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Scale-free ferroelectricity induced by flat phonon bands in HfO₂

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Discovery of robust yet reversibly switchable electric dipoles at reduced dimensions is critical in advancing nanoelectronics devices. Energy bands flat in momentum space generate robust localized states that are activated independently of each other. We determined flat bands exist and induce robust yet independently switchable dipoles exhibiting a unique ferroelectricity in HfO₂. Flat polar phonon bands in HfO₂ cause extreme localization of electric dipoles within its irreducible half-unit-cell-widths (~3 Å). Contrary to conventional ferroelectrics with spread dipoles, those intrinsically localized dipoles are stable against extrinsic effects such as domain walls, surface exposure, and even down-to-angstrom-scale miniaturization. Moreover, the sub-nm-scale dipoles are individually switchable without creating any domain-wall energy cost. This offers unexpected opportunities for ultimately-dense unit-cell-by-unit-cell ferroelectric switching devices directly integrable into silicon technology.

Ferroelectricity arises from spontaneous ordering of electric dipoles in a crystal which is reversibly switched to opposite directions under an applied electric field. A ferroelectric oxide HfO₂ recently emerged as an interesting material because of its robust electric dipoles at nanometers thicknesses and the ability to directly integrate into silicon devices (1–3). The switchability of electric dipoles in HfO₂, a fluorite structure, is expected to be different from that in ABO₃ perovskite-structure oxides (4) as hinted by its large coercive field (5, 6) and slow domain propagation (7). Unfortunately, the underlying reasons for the stable ferroelectricity and distinct switchability of HfO₂ at an atomic level are poorly understood. The relationship between structure and ferroelectric properties of HfO₂ is crucial for their use in advanced nanoelectronic devices like non-volatile memories and low-power logic (2).

We reveal that ferroelectric HfO₂ possess switchability that is robust even down to irreducible, sub-nano-scale dimensions. This behavior is due to the flat phonon bands intrinsic to the material. While flat bands of electrons, photons, and magnons are known to cause exotic phenomena such as electron lattice (8), graphene superconductivity (9), photon-(10) and magnon-localization (11), flat bands of polar phonons and their consequences in ferroelectrics are not well understood. The emergence of flat phonon bands in HfO₂ provides a missing link to extend those exotic phenomena to ferroelectrics.

We used first-principles calculations to discover flat bands of polar phonons and consequent localized dipoles, which

induces a scale-free ferroelectric order in HfO₂. This order contains a lateral array of vertically-aligned polar layers separated by nonpolar spacer layers that are each of half unit-cell width (~2.5 Å). The presence of the spacers in HfO₂ laterally localize the vertical dipoles within its half-unit-widths in a step-like manner from one polar layer to the next. Contrary to conventional ferroelectrics whose spread dipoles fade away below critical nano-dimensions (4, 12–15), the localized dipoles stable and switchable down to sub-nm scale allow storage of bits in angstrom-size lateral domains without costing any domain-wall formation energy. Vanishingly zero interactions between the ferroelectric dipoles, evidenced by flat bands in HfO₂, explain the unusual phenomena of its large coercive field (5, 6) compared to conventional ferroelectrics (16–21) and extremely slow domain propagation (7). As HfO₂ is already integrated into Si-technology, fabrication of ultimately dense memories could be accomplished by exploiting its irreducible unit-cell-scale switchability.

To determine the origin of unusual structural features of the orthorhombic phase of HfO₂ (*Pca2*₁), we analyzed the sequence of symmetry lowering steps starting with the cubic $Fm\bar{3}m$ structure of HfO₂, known to be stable above 2870 K (22). Upon cooling, it transforms into tetragonal *P4*₂/*nmc* phase at 2870 K, and then to monoclinic phase at *T* = 2000 K. In contrast, the ferroelectric orthorhombic phase is stabilized in thin films at room temperature (1). Phonon spectrum of the high temperature cubic phase (Fig. 1A) reveals the dominant phonon instability with x'_2 symmetry at $\omega = -i228$

