Ferroelectricity in binary oxides including hafnia and zirconia has riveted the attention of the scientific community due to the highly unconventional physical mechanisms and the potential for the integration of these materials into semiconductor workflows. Over the last decade, it has been argued that behaviours such as wake-up phenomena and an extreme sensitivity to electrode and processing conditions suggest that ferroelectricity in these materials is strongly influenced by other factors, including electrochemical boundary conditions and strain. Here we argue that the properties of these materials emerge due to the interplay between the bulk competition between ferroelectric and structural instabilities, similar to that in classical antiferroelectrics, coupled with non-local screening mediated by the finite density of states at surfaces and internal interfaces. Via the decoupling of electrochemical and electrostatic controls, realized via environmental and ultra-high vacuum piezoresponse force microscopy, we show that these materials demonstrate a rich spectrum of ferroic behaviours including partial-pressure-induced and temperature-induced transitions between ferroelectric and antiferroelectric behaviours. These behaviours are consistent with an antiferroionic model and suggest strategies for hafnia-based device optimization.

The discovery of ferroelectricity in hafnia took the scientific community by surprise. These findings represented the first reliable observation of ferroelectricity in binary oxides, suggesting a mechanism very different from that in classical ABO$_3$ perovskites. Importantly, hafnia and related binary oxides allow for integration with semiconductor manufacturing workflows, a long-standing challenge for the ferroelectric community spurred by potential applications in non-volatile random access memories, tunnelling barriers, field-effect transistors and multiferroic devices. It is notable that initial reports of ferroelectricity in hafnia and zirconia were followed by an exponentially rapid growth of groups active in the area. Furthermore, this discovery has stimulated the investigation of ferroelectricity in conventionally non-ferroelectric polar materials including Mg$_x$Zn$_{1-x}$O, Al$_x$B$_{1-x}$N and Al$_{1-x}$Sc$_x$N, suggesting that ferroelectricity can be ubiquitous in nitrides and oxides.

From the first reports on ferroelectricity in hafnia, controversy emerged on the origins of the switchable spontaneous polarization in this material. Early density functional theory calculations
demonstrated the feasibility of intrinsic polarization instability in these structures; however, experimental studies have demonstrated that many aspects of ferroelectric behaviour in hafnia are considerably complex compared to classical ferroelectrics. These include a more exaggerated wake-up effect, that is, when classical ferroelectric hysteresis loops emerge after cycling of the fabricated devices. Similarly, ferroelectric behaviours in hafnia-based systems possess an anomalously strong dependence on electrode interfaces and preparation conditions. Jointly, these observations suggest that ferroelectric-like behaviours in these materials either originate or are mediated by alternative mechanisms. The former can include the formation of mesoscale chemical dipoles and vacancy ordering, whereas the latter suggest the potential coupling between ferroelectric and ionized or strained subsystems. Additionally, a large discrepancy between nanoscale free-surface- and bulk-capacitor-based measurements has been observed throughout the community, further suggesting that complex mechanisms underpin hafnia’s functionality.

Driven by these considerations, a number of groups have proposed that ferroelectricity in hafnia can be mediated by atomic defects, most notably oxygen vacancies. Furthermore, the polymorphism of hafnia was proposed to be associated with multiple factors including strain, doping, field-induced phase transitions and changes in oxygen stoichiometry resulting in complexities associated with stabilizing the ferroelectric orthorhombic phase.

