nature communications

Article

https://doi.org/10.1038/s41467-025-59519-2

Hidden structural phase transition assisted ferroelectric domain orientation engineering in Hf_{0.5}Zr_{0.5}O₂ films

Received: 28 April 2024

Accepted: 25 April 2025

Published online: 07 May 2025

Check for updates

Yuyan Fan $\mathbb{O}^{1,2}$, Shunda Zhang³, Zhipeng Xue^{1,2}, Yulong Dong^{1,2}, Danyang Chen $\mathbb{O}^{1,2}$, Jiahui Zhang³, Jingquan Liu \mathbb{O}^1 , Mengwei Si \mathbb{O}^1 , Chunlai Luo⁴, Wenwu Li $\mathbb{O}^4 \boxtimes$, Junhao Chu⁴, Yanwei Cao $\mathbb{O}^3 \boxtimes$, Zhen Wang $\mathbb{O}^5 \boxtimes \&$ Xiuyan Li $\mathbb{O}^1 \boxtimes$

The polarization of HfO₂-based ferroelectrics originates from the metastable orthorhombic phase formed during the tetragonal to monoclinic phase transition and is typically controlled by tuning the phase content. However, another way to control polarization via modulating ferroelectric domain orientations remains underexplored. This work uncovers a hidden tetragonalorthorhombic phase transition pathway to engineer domain orientations and further polarization in polycrystalline Hf_{0.5}Zr_{0.5}O₂ using single-crystalline TiN substrates. Specifically, $(001)_{0}$ and/or $(010)_{0}$ domains, which fully contribute to remanent polarization under an electric field, are controllable in Hf_{0.5}Zr_{0.5}O₂ on TiN (001) and (111), enhancing remanent polarization compared to that on TiN (110). The key is the hidden transition from the tetragonal phase's longest **c**-axis to the orthorhombic phase's shorter $\mathbf{b}_0/\mathbf{c}_0$ -axis, alongside the reported one to the longest \mathbf{a}_{0} -axis, assisted by periodic dislocations at the TiN/Hf_{0.5}Zr_{0.5}O₂ interface. These findings shed light on governing the polarization of Hf_{0.5}Zr_{0.5}O₂ films by controlling the interface dislocations and further domain orientations.

 HfO_2 -based ferroelectrics have attracted great attention in terms of both ferroelectric (FE) material science and non-volatile memory applications since their discovery in 2011^{1-15} . Optimizing properties, including remanent polarization (P_r), retention, endurance, switching speed, etc., have been significant issues for ferroelectric memories. It has been well agreed that the ferroelectricity of HfO_2 -based thin films originates from a metastable $Pca2_1$ orthorhombic (O) phase, which is formed during the tetragonal (T) to monoclinic (M) phase transition in thermal annealing^{5,16–18}. Therefore, FE characteristics are typically observed with the coexistence of T-, O-, and M-phases and polycrystalline structure in the films, though epitaxial FE O-phase and FE rhombohedral phase films also have been demonstrated¹⁹⁻²⁴. Thus, the key to controlling the FE properties mainly lies in controlling the phase composition of the films and the content of the O-phase. In the past decade, intensive studies have focused on maximizing the quantity of O-phase through optimization of material and process parameters, such as dopants and doping concentration^{1,8,25-27}, deposition methods and parameters²⁸⁻³², annealing conditions^{33,34}, electrode materials^{35,36}, oxygen vacancy (V_O) concentration^{26,37-39}, film thickness^{40,41}, etc. And, a linear relationship between the content of O-phase and P_r has been established^{26,42}.

¹National Key Lab of Micro/Nano Fabrication Technology, School of Integrated Circuits, Shanghai Jiao Tong University, Shanghai 200240, PR China. ²Department of Micro/Nano Electronics, School of Integrated Circuits, Shanghai Jiao Tong University, Shanghai 200240, PR China. ³Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, PR China. ⁴Shanghai Frontiers Science Research Base of Intelligent Optoelectronics and Perception, Institute of Optoelectronics, Department of Materials Science, Fudan University, Shanghai 200433, PR China. ⁵Department of Physics, University of Science and Technology of China, Hefei 230026 Anhui, People's Republic of China. ^{Image} e-mail: liwenwu@fudan.edu.cn; ywcao@nimte.ac.cn; wangzhen03@ustc.edu.cn; xiuyanli@sjtu.edu.cn