cm^{-1} , which involves anti-parallel x-displacements of neighboring oxygen atoms in yz plane (Fig. 1B). The cubic structure transforms into a tetragonal structure through the condensation of an x'_2 phonon with zero net polarization. Among the four phonons condensing in the transformation from tetragonal to orthorhombic (fig. S1), we focus on (i) the Γ_{15}^+ phonon with all oxygen atoms moving along z-direction (Fig. 1C) generating a uniform polarization, and (ii) the cell-doubling anti-polar phonon Γ_5^+ , where oxygen atoms in neighboring xz planes move along the z-axis in an antiparallel manner (Fig. 1D) providing A-type ordering with zero net polarization. Similar to strained ZrO_2 (23), ferroelectricity of HfO_2 is improperly caused by the nonlinear interaction of stable Γ_{15}^+ and X_5 phonons with the primarily instability of x'_2 phonon.

An unusual aspect of the ferroelectric order originates from polar Γ_{15}^+ and anti-polar Γ_5^+ phonons condensing with exactly identical amplitudes, which generate a dipolar partitioning into two types (24) of alternating atomically thin layers (Fig. 1E). The first type is the spacer with zero z-displacements of oxygen atoms and the second is the ferroelectric layer with parallel z-displacements of its oxygen atoms. Thus, spacers are dead layers that screen the elastic interaction between the ferroelectric active layers. Experimental evidence for these layers can be seen in a study employing transmission electron microscopy (25), which named them as minor and major layers, respectively. The structural characteristics of the spacer layers is discussed in fig. S2.

Natural dipolar partitioning in orthorhombic HfO_2 has spectacular consequences to its polarization domain structure, contrary to that of perovskite ferroelectric PbTiO_3 . As the local polarization vanishes in the spacer layer even in uniformly polarized HfO_2 , it inherently hosts a domain wall of vanishing thickness between oppositely polarized (180°) domains (Fig. 2A). Such a domain wall is essentially strain-free (Fig. 2, ε_i where $i = x, y$, and z , fig. S3), with little change in the local structure and supporting unsuppressed bulk polarization in its neighborhood. This should lead us to expect a high energy cost of a sharp domain wall in HfO_2 due to the $g \left| \vec{\nabla} \times \vec{P} \right|^2$ term. But $g \sim 0$ is evident in its flat band of polar phonons (Fig. 2B, supplementary text S1) and makes a sharp domain wall feasible. This flatness of the polar bands results in a phonon velocity of nearly zero (Fig. 2D). The origin of the flatness is discussed with a spring model in fig. S4. The Γ point phonon in the flat band of the lowest frequency (black line in Fig. 2B) involves atomic displacements of all the modes condensed during cubic to orthorhombic transition, and that of higher frequency (red line in Fig. 2B) involves polar and antipolar modes. Physically, the elastic interaction between ferroelectric domains is screened by the spacer layer.

With contribution mostly from dipole-dipole interactions, the domain wall energy of HfO_2 is weakly negative ($\sim -18 \text{ mJ/m}^2$, supplementary text, section 2). In contrast, a domain wall separating the 180° polar domains in PbTiO_3 is diffuse, with a width of a few unit cells and the polarization is suppressed significantly in its neighborhood (Fig. 2C). This difference is because some of the polar atomic displacements are shared between adjacent domains in PbTiO_3 . The parameter g is sizeable, as evident in its dispersed polar phonons (26) and a finite phonon velocity in PbTiO_3 (Fig. 2D).

We seek to establish the stability and switchability of half-a-unit-cell-wide polar domain sandwiched between the spacers by simulating reversal of its local polarization (Fig. 3A and fig. S6). The 2D layer with flipped polarization has a robust stability, with a large energy barrier of 1.34 eV that prevents it from switching back to the uniformly polarized state (Fig. 3B). The switching of polarization in the adjacent layer (Fig. 3B) results in a domain consisting of two ferroelectric layers sandwiching a spacer, following a path with a comparable energy barrier of 1.38 eV. Low dependence of domain wall energy on the width of polar domains reveals weak inter-domain wall interaction as expected from the flat bands. In contrast, our simulation of a single-unit-cell-wide domain in PbTiO_3 (Fig. 3C) has substantially reduced polarization at the diffused domain wall, and its marginal stability is evident in its tendency to expand spontaneously (with a small energy barrier of 0.024 eV) to domains of larger width (Fig. 3D). Despite the strongly knit three-dimensional crystal structure of HfO_2 , our results establish that it consists of weakly interacting 2D polar layers, allowing stable and switchable ferroelectric domains at the ultimate limit of width (2.7 Å).

