and K. M. Rabe, *Polarization switching in ferroelectric HfO₂ from first-principles lattice mode analysis*, *Phys. Rev. B* **111**, 134106 (2025).
- [65] D. H. Choe, S. Kim, T. Moon, S. Jo, H. Bae, S. G. Nam, Y. S. Lee, and J. Heo, *Unexpectedly low barrier of ferroelectric switching in HfO₂ via topological domain walls*, *Mater. Today* **50**, 8 (2021).
- [66] D. Fan, T. Y. Zhu, and S. Liu, *Unexpected density functional dependence of the antipolar Pbcn phase in HfO₂*, *npj Comput. Mater.* **11**, 140 (2025).
- [67] S. S. Zhou, S. H. Qin, and A. M. Rappe, *Domain wall reactions in multiple-order parameter ferroelectrics*, *Phys. Rev. Lett.* **134**, 136802 (2025).