Likewise, scaling effects have been observed to increase the complexity of hafnia-based systems. Unlike conventional ferroelectrics (for example, perovskites such as BaTiO₃), where the polarization is known to diminish with reducing crystal size, in hafnia systems, the stability of the non-equilibrium phases increases with decreasing crystal size. Several groups have experimentally shown a strong dependence of the phases present on film thickness. For example, films that are thicker than approximately 15 nm often show increased phase fractions of the equilibrium, non-ferroelectric monoclinic phase, and adding artificial interfaces to disrupt the lattice has been successful in stabilizing the non-equilibrium phase to larger thicknesses. These observations point to a large surface/interface energy contribution to phase stability in the hafnia system, which has been well-known in fluorite oxides since early work on ZrO₂ (ref. 32). Computational efforts have corroborated this surface/interface effect on phase stability, where different thickness regimes of metastable phase formation have been shown to be 5, 15 and approximately 35 nm in HfO₂, HfₓZr₁₋ₓO₂ (HZO) and ZrO₂, respectively. Furthermore, recent computational and experimental reports have shown there is, practically, no size limit for ferroelectricity in hafnia-based systems. Specifically, Zhao et al. showed that the polar phase is stabilized by an anti-polar mode that results in extreme size scaling, and Cheema et al. have shown experimental evidence for reversible polarization in films that are only one unit cell thick. Given that surfaces and interfaces play a large role in phase stability, changes of electrochemical boundary conditions will strongly impact a system that is stabilized by surface energy.

While discussing the state-of-the-art understanding of ferroelectricity in hafnia, we note that over the last decade, anomalous ferroelectric-like behaviours were also observed by the classical ferroelectrics community. For example, observations of hysteresis loops and switchable remanent polarization in materials where polarization exists in the bulk but is expected to disappear in thin layers, or in materials that do not have polarization instability, were reported. The characteristic aspect of these systems is the presence of a continuum of polarization states (as opposed to the binary polarization in classical ferroelectrics) and a sensitivity to environmental conditions. Furthermore, often these phenomena could be generally observed on free surfaces via piezoresistance force microscopy (PFM), but the device structures formed from these films could not be observed. In these cases, it was argued that the coupling between the bulk ferroelectric instability and surface electrochemistry can give rise to new ferroionic states. More generally, these studies pointed to the possible key role of electric-potential compensation phenomena at ferroelectric surfaces and interfaces beyond a classical dead-layer model.

Here we argue that the observed ferroelectric behaviours in hafnia can be ascribed to the interplay between bulk antiferroelectric instability and nonlinear surface (or interface) charge compensation, manifested in the bulk and at the interfaces, respectively. This fundamental disparity in the spatial localization of bulk ferroelectric instability and interfacial behaviours renders non-local polarization switching and phase evolution, resulting in complex time and voltage responses. To explore these assertions, we aim to control the ionic and electrostatic degrees of freedom separately. Note that while this separate control is highly challenging to achieve at the internal interfaces (simply because biasing affects both electrostatic and electrochemical potentials jointly), such control can be readily accomplished at the surfaces via the partial pressure of oxygen and temperature. As such, with the decoupling of the electrochemical and electrostatic controls realized via environmental and ultra-high-vacuum PFM, we show that these materials demonstrate a rich spectrum of ferroic behaviours including oxygen partial-pressure-induced and temperature-induced transitions between ferroelectric and antiferroelectric behaviours.

**Structural phase identification**

As a model system to explore hafnia-based antiferroelectric instabilities, we chose a 17 nm HZO thin film grown via plasma-enhanced atomic layer deposition (ALD) on a silicon substrate with TaN bottom electrodes (Methods). To evaluate the intrinsic material properties of HZO, we employ structural and chemical characterization as seen in Fig. 1. The atomic force microscopy (AFM) topography reveals a surface morphology consisting of 25 nm average grain sizes (Fig. 1a) and a root-mean-square roughness of 1.2 nm, consistent with previous reports of ALD-prepared HZO. Fig. 1b shows the cross-section of a HZO film (in the awoken state), taken using atomically resolved high-angle annular dark-field scanning transmission electron microscopy (STEM) micrographs, where a single grain making up the full thickness of the film is observed, together with the TaN bottom electrode and the top protective cap (Pt) used for sample preparation. Position-averaged convergent electron beam diffraction (PACBED) measurements were also acquired to facilitate the determination of the phases (Fig. 1b). Although a lack of a mirror plane should be observed across the dashed axis bisecting the pattern for the Pca₂ structure, the experimental pattern shown in Fig. 1b reveals a more symmetric distribution. These results together with the presences of weak reflections in the fast Fourier transform reveal a coexistence of two orthorhombic phases, including Pca₂ (polar) and Pbca (anti-polar), oriented along the [110] and [101] directions, respectively, as shown in Fig. 1b (right panel), establishing the presence of competing ferroelectric–antiferroelectric states.