Domains, as another critical fundament for FE materials in addition to the crystal phase, also play a crucial role in controlling FE properties as well known. A FE, or a polar domain, is conventionally defined as a spatial region within a single crystal or grain where the direction of spontaneous polarization remains consistent. While factors such as domain size, shape, and domain walls can affect various ferroelectric properties, the P_r of an FE film is specifically influenced by the out-of-plane component of spontaneous polarization, which is determined by the domain orientation in the film⁴³. For epitaxial ferroelectrics usually with a single-crystalline structure, the texture of the crystal is fixed, and its symmetry is broken in different directions, resulting in multiple domains separated by domain walls^{44,45}. As for HfO₂-based FE films typically with polycrystalline structure and multiple phases, however, not only are multiple domains formed within a crystal grain, but the texture of crystal grains is also relatively flexible, both influencing the contribution of spontaneous polarization to P_{r} as shown in Supplementary Fig. S12. To enhance Pr value, the goal is to achieve as many FE domains as possible which could contribute to P_r as large as possible in O-phase occupied areas, such as $(001)_{O}$ -oriented domains. Meanwhile, it has been reported that the $(010)_{0}$ -oriented domains, whose polarization direction initially lies in-plane of the film, could transform into $(001)_{\Omega}$ -oriented domains under an electric field^{46,47}. So, the goal to engineer domain orientations to get larger P_r becomes to obtain a dominance of (001)₀- and/or (010)₀-oriented FE domains. And, achieving the goal requires engineering both the macroscopic texture of grains and specific domain orientations inside the grains.

The engineering of the texture of HfO_2 -based films has been greatly done by employing single-crystalline substrates, such as yttrium-stabilized zirconia (YSZ)^{21,48–55}, SrTiO₃ (STO)^{20,23,56–59}, and even TiN^{55,60,61}, while the control of domain orientations inside the grains remains a challenge. Notably, the polarized O-phase (*Pca2*₁) generally transforms from the T-phase in HfO₂-based films, so the understanding

and controlling of the specific T-O phase transition pathway is crucial for controlling domain orientations within the crystal grains. For easy comparison of these two phases, a double-sized T-phase unit cell $(a = b = \sqrt{2}a_T, c = c_T)$ has been used^{33,62}. It has been declared that the longest **c**-axis of the T-phase should transform into the longest **a**₀-axis of the O-phase, while the equivalent **a**- and **b**-axes of the T-phase should shift to the similar **b**₀- and **c**₀-axes of the O-phase in T-O phase transition based on lattice parameter differences between T- and O-phases⁶³. And, through such a T-O transition pathway, a study has successfully achieved $(001)_0/(010)_0$ -oriented domains in 7%-YO_{1.5}substituted HfO₂ (YHO-7) films by precisely controlling the epitaxial (100)-oriented T-phase on single-crystalline YSZ (001)⁶². Such a transition way, however, requires strict control of the single-crystalline structure of the T-phase, which is quite challenging for HfO₂-based films and limits their applications greatly.

Here, we conceive that if a T-O phase transition pathway from other orientations of T-phase to (001)0- and/or (010)0-oriented O-phase could be achieved together with the reported one as mentioned above, it would be promising to engineer the dominance of $(001)_{0}$ and/or $(010)_{0}$ oriented domains even in a polycrystalline structure in HfO₂-based films, as schematically shown in Fig. 1. Therefore, in this work, we propose a potential way to approach this goal through controlling the interface dislocations between Hf_{0.5}Zr_{0.5}O₂ (HZO) films and single-crystalline TiN substrates. We perform a systematic investigation of crystalline texture, domain orientation, and interface structure as well as polarization-electric field (P-E) characteristics in HZO on TiN substrates with three different orientations. Our results show that (001)₀- and/or (010)₀-oriented domains can be controlled in polycrystalline and multiple phases of HZO on TiN (001) and (111) with enhanced P_r values in contrast to HZO on TiN (110). This is achieved through a hidden T-O transition pathway from the longest c-axis of the T-phase towards the relatively shorter $\mathbf{b}_{0}/\mathbf{c}_{0}$ -axis of the O-phase, in addition to the reported one towards the





double-sized T-phase unit cell). The direction of polarization (P) should align with the **c**-axis of the O-phase. If hidden T-O transition pathways toward $(010)_{O}$ - and $(001)_{O}$ -oriented O-phases can be realized, it would provide greater flexibility, enabling the engineering of domain orientations and further P_r in polycrystalline HfO₂-based films.