We provide a possible explanation of the puzzling observation that the coercive field of polarization switching observed in HfO_2 is unusually large and even comparable to the activation field (E_a). The coercive field in conventional ferroelectrics is typically a tenth of the activation field (Fig. 4A) (16), as polarization switching occurs by nucleation and the growth of ferroelectric domains of reversed polarization. Due to such collective behavior, E_c is generally reduced by a factor proportional to the width of the domain wall (27). In HfO_2 , domain walls are vanishingly thin and the resulting reduction in E_c (Fig. 4A) is marginal. With weakly interacting domain walls and zero group velocity of the relevant polar modes ($g \sim 0$, by the flat bands of HfO_2), domain walls do not propagate efficiently and can move only by hopping over a large energy barrier (Fig. 3B), suggesting that their sluggish motion observed experimentally could be an intrinsic property (7, 28). In contrast, a domain wall in PbTiO_3 encounters a much smaller energy barrier of 0.024 eV (Fig. 3D) and its motion leads to rapid expansion of its polar domain.

We demonstrate the scale-free nature of polarization switching in HfO_2 by comparing reversal of uniform and local

polarization (Fig. 4B). Energetics of local and uniform polarization switching in HfO_2 are strikingly similar. Flipping the polarization of a single layer is nearly energetically equivalent (per layer) to flipping the polarization of all layers. In contrast, reversal of local polarization in a single unit cell wide region is energetically forbidden in PbTiO_3 . Total energy along the polarization reversal in consecutive 2D polar domains in HfO_2 is a periodic function of the number of unit-cell-width domains switched (Fig. 4C). The equal multi-stability and identical switching barriers show absolutely scale-free behavior that can be labeled by the integer (number of unit cells) and be a basis for a multi-level device whose number of states are similar to the number of lateral unit-cells. In contrast to this multi-state polar nature in HfO_2 , only bi-stability in PbTiO_3 is evident from its uniformly polarized states ($\pm P_0$) which are more stable than the rest of the intermediate polar states (Fig. 4C, bottom).

To establish the intrinsic size limit on ferroelectricity in HfO_2 , we simulated Hf-terminated slabs (Fig. 4D) perpendicular to (i) (010) axis with in-plane polarization, and (ii) (001) axis with out-of-plane polarization. The polarization in a ferroelectric layer of (010) slabs survives in a scale-free manner down to 1.5-unit-cell thickness with spacers acting as natural protective coatings. The polarization retains its bulk value in (001) slabs down to single-unit-cell thickness, as expected from the improper nature of fluorite ferroelectricity (29). Thus, the intrinsic lateral and perpendicular size limits on ferroelectric order in HfO_2 films are 0.75 and 0.51 nm, respectively (fig. S5). Robust ferroelectric order appears to exist down to 1 nm thickness, as recently reported (30), which verifies one of our predictions. Now the storage size limitation is only from the electrode and transistor used to interface with it for readout operations.

As HfO_2 is already compatible in Si-electronics, our discovery of independently switchable polar layers could provide opportunities to realize ultra-dense and low cost FeRAM or FeFET for memory or logic device applications (figs. S11 and S12). In addition, possibility of unit-cell-by-unit-cell dipolar control provides different opportunities for deterministic multilevel switching (figs. S6, S7, and S12), ultimately down to the angstrom scale.

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SUPPLEMENTARY MATERIALS

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Materials and Methods
Supplementary Text S1 to S3
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Fig. 1. Structural origin of alternating ferroelectric and nonpolar layers in orthorhombic HfO_2 . (A) Phonon dispersion of the cubic phase; each red dot labeled b, c, and d denotes primary instability of (B) X_2' mode, (C) Γ_{15}^2 , and (D) Y_5^2 , where arrows denote u , the displacements of oxygen atoms. (E) Polar Γ_{15}^2 and anti-polar Y_5^2 phonons condense in-phase with equal magnitude to generate orthorhombic structure consisting of alternating spacer layer and ferroelectric layer with up (top), and down (bottom) polarization, respectively. Silver balls denote Hf atoms, red and blue balls denote oxygen atoms in ferroelectric layer with up and down polarization, respectively, and green balls indicate oxygen atoms belonging to the spacer layer.