To identify the relative phase fractions within the HZO thin film, Fig. 1c shows grazing incidence X-ray diffraction results differentiating the monoclinic phase from the orthorhombic phase, and finding an 80.9% orthorhombic phase. Grazing incidence X-ray diffraction is performed because the grazing incidence angle is near the critical angle for the hafnia films. This, in turn, leads to an increased sampling volume and signal-to-noise ratio in the X-ray diffraction scan. Importantly, both orthorhombic phases, Pbca and Pca₂, are virtually indistinguishable from the tetragonal phase via X-ray diffraction; thus, the corresponding peak is labelled as orthorhombic/tetragonal. Lastly, chemical homogeneity can strongly influence the ferroelectric properties of HZO. As seen from Fig. 1d, a relatively uniform distribution of hafnium (green), zirconium (blue) and oxygen (red) is observed. Moreover, the average profiles shown in Fig. 1e show a relatively uniform z profile of the individual constituents.
Environmenally dependent electromechanical response

To investigate the coupling between the bulk ferroelectric instability and surface electrochemistry, band excitation (BE) PFM measurements were performed in three different environments on pristine HZO—that is, ambient, glove box (<10 ppm O₂) and ultra-high vacuum (2 × 10⁻¹⁰ torr) environments—to control the effective partial pressure of oxygen. Note that in contrast to single-frequency PFM, BE-PFM uses a non-sinusoidal signal with a defined band in frequency space to independently detect the resonance frequency and response amplitude, ultimately mitigating the topographic crosstalk⁴³. Figure 2 shows classical box-in-a-box poling experiments acquired in all three environments using +7 V and -7 V d.c. biases to pole 600-nm-wide and 300-nm-wide areas, respectively (solid and dotted boxes in Fig. 2a). Figure 2a,d displays the BE-PFM amplitude and phase, respectively, acquired after poling in ambient conditions. Here, the formation of domain walls and oppositely poled regions is not observed. Interestingly, localized regions of the BE-PFM phase (Fig. 2d) seem to vary across the region of interest, suggesting the presence of additional mechanisms, such as non-uniform polarization or surface states. As the environmental oxygen partial pressure is reduced (that is, we move towards glove box measurements), localized areas with decreased amplitude are observed (Fig. 2b,e) in the +7 V poled region. By contrast, as the environmental oxygen partial pressure is further reduced to ultra-high vacuum conditions, clear domain wall formation and polarization switching is observed within the poled regions (Fig. 2c,f) with the presence of localized unswitched areas in the +7 V poled region, suggesting possible localized defect clusters or non-ferroelectric monoclinic phases.

Next, HZO hysteresis loops were measured via BE piezoresponse spectroscopy (BEPS) in the ambient, glove box and ultra-high vacuum environments at 300 K, and the results are shown in Fig. 3. Here, classical hysteresis loops measured via PFM experiments are presented in the off-field state, where the PFM signal is measured at the zero-bias state after the application of a short bias pulse. This experimental protocol is chosen to minimize the contribution of electrostatic forces in the measured signal⁴⁴,⁴⁵. In the interpretation of these measurements, we postulated that the domain formed below the tip does not appreciably relax on the transition to zero probe d.c. bias; that is, the domain walls are strongly pinned⁴⁶. However, this assumption is not necessarily justified for materials, such as ferroelectric relaxors, with highly mobile domain walls or materials with competing order parameters such as antiferroelectrics. Hence, here we present both on-field and off-field measurements.