Fig. 2 | Synchrotron-based GIXRD results of pristine $Hf_{0.5}Zr_{0.5}O_2$ films on singlecrystalline TiN substrates with different orientations. a Schematic of the device structure and the synchrotron-based GIXRD measurement setup. The 2D GIXRD image of HZO **b** on TiN (001), **c** on TiN (111), and **d** on TiN (110). (111)_O/(011)_T and $\{002\}_O/(110)_T/(002)_T$ diffraction rings are identified and marked, respectively. The

intensity-azimuth angle (γ) curves of $\{002\}_0/(110)_T/(002)_T$ and $(111)_0/(011)_T$ peaks of HZO **e** on TiN (001), **f** on TiN (111), and **g** on TiN (110). The bottom row illustrates the preferred out-of-plane orientations of specific lattice planes of T- and O-phases in HZO films on TiN (001), (111), and (110), concluded from the GIXRD results.

longest $\mathbf{a}_{\mathbf{0}}$ -axis of the O-phase. Such a hidden phase transition pathway is assisted by the periodic dislocations at the bottom HZO/TiN interface and occurs during the cooling down of the annealing process and possibly in polarization switching cycling as well. Our research highlights the potential for engineering domain orientations and further FE properties in polycrystalline HZO films.

Results and Discussion

Crystalline texture of HZO on different orientations of TiN substrate

The crystalline textures of 10 nm HZO films on single-crystalline TiN (001), (110), and (111) substrates were investigated using the synchrotron-based grazing incidence X-ray diffraction (GIXRD)

technique. The setup and the device structure are schematically shown in Fig. 2a. The excellent single crystallinity of TiN substrates is demonstrated in Supplementary Fig. S1. Although the quality of TiN (111) is not as good as other orientations, it would not fundamentally change the properties of HZO films grown on top (see section (A) of the Supplementary Note). Figure 2b–d shows the 2D GIXRD images of HZO on TiN (001), (111) and (110), respectively, where (111)_O/(011)_T and $\{002\}_O/(110)_T/(002)_T$ diffraction rings at around 30.5° and 35.5° are identified and marked. Here $\{002\}_O$ includes information of $(200)_O$, $(020)_O$, and $(002)_O$ due to their similar lattice distance. Unfortunately, the information of $\{110\}_O$ cannot be obtained directly because the diffraction ring is obscured by the light spot in the center. Firstly, the content of the O-phase among the samples was determined by



Fig. 3 | HRTEM images of $Hf_{0.5}Zr_{0.5}O_2$ films before wake-up on different orientations of TiN substrate. a For HZO on TiN (001), in O-phase occupied areas, the (010)_O-oriented domains are dominant, and the (001)_O-oriented domains appear in a small part of the observed areas. b For HZO on TiN (111), the (010)_O-oriented domains are dominant. c For HZO on TiN (110), the (110)_O-, (101)_O-, and (011)_Ooriented domains are dominant.

analyzing the XRD results and performing investigations with Raman spectroscopy (see section (B) of the Supplementary Note). Interestingly, no obvious difference is observed among HZO films on TiN substrates with different crystalline orientations. This suggests that the orientation of the bottom TiN has a limited effect on adjusting the total content of the O-phase.

Then the in-plane and out-of-plane textures are taken into account. From the marked rings in Fig. 2b-d, the peak intensities of $\{002\}_{O}/(110)_{T}/(002)_{T}$ and $(111)_{O}/(011)_{T}$ for HZO on TiN (001), (111), and (110) were extracted as a function of γ (the azimuth angle) in Fig. 2e-g, respectively. For HZO on TiN (001) and (111), the intensity of the $\{002\}_{O}/(110)_{T}/(002)_{T}$ peak is higher at around $\gamma = 90^{\circ}$ (out-of-plane) than around $\gamma = 30^{\circ}$ and 150° (in-plane), while the $(111)_{O}/(011)_{T}$ peak intensity shows peaks near $y = 35^{\circ}$ and 145°. Both indicate a highly outof-plane orientation of $\{002\}_O$ and $(110)_T/(002)_T$. In contrast, for HZO on TiN (110), two round peaks in the intensity of $(111)_{O}/(011)_{T}$ are observed at $\gamma = 55^{\circ}$ and 125°, indirectly indicating the preferential orientation of $\{110\}_{\Omega}$ and $(112)_T/(020)_T$ at $y = 90^\circ$. A detailed analysis of XRD results is presented in section (C) of the Supplementary Note. These observations suggest that the texture of the T/O grains in HZO films can be engineered by controlling the orientation of the TiN substrate. And, $\{002\}_O/(110)_T/(002)_T$ grains can be controlled out-ofplane by using TiN (001) and TiN (111) substrates, which is the base to further obtain (001)₀- and/or (010)₀-oriented domains. Note that the above diffraction information of $(110)_T$ and $(002)_T$ is obtained based on the original unit cell of the T-phase. With a double-sized unit cell, it should be written as (200)- and (002)-textured. This notation is also used in the following text.