Fig. 2. Flat bands and zero-width domain wall in HfO_2 , contrary to the diffused domain wall in PbTiO_3 . (A and C) Atomic structure of the domain wall and variation in local polarization along the direction perpendicular to the domain walls in (A) HfO_2 and (C) PbTiO_3 . Red and black lines correspond to the local polarization averaged over their half and single unit cells, respectively. While $(\vec{\nabla} \times \vec{P} = \frac{\partial P_z}{\partial y})$ is small and spreads over a few unit cells away from the domain wall in PbTiO_3 , it is singularly large and highly localized at the domain wall in HfO_2 . (B) This is due to its low energy cost ($g \sim 0$) guaranteed by the flatness of polar phonon bands involving the polar and anti-polar modes condensed in orthorhombic HfO_2 . Flat polar bands are marked with black and red lines and eigenmodes at Γ and Y in the bands are depicted in insets. This flatness of the bands in HfO_2 is in sharp contrast to a dispersive band in PbTiO_3 [(B), top, inset]. (D) Phonon velocities of the flat bands in HfO_2 are nearly zero, while that of polar band in PbTiO_3 has a finite value. For PbTiO_3 , black balls denote Pb atoms, and sky-blue and red balls denote Ti and oxygen atoms, respectively.

Fig. 3. Robust stability of a half-unit-cell-width ferroelectric domain. (A) Atomic structure of the thinnest domain and variation in polarization along the direction perpendicular to the domain walls in HfO₂. (B) Energy along the path of polarization switching of HfO₂ starting from the uniformly polarized structure [(B), left inset] to a state with reversed polarization in two layers [(B), right inset] passing through the state in (A). (C) In contrast to the domain polarization that is unsuppressed relative to bulk P in HfO₂ (A), it is substantially suppressed inside the switched domain as well as a few unit cells away from the domain wall of PbTiO₃. (D) Remarkably, the robust stability of a half-unit-cell-wide domain of HfO₂ (B) is in complete contrast with the marginal stability of single-unit-cell domain in PbTiO₃ which spontaneously expands to wider domains. Successive switching in the next layer [(B), red line] of HfO₂, has an energy barrier comparable to the first switching process [(B), blue line] in HfO₂, in contrast to a small energy barrier of successive switching in PbTiO₃ (D).

Fig. 4. Experimental activation and coercive fields revealing unusual switching behavior of HfO₂ and simulated energetics demonstrating its perfectly scale-free 2D domain switching of 0.27nm width. (A) Experimental values of activation (E_a) and coercive (E_c) fields for various ferroelectrics [BaTiO₃, (16); Pb(Zr,Ti)O₃, (17, 18); BiFeO₃, (19, 21); Pb(MgNb)O₃, (20); PbTiO₃, (21); (Hf,Zr)O₂, (5, 6)]. While E_c is 10 times smaller than E_a in conventional ferroelectrics, these are comparable in HZO, implying that collective and individual domain switching occur at the same field. (B) Calculated energy curves along paths of switching uniform and local (one-unit-cell) polarization in HfO₂ (top) and PbTiO₃ (bottom). (C) Energy of unit-cell-by-unit-cell width switching: while switching of local polarization in consecutive unit cells in PbTiO₃ shows bi-stable ($\pm P_0$) behavior (bottom), domains of any width in HfO₂ are equally stable with the same energy barrier of switching (top) showing its multi-state and scale-free ferroelectric behavior in stability and switchability. (D) Schematic of HfO₂-based capacitive memory device with ultrahigh density because the improper ferroelectricity allows no critical thickness, as confirmed with first-principles calculations [(D), right] and there is no critical lateral width of ferroelectricity in HfO₂ [(D), bottom] due to the presence of spacer layers.