Figure 3a,d shows the on-field and off-field switching behaviour in ambient conditions, respectively. Here, clear pinching of the on-field hysteresis loop close to 0 V is observed, indicative of antiferroelectric-like behaviour. Notably, the pinched loop is slightly offset from 0 V, suggesting the presence of a built-in potential.
Examination of the off-field loop also shows antiferroelectric-like behaviour, suggesting the metastability of the bias-induced polar phase. However, in an argon environment (that is, glove box measurements), a lower degree of pinching accompanied by a narrowing of the hysteresis loop is observed in the on-field state with no remanent ferroelectric switching observed in the off-field state (Fig. 3b,e and Supplementary Fig. 9), indicating a paraelectric-like phase. By contrast, in ultra-high vacuum conditions (2 × 10⁻¹⁰ torr), a widening of the on-field loop with the absence of pinching is observed, indicating the onset of ultra-high vacuum conditions (2 × 10⁻¹⁰ torr), a widening of the on-field hysteresis loop is observed in the on-field state with no remanent switching can be observed in all environments, as expected; however, differences in the hysteresis loop shape are readily observed, suggesting that in reducing environments (ultra-high vacuum), oxygen vacancies can migrate and/or be created within the PFM probing volume, inducing unprecedented responses, similar to recently reported observations. Importantly, environmentally induced surface effects, such as the propensity for surface adsorbates or oxygen vacancy formation at the surface, can have a substantial impact on the ferroelectric behaviour, as seen in HZO.

These observations suggest the electrochemical state of the surface strongly couples to the ferroelectric behaviour in the hafnia system. In other words, as the environmental oxygen partial pressure and total pressure are reduced via ultra-high vacuum, the chemical potential driving force will reduce the compensating mechanisms (for example, surface absorbates or ionic species) and subsequently decrease the oxygen content at the surface, which is expected to increase the negative surface charge (that is, compensated oxygen vacancies), potentially giving rise to the observed ferroelectric stability. As such, it is worth mentioning that the placement of conductive electrodes on hafnia's surface can also provide the necessary interfacial charge to stabilize the ferroelectric behaviour, congruent with previous reports.

### Phenomenological Landau-type modelling

To gain further insight, we apply a previously developed formalism for an antiferroelectric film coupled to surface electrochemical reactions. This phenomenological formalism considers competing polar and structural anti-polar distortive long-range orders in (Hf,Zr)O₂ at the mesoscopic level with the possible role of doping and oxygen vacancies, in the presence of a finite surface (or interface) density of ionic and electronic states (Supplementary Sections A and B). We use this formalism to plot the phase diagram of a 20-nm-thick HZO film as temperature versus relative oxygen pressure (Fig. 4a), where the dashed curves separate the different types of loops corresponding to the non-polar antiferroelectric phase (AFEI), the intermediate paraelectric-like phase (PE) and the ferroelectric-like ferroionic phase (FEI). This classification is valid for quasi-static
changes of the applied voltage and is based on the shape of polarization hysteresis loops, which continuously transform from a double antiferroelectric-type loop through a hysteresis-less PE curve towards a single ferroelectric-type loop, as shown in Fig. 4a. Importantly, the experimentally measured hysteresis loops acquired as a function of relative oxygen partial pressure are in great qualitative agreement with the phenomenological Landau-type modelled loops, suggesting that the experimentally observed behaviour is due to the proposed AFEI–PE–FEI transition mechanisms, that is, the interplay between bulk antiferroelectric instability and nonlinear surface charge compensation. Also, it is important to consider that the modelled behaviour indicates that the antiferroelectric-type loops transform to the ferroelectric type with the increase of the applied voltage frequency (Supplementary Figs. 4 and 5). For comparison, average off-field hysteresis loops of 80-nm-thick BaTiO3 are shown in g–i, acquired in ambient, argon and ultra-high vacuum environments, respectively. Top (a–c) and bottom (d–i) panels correspond to an on-field and off-field hysteresis loop, respectively. All data are presented as mean values ± standard deviation.