Domain orientations tuning with different orientations of the substrate

To obtain microscopic information on the domains inside the O-phase grains, high-resolution scanning/transmission electron microscopy (S/

HRTEM) investigations on these samples in the pristine state were further carried out, as shown in Fig. 3. The out-of-plane growth direction of the film in different areas can be determined from their corresponding Fast Fourier Transform (FFT) patterns. Consistent with GIXRD results, most of the areas exhibit T-phase in all films (see Supplementary Fig. S14), while O-phase crystals/domains are also observed clearly. In principle, three orientations of domains are predictable from each kind of O-phase texture, for example, $(100)_{0}$, $(010)_{0}$ and $(001)_{0}$ oriented domains are expected from $\{002\}_{0}$ texture. Very interestingly, however, $(010)_{0}$ -oriented domains are dominantly present in O-phase grains on TiN (001), while $(001)_{O}$ -oriented ones appear in some areas from multiple image statistics (Fig. 3a). Both types of domains can contribute to P_r completely. Namely, the (100)₀oriented domain, which has no contribution to P_r , is avoided. For HZO films on TiN (111), as shown in Fig. 3b, (010)₀-oriented domains are also predominantly present, while (001)₀-oriented domains are not found along with $(100)_{0}$ -oriented ones in the observed areas. Additionally, a minor fraction of $(111)_{\Omega}$ -oriented domains is also observed in this case (see Supplementary Fig. S15). In contrast, all three kinds of $(101)_{0}$ -, $(110)_{0}$, and $(011)_{0}$ -oriented domains predicted from the out-of-plane texture of {110}o in XRD results are observed in HZO grains on TiN (110). Since the co-axes (aligned with the spontaneous polarization direction) of $(101)_{O}$ - and $(011)_{O}$ -oriented domains form a 45° angle with the out-of-plane direction, they can only contribute partially to P_r , while the $(110)_{O}$ -oriented domains have no contribution to P_r due to the in-plane c_0 -axis orientation. Thus, these domains are limited to getting high P_r theoretically. Nevertheless, these results clearly demonstrate the tuning effect of TiN substrate orientation on domain orientations in HZO. And, the goal to get the dominance of $(001)_{0}$ and/or $(010)_{0}$ -oriented domains in polycrystalline HZO is achievable by employing a TiN (001) substrate and possibly by using TiN (111) as well.

P_r engineering beyond O-phase content controlling

The effect of domain orientation on the P_r value of HZO is further considered. As mentioned in the introduction part, the Pr value of HZO is conventionally controlled by the content of the O-phase. Our HZO films on different orientations of TiN substrates show a similar content of O-phase but different domain orientations. And, in principle, the predominant (001)₀- and/or (010)₀-oriented domains in HZO on TiN (001) and (111) should enable enhanced P_r performance in contrast to that on TiN (110) even though O-phase content is similar. To confirm this, we experimentally investigated the P-E characterizations of the above samples. Figure 4a-c shows P-E curves of HZO films on three orientations of TiN substrates in the pristine state and after wake-up. Pristinely, all devices displayed an antiferroelectric (AFE)-like characterization, consistent with a large T-phase content in this state. After wake-up, typical FE P-E hysteresis curves were observed for all three samples. The comparison of P_r values after wake-up in three cases is shown in Fig. 4d. Clearly, the 2Pr of HZO on TiN (001) is slightly larger than that of HZO on TiN (111) but notably higher than that on TiN (110). The slightly smaller P_r of HZO on TiN (111) than that on TiN (001) should be due to the effect of a small part of (111)₀-oriented domains whose spontaneous polarization contributes to P_r partly. Therefore, these results are exactly as expected from the predominant orientation of domains in HZO on each substrate. In addition, Pr evolutions in wake-up were also conducted as shown in Fig. 4e. During the polarization switching cycling, the difference in the P_r values of HZO films on TiN (001)/(111) from HZO on TiN (110) becomes larger. Thus, HZO films on TiN (001)/(111) exhibit an enhanced wake-up effect compared with those on TiN (110), macroscopically. Furthermore, Fig. 4f compares the relationship between P_r and O-phase content in the reported literature^{26,42} and this work. Despite the reported linear relationship, our results directly and clearly demonstrated that the P_r value can be controlled by domain orientations beyond the O-phase content.



Fig. 4 | Electrical characterizations of $Hf_{0.5}Zr_{0.5}O_2$ capacitors with different orientations of TiN substrate. P-E hysteresis curves of HZO capacitors **a** on TiN (001), **b** on TiN (111), and **c** on TiN (110) in the pristine state and after wake-up. **d** The comparison of after-wake-up P-E hysteresis curves of HZO capacitors on different

orientations of TiN substrate. **e** The wake-up evolution of HZO capacitors on different orientations of TiN substrate. **f** The linear relationship between the value of P_r and the O-phase content of HZO film reported in literature^{26,42} and in our work.