A critical component of the modelled behaviour is the dynamic electric field dependencies on the out-of-plane polarization (black curves), and on the positive (red curves) and negative (blue curves) surface charges, which are calculated for decreasing oxygen pressure and different relaxation times between the positive ($r_p$) and negative ($r_n$) screening charges, $r_n \ll r_p$ (Fig. 4b–d). A clear increase in the hysteresis loop opening, or the ferroelectric-like behaviour, can be seen with decreasing relative oxygen partial pressure (Fig. 4b–d), which is accompanied by an increase in negative surface charges (potentially compensated oxygen vacancies) and relatively constant positive surface charges. Congruently, the corresponding normalized dielectric susceptibilities $\chi/\chi_0$ (where $\chi_0$ is the zero electric field susceptibility) are shown in Fig. 4e–g (the calculation parameters, selected based on experimental observations, are listed in Supplementary Table I). The susceptibility, corresponding to FEI-type states, has two peaks standing on a wide high `base'. The frequency behaviour of the $\chi/\chi_0$ values in the FEI state is different from the behaviours in the ferroelectric and PE states. Indeed, $\chi/\chi_0$ in the ferroelectric state has two sharp peaks at a coercive field (without any base), which remain unchanged in a wide frequency range; and $\chi/\chi_0$ in the PE state has a frequency-sensitive central maximum without any side peaks. In the FEI state, the decrease of oxygen pressure leads to the continuous decrease of the base height, its horizontal shift and an increase of the peaks’ height. Note that the features of the polarization loops, characteristic to AFEI states, can be seen at much lower frequencies of applied bias (compare Supplementary Figs. 2 and 3 with Supplementary Figs. 4 and 5).

Fig. 3 | BEPS hysteresis loops. a–f. Average on-field and off-field hysteresis loops of HZO over two cycles, acquired from a 10 × 10 grid over a 1-µm-wide area in three different environments: ambient (a and d), argon (b and e) and ultra-high vacuum (c and f). g–i. For comparison, average off-field hysteresis loops of 80-nm-thick BaTiO3, are shown in g–i, acquired in ambient, argon and ultra-high vacuum environments, respectively. Top (a–c) and bottom (d–i) panels correspond to an on-field and off-field hysteresis loop, respectively. All data are presented as mean values ± standard deviation.
Ferroionic temperature dynamics

We further proceed to explore the temperature dynamics in an effort to probe the complex HZO ionic-electrostatic-mediated phase diagram. Here, we note that in classical ferroelectrics, the hysteresis loops are weakly dependent on temperature away from the phase transition, and generally expected to remain symmetric. At the same time, ferroionic systems were predicted to give rise to a broad range of temperature-mediated behaviours, including the transitions between ferroelectric-like and antiferroelectric-like behaviours.

Accordingly, we collected temperature-dependent BEPS hysteresis loops under ambient and ultra-high vacuum conditions (Fig. 5) to vertically transverse the predicted complex phase diagram in a high and low oxygen partial pressure environment, respectively. Figure 5a–c shows hysteresis loops acquired at 360, 420 and 500 K in ambient conditions with the on-field and off-field shown in the left and right panels, respectively. At 360 K (Fig. 5a), a clear pinching of the hysteresis loop is still observed in the on-field state, indicating antiferroelectric-like behaviour; however, the off-field begins to lose the metastable bias-induced polar phase observed in Fig. 3d, that is, the loop opening with negative bias. Furthermore, as the temperature is increased to 500 K, the pinched hysteresis loops begin to collapse, similar to Fig. 3b,e, suggesting the onset of a paraelectric-like phase transition. Jointly, these observations imply HZO begins to undergo an antiferroelectric to paraelectric phase transition at elevated temperatures (>500 K) under ambient conditions, in great agreement with the predicted complex phase diagram in Fig. 4a.