A hidden T-O phase transition pathway resulting in domain orientation tuning

Finally, we discuss how the domain orientations and P_r values are affected by the orientation of the TiN substrate. It is particularly important to understand how the (100)₀-oriented domain, whose polarization has no contribution to P_{r_i} is avoided in HZO films on TiN (001) and (111), which is critical for enhancing the P_r value. As introduced, the T-O phase transition pathway is the key to understanding. By employing synchrotron-based in-situ GIXRD investigation for HZO on TiN (001) in annealing (see section (D) of the Supplementary Note), we confirmed that the $\{002\}_{O}$ -oriented O-phase (mixture of $(200)_{O}$, $(020)_{O}$, and $(002)_{O}$ is transformed from $(110)_{T}/(002)_{T}$ -oriented T-phase, which aligns with the GIXRD and S/HRTEM results discussed earlier. To get more intuitive insights, in-situ TEM investigations in thermal annealing were further performed. As demonstrated in Fig. 5a, b, (002)_T-oriented T-phase nucleated first in the heating process, observed under the microscope at 550 °C. After cooling to room temperature (RT), it transited to $(020)_{\Omega}$ -oriented O-phase partly, with remaining T-phase part intergrown with transited O-phase in the same grain. Namely, a T-O transition pathway, where the longest c-axis of the T-phase transforms to the shorter $\mathbf{b}_{\mathbf{0}}$ -axis of the O-phase, is observed. Interestingly, this transition pathway is fundamentally different from the previously reported one where the longest c-axis of the T-phase transforms to the longest ao-axis of the O-phase, so we consider it a hidden T-O phase transition pathway. Moreover, the reported T-O transition from $(110)_{T}$ -oriented T-phase to $(020)_{O}$ -oriented O-phase is also observed (see Supplementary Fig. S17). The $(002)_{0}$ -oriented one observed in some areas in the HRTEM images may arise from this transition as well, considering the similar lattice constants of b_0 and c_0 . Therefore, through both the hidden and reported T-O phase transition pathways, the dominance of $(020)_{0}$ and $(002)_{0}$ oriented O-phase (i.e., $(010)_{\Omega}$ and $(001)_{\Omega}$ oriented domains) whose spontaneous polarization could completely contribute to P_r under the electric field, is achieved in O-phase areas of polycrystalline HZO on TiN (001) after annealing.

Next, we discuss how the hidden transition happens. Notably, despite the large interface lattice mismatch between TiN and HZO. epitaxial growth of T/O grains is realizable locally through periodic dislocations. The period of the interface dislocations is determined by the lattice mismatch between HZO and TiN. More specifically, as shown in Fig. 5c and the amplified atom arrangement images derived from it, the a-axis of the T-phase aligns with that of TiN at the interface, with periodic dislocations occurring every 5 double-sized T-phase unit cells with 6 TiN unit cells, forming a (002)-oriented T-phase. This is understandable because the lattice constant along the a-axis of the T-phase is about 6/5 of that in TiN. The intergrown (020)₀-oriented O-phase also follows similar interface dislocations. Additionally, as shown in Fig. 5d, the strain map derived from Fig. 5c indicates that the lattice-mismatch-induced stress is primarily concentrated at the interface dislocations but released within the film. Therefore, it is considered that the interface dislocations provide tolerance, enabling the hidden phase transition inside HZO grains with the release of strain. In this way, the **a**-axis of the T-phase transforms to the **c**₀-axis of the O-phase, while the longest c-axis of the T-phase transforms to the shorter $\mathbf{b}_{\mathbf{0}}$ - rather than the longest $\mathbf{a}_{\mathbf{0}}$ -axis of the O-phase, resulting in $(010)_{O}$ -oriented domains while avoiding $(100)_{O}$ -oriented ones. This is also understandable because the (100)_O plane exhibits a buckling structure, with Hf/Zr atoms shifting along the out-of-plane (**a**₀-axis) direction, which disturbs the flatness of the $(100)_0$ plane, introducing strain and raising its formation energy (see Supplementary Fig. S18). Moreover, the lattice constant along the **a**-axis of the T-phase is similar to that along the c_0 -axis of the O-phase, making this transition easier to happen.