Lastly, Fig. 5d–i shows the average on-field, off-field and on-field differential hysteresis loops acquired at 108, 360 and 420 K from a 1 μm area (10 × 10 grid) in ultra-high vacuum. At 108 K, the on-field loops (Fig. 5d, left panel) display an observable pinching near 0 V while the off-field loops (Fig. 5d, right panel) have an asymmetric response, particularly along the piezoresponse axis, similar to Fig. 4i–l. Interestingly, when evaluating the on-field differential dP/dV spectra (Fig. 5i), two clear kinks are observed, corresponding to the pinching of the on-field loop (dotted circles, Fig. 5g–i). Here we identify the first-order changes in dP/dV to be associated with antiferroelectric behaviour. Upon increasing the temperature to 360 K, no pinching was observed, which is readily apparent from the dP/dV loops (Fig. 5h). Furthermore, the off-field loops at 360 K have a distinctly different switching behaviour, namely, a decrease in the coercive field relative to the hysteresis loops acquired at 108 K, which is in remarkably good agreement with the predicted behaviour shown in Fig. 4a. Lastly, at 420 K, the on-field loop pinching (Fig. 5f, left panel) reappears, which is confirmed via the kinks in the dP/dV spectra (Fig. 5i), suggesting a temperature-induced ferroelectric–antiferroelectric instability. Exploring the off-field response at 420 K reveals symmetric hysteresis loops with a larger coercive voltage, potentially originating from mechanisms such as ionic motion, which is certainly plausible at
Outlook

To summarize, here we reveal a strong dependence of the ferroelectricity in hafnia on the external environment, explored over a range of partial pressures and temperatures. These observations confirm that the electrochemical state of the surface strongly couples to the ferroelectric phase transition and stability in these materials and is inseparable from ferroelectricity. These observations can be described in terms of the antiferroionic model of coupled antiferroelectric bulk and surface electrochemical phenomena. Importantly, the free energies of the various hafnia phases are compositionally dependent, and the surface energy term will impact them each differently. As such, we expect that the observed behaviour of the ferroionic response would hold for any ferroelectric fluoride, but the phase diagrams will differ depending on composition (for example, the relative O₂ pressure and temperature boundaries may differ).

Overall, these mechanisms can provide a general explanation for the range of the unusual phenomena obtained in hafnia and similar binary oxides, including the slow evolution of the ferroelectric properties, the dependence on processing conditions and the observed discrepancy between ferroelectric measurements acquired on a free surface and those in a capacitor geometry. This, in turn, creates novel opportunities for the discovery and optimization of these material systems, such as circumventing the wake-up effect, which is enabled via independent ionic control.

Online content
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Methods

Material synthesis
Metal–insulator–metal TaN/HZO/TaN devices were prepared on 500-µm-thick silicon substrates. The planar bottom TaN electrode was deposited through a d.c. sputtering process from a sintered TaN target to a thickness of 100 nm at room temperature. Next, an Oxford FlexAL II Plasma-Enhanced Atomic Layer Deposition system was used to grow a HZO film to a thickness of 17 nm at 260 °C using tetrakis(ethylmethylamido)hafnium (TEMA Hf) and tetrakis(ethylmethylamido)zirconium (TEMA Zr) as HfO₂ and ZrO₂ precursors, respectively, in 5:5 super cycle ratios to control film composition. An oxygen plasma was employed as the oxidant. Following HZO deposition, a 20-nm-thick planar TaN top electrode was prepared through an identical process to that of the bottom electrode, and the film stack was annealed within an Allwin21 AccuThermo 610 Rapid Thermal Processor for 30 seconds under a N₂ atmosphere. For the sample for PFM measurements, the entire film was exposed to a SC-1 (5:1, H₂O/30% H₂O₂ in H₂O/30% NH₄OH in H₂O) etch solution at 60 °C for 45 minutes to fully remove the top electrode layer. To prepare electrodes, 50-nm-thick Pd electrodes were deposited through a shadow mask, and the exposed TaN was removed using the SC-1 treatment. The discrete Pd pads served as a hard mask.

Polarization measurements
Polarization versus electric field measurements were performed with a Radiant Technologies Precision LC II ferroelectric tester with a measurement period of 1 ms. An Instec hot-stage probe station equipped with a turbo molecular pump was used to measure performance at ambient and high vacuum conditions at 300 K, 360 K and 420 K.

Atomic force microscopy measurements
All PFM measurements were captured using Budget Sensor Multi75E-G Cr/Pt-coated AFM probes (-3 N m⁻¹). BE was achieved by coupling the AFM measurements with an arbitrary wave generator and data acquisition electronics based on a National Instruments fast data acquisition card. Custom software was used to generate the probing signal and store local BE and hysteresis loops. All BE-PFM measurements were collected using frequencies ranging from 300–400 kHz, with subsequent simple harmonic oscillator fits applied to the collected spectra to extract amplitude and phase at the resonance frequency. Ambient PFM measurements were taken using an Oxford Instruments Cypher AFM instrument. Glove box measurements were taken using a Bruker Dimension Icon fitted inside a MBRAUN MB200B series glove box. Ultra-high vacuum measurements were taken via a modified ultra-high vacuum Omicron AFM–STM microscope (STM, scanning tunnelling microscopy) controlled from a Nanonis real-time controller at a pressure of ~2 × 10⁻⁶ torr. For all PFM measurements, the same pristine HZO sample was used. However, additional measurements on multiple samples highlighting reproducibility can be found in the Supplementary Information (Supplementary Fig. II). For all post-poling images (Fig. 2), images were acquired directly after writing with a PFM tip bias of ±7 V.

Scanning transmission electron microscopy measurements
STEM images were acquired in a Thermo Fisher Themis operated at 200 kV, using a high-angle annular dark field, a probe convergence angle of 17.9 mrad and a camera length that resulted in acceptance angles between 60 and 200 mrad. A set of 20 frames was collected using a dwell time per pixel of 10 µs at 200 keV during 10 min using a Super-X Energy-dispersive X-ray spectroscopy detector. The maps were constructed using N Ka, O Kα, Zr Kα, Hf Lα, Ta Lα and Pt Lα lines. PACBED patterns were formed by averaging convergent-beam electron diffraction patterns while scanning the sample with the STEM probe, using a convergence semi-angle of 17.9 mrad and 500 ns dwell time. Patterns were collected during 1 s over the scanned area using a Ceta camera from Thermo Scientific. PACBED patterns were calculated by multislice computer simulations using the Dr. Probe v.1.9 software package (https://doi.org/10.1016/j.ultramic.2018.06.003) and compared with experimental patterns to determine the phases and estimate samples thickness.

Theoretical modelling and analysis
Data supporting the theoretical results were visualized in Mathematica 12.2 (https://www.wolfram.com/mathematica) and can be found at the Notebook Archive (https://github.com/SergeiVKalinin/SergeiVKalinin-Hafnia_NatureMaterials2023/blob/main/abs_HZO-2023_ANM.nb). Thresholding for coercive field and remanent polarization maps was acquired using a ±1 V and ±0.2 a.u. threshold, respectively.

Data availability
The data that support the findings of this study are available from the corresponding authors upon request. Data supporting the theoretical results were visualized in Mathematica 12.2 (https://github.com/SergeiVKalinin/SergeiVKalinin-Hafnia_NatureMaterials2023/blob/main/abs_HZO-2023_ANM.nb). Source data are provided with this paper.

Code availability
Detailed information related to the codes used in this manuscript is available in the Supplementary Information files or from the corresponding authors upon request.

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Author contributions
K.P.K. performed and conceived experiments; A.N.M. and E.A.E. performed theoretical calculations; Y.L. performed ambient PFM measurements; S.T.J., S.S.F., T.M. and J.F.I. grew samples and performed bulk characterization; S.C. and E.C.D. performed STEM and analysis; and K.P.K. and S.V.K conceived the project. All authors contributed to discussions and the final manuscript.

Competing interests
The authors declare no competing interests.
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