As for HZO on TiN (111), the transition from the longest **c**-axis of (110)_T-oriented T-phase to the shorter **c**₀-axis of the intergrown O-phase is observed, leading to $(010)_{O}$ -oriented domains and avoiding



Fig. 5 | **Hidden T-O transition pathway in Hf_{0.5}Zr_{0.5}O₂ on TiN (001). a**, **b** The insitu HRTEM images in annealing showing the hidden T-O transition pathway from the **c**-axis of T-phase to the **b**₀-axis of O-phase. Solid red lines mark grain boundaries in the film, and dashed lines highlight the T-O phase boundaries within a single grain. **c** The HRTEM image showing the intergrowth of T- and O-phases within a grain of HZO on TiN (001) after annealing. The amplified atom arrangement images on the right reveal periodic dislocations at the interface between HZO and TiN

(001), occurring at regular intervals of every 5 HZO cells with 6 TiN cells. **d** The strain map calculated from diffraction spots marked by the circle. Periodic dislocations are generated at the interface with the release of strain, which contributes to local epitaxial growth of HZO on TiN (001). **e** Schematics of the hidden T-O transition pathway observed from the HRTEM images. The **c**-axis of the T-phase transforms into the **b**₀-axis of the O-phase. Simultaneously, the **a**- and **b**-axes of the T-phase transform into **c**₀- and **a**₀-axes of the O-phase, respectively.

 $(100)_{O}$ -oriented ones like the case on TiN (001) (Supplementary Fig. S19b). $(001)_{O}$ -oriented domains are not observed, possibly due to the different space tolerance at the interface or the limited areas observed. As for HZO on TiN (110), both reported and hidden T-O transitions occur possibly, forming three kinds of $(101)_{O}$ -, $(011)_{O}$ -, and $(110)_{O}$ -oriented domains due to its different interface structure (Supplementary Fig. S19c).

In addition, considering the wake-up difference on three orientations of TiN substrates, our recent study demonstrated that the T-O phase transition continues in polarization switching cycling, resulting in a wake-up effect from AFE-like characteristics to FE properties⁶⁴. S/HRTEM images of HZO films on TiN (001) after wake-up reveal a significant increase in $(020)_O/(002)_O$ -oriented O-phase while a reduction in $(110)_T/(002)_T$ -oriented T-phase, confirming a substantial T-O transition during wake-up (Supplementary Fig. S21), consistent with the P-E loop changes in Fig. 4. T-O phase transition under polarization switching cycling is like a continuation of T-O phase transition in thermal annealing. Both should happen through the pathway with the smallest energy barrier. So, we consider that a similar T-O phase transition pathway also appears in the wake-up of HZO, which is indicated by the intergrowth grain in TEM images. Since the T-phase content is very high and the T-O phase transition is not sufficient before wake-up, the P_r difference is not obvious in the pristine state. While the T-O phase transition becomes much more sufficient after wake-up in polarization switching, the P_r difference becomes much more obvious.

In conclusion, the control of $(001)_{O}$ - and/or $(010)_{O}$ -oriented domains in O-phase grains of polycrystalline HZO, whose spontaneous polarization can contribute to P_r completely, has been achieved along with enhanced P_r by employing TiN (001) and TiN (111) singlecrystalline substrates. This achievement benefits from a hidden transition from the longest **c**-axis of the T-phase to the shorter **b**_O- or **c**_O-axis of the O-phase in intergrown T/O grains assisted by the periodic interface dislocations in addition to reported one from the longest **c**-axis of the T-phase to the longest **a**_O-axis of O-phase. These findings shed light on governing the domain orientations and FE properties of HZO by controlling the interface dislocations.

Methods

Device fabrication

(1) Synthesis of TiN bottom electrodes: epitaxial TiN thin films were deposited on (001)-, (110)-, and (111)-oriented MgO substrates by a homemade magnetron sputtering epitaxy system using a 2-inch Ti

(purity of 99.995%) target and the N₂ (purity of 99.999%) reactive gas. The base vacuum pressure of the growth chamber is 3×10^{-8} Torr. The TiN films were deposited at a temperature of 1100 °C under a pure nitrogen pressure of 0.02 Torr. During the deposition, all three MgO substrates were mounted on a rotatable SiC absorber heated by a laser. The temperature of MgO substrates was monitored at the back side of the SiC absorber using an infrared pyrometer. To ensure uniformity, the sample holder was rotated at a speed of 5 rpm throughout the deposition. The radio frequency (RF) generator power was kept at 100 W throughout the entire deposition process.

(2) Growth of HZO films: HZO films were deposited on TiN bottom electrodes using thermal ALD (TFS200 Beneq Thermal/Plasma Enhanced Atomic Layer Deposition) at a substrate temperature of 250 °C. Hf(N(CH₃)₂)₄, Zr(N(CH₃)₂)₄, and H₂O were used as the Hf precursor, Zr precursor, and oxygen source, respectively. The growth rates per cycle of HfO₂ and ZrO₂ were nearly identical (0.09 and 0.07 nm/cycle, respectively). Therefore, HZO films with a 0.5:0.5 Hf: Zr ratio could be deposited by using a 1:1 HfO₂:ZrO₂ ALD cycle ratio, with a 0.5 s H₂O dose time in each cycle.

(3) Growth of top electrodes: first, 30-nm-thick poly-TiN top electrodes were deposited via reactive magnetron sputtering at room temperature through a hard shadow mask with three different hole sizes (-6800, 11,800, 38,000 μ m²). The base pressure was reduced to 4×10^{-4} Pa, the sputter power was set to 250 W, and the gas atmosphere consisted of Ar: N₂ in a ratio of 50:4 sccm. Then, 30-nm-thick W electrodes were deposited without removing the hard mask, the sputter power for W is 80 W and the atmosphere is Ar = 30 sccm. After the top electrode deposition, post-metallization annealing (PMA) was performed for 30 s at 550 °C in an N₂ atmosphere to promote the crystallization of the HZO films.

Electrical characterizations

The electrical measurements were carried out using a Cascade Microtech Summit 11000 B-S Semi-automated Probe Station, which is a commonly used apparatus for such purposes in the field. During all electrical measurements, a bias voltage was applied to the top electrode, and the bottom electrode was grounded. Polarization-electric field curves were measured utilizing a semiconductor parameter analyzer (Keithley 4200A-SCS) operating at a frequency of 1 kHz. Meanwhile, endurance tests were conducted at a frequency of 250 kHz with an applied electric field of 3.5 MV/cm.

Structural characterizations

(1) GIXRD characterizations: the 2θ - ω scans were conducted using a high-resolution X-ray diffractometer (Bruker D8 Discovery). Monochromatic Cu K α radiation with a wavelength of 1.5406 Å was utilized for this purpose. The GIXRD measurements were carried out at the 02U2 beamline situated within the Shanghai Synchrotron Radiation Facility (SSRF), where a fixed energy of 10 keV ($\lambda = 1.24$ Å) and an incidence angle of 3° were employed. 2θ of high energy X-ray $(\lambda_1 = 1.24 \text{ Å})$ is converted into Cu-K α form $(\lambda_2 = 1.54 \text{ Å})$ based on $\lambda_1/2$ $\sin\theta_1 = \lambda_2 / \sin\theta_2$ for a convenience. For in-situ 2D-GIXRD investigation during the thermal annealing process, crystalline information was captured by a MarCCD 225 detector every 3 s during annealing in N₂. The thermal annealing procedure consisted of three distinct stages: heating at a controlled rate of 20 °C/min, holding the temperature at 550 °C for 5 min, and cooling at a 30 °C/min rate. The 2D diffraction images obtained were processed and converted into one-dimensional XRD data using Fit2D and Dioptas software, enabling detailed analysis of the structural evolution during the annealing process.

(2) Raman spectroscopy: Raman measurements were carried out at room temperature with a Raman microscope (Renishaw inVia Qontor), using a 532 nm wavelength laser, 100× objective lens, and 100 s total measurement time per spectrum.

(3) TEM characterizations: STEM samples were prepared using a focused ion beam with Ga⁺ ions to a thickness of ~30 nm. Scanning transmission electron microscopy (STEM) and High-Resolution Transmission Electron Microscopy (HRTEM) imaging were performed on a Thermo Scientific Themis Z microscope operating at 300 keV and equipped with a spherical aberration corrector for the condenser lens. The atomic-resolution high-angle annular dark-field (HAADF) STEM image was collected with a 25-mrad convergent angle and a collection angle of 41-200 mrad. The analysis of the FFT patterns was employed to determine the phase of HZO. The in-plane strain map (ε_{rr}) was calculated using the Geometric Phase Analysis (GPA) method. A PicoFemto in-situ MEMS heating TEM holder was employed to investigate the temperature-dependent structural evolution of the HZO film using high-resolution imaging. The sample was heated from RT to 550 °C at a rate of 20 °C per minute, held at 550 °C for 1.5 h, and then cooled down to RT at a rate of 30 °C per minute.

Data availability

The data generated in this study are provided in the Source Data file. Source data are provided with this paper.

References

- Böscke, T. S., Müller, J., Bräuhaus, D., Schröder, U. & Böttger, U. Ferroelectricity in hafnium oxide thin films. *Appl. Phys. Lett.* **99**, 102903 (2011).
- Böscke, T. M. J., Bräuhaus, D., Schröder, U. & Böttger, U. Ferroelectricity in hafnium oxide CMOS compatible ferroelectric field effect transistors. In 2011 IEEE International Electron Devices Meeting (IEDM 2011) 24.25, 24 (IEEE, 2011).
- 3. Müller, J. et al. Ferroelectricity in HfO2 enables nonvolatile data storage in 28 nm HKMG. In 2012 Symposium on VLSI Technology (VLSIT) (IEEE, 2012).
- 4. Müller, J. et al. Ferroelectricity in simple binary ZrO₂ and HfO₂. *Nano Lett.* **12**, 4318–4323 (2012).
- Huan, T. D., Sharma, V., Rossetti, G. A. & Ramprasad, R. Pathways towards ferroelectricity in hafnia. *Phys. Rev. B* 90, 064111 (2014).
- 6. Park, M. H. et al. Ferroelectricity and antiferroelectricity of doped thin HfO₂-based films. *Adv. Mater.* **27**, 1811–1831 (2015).
- Fujii, S. et al. First demonstration and performance improvement of ferroelectric HfO₂-based resistive switch with low operation current and intrinsic diode property. in 2016 IEEE Symposium on VLSI Technology (IEEE, USA).
- Kim, S. J., Mohan, J., Summerfelt, S. R. & Kim, J. Ferroelectric Hf_{0.5}Zr_{0.5}O₂ thin films: a review of recent advances. JOM **71**, 246–255 (2018).
- Toriumi, A. et al. Material perspectives of HfO₂-based ferroelectric films for device applications. in *IEEE International Electron Devices Meeting* (IEEE, 2019).
- Sebastian, A., Le Gallo, M., Khaddam-Aljameh, R. & Eleftheriou, E. Memory devices and applications for in-memory computing. *Nat. Nanotechnol.* 15, 529–544 (2020).
- 11. Cheema, S. S. et al. Enhanced ferroelectricity in ultrathin films grown directly on silicon. *Nature* **580**, 478–482 (2020).
- 12. Mikolajick, T., Schroeder, U. & Slesazeck, S. The past, the present, and the future of ferroelectric memories. *IEEE Trans. Electron Devices* **67**, 1434–1443 (2020).
- Mulaosmanovic, H. et al. Ferroelectric field-effect transistors based on HfO₂: a review. *Nanotechnology* **32**, 502002 (2021).
- Schroeder, U., Park, M. H., Mikolajick, T. & Hwang, C. S. The fundamentals and applications of ferroelectric HfO₂. *Nat. Rev. Mater.* 7, 653–669 (2022).
- Silva, J. P. B. et al. Roadmap on ferroelectric hafnia- and zirconiabased materials and devices. *APL Mater.* **11**, 089201 (2023).

- Sang, X., Grimley, E. D., Schenk, T., Schroeder, U. & LeBeau, J. M. On the structural origins of ferroelectricity in HfO₂ thin films. *Appl. Phys. Lett.* **106**, 162905 (2015).
- Barabash, S. V. Prediction of new metastable HfO2 phases: toward understanding ferro- and antiferroelectric films. *J. Comput. Electron.* 16, 1227–1235 (2017).
- Xu, L. et al. Kinetic pathway of the ferroelectric phase formation in doped HfO₂ films. J. Appl. Phys. **122**, 124104 (2017).
- Fina, I. & Sánchez, F. Epitaxial ferroelectric HfO₂ films: growth, properties, and devices. ACS Appl. Electron. Mater. 3, 1530–1549 (2021).
- Song, T. et al. Epitaxial ferroelectric La-doped Hf_{0.5}Zr_{0.5}O₂ thin films. ACS Appl. Electron. Mater. 2, 3221–3232 (2020).
- Suzuki, T., Shimizu, T., Mimura, T., Uchida, H. & Funakubo, H. Epitaxial ferroelectric Y-doped HfO₂ film grown by the RF magnetron sputtering. Jpn. J. Appl. Phys. 57, 11UF15 (2018).
- El Boutaybi, A., Maroutian, T., Largeau, L., Matzen, S. & Lecoeur, P. Stabilization of the epitaxial rhombohedral ferroelectric phase in ZrO₂ by surface energy. *Phys. Rev. Mater.* 6, 074406 (2022).
- 23. Wei, Y. et al. A rhombohedral ferroelectric phase in epitaxially strained Hf_{0.5}Zr_{0.5}O₂ thin films. *Nat. Mater.* **17**, 1095–1100 (2018).
- 24. Zhang, Y., Yang, Q., Tao, L., Tsymbal, E. Y. & Alexandrov, V. Effects of strain and film thickness on the stability of the rhombohedral phase of HfO₂. *Phys. Rev. Appl.* **14**, 014068 (2020).
- Mueller, S. et al. Incipient ferroelectricity in Al-doped HfO₂ thin films. Adv. Funct. Mater. 22, 2412–2417 (2012).
- Schroeder, U. et al. Recent progress for obtaining the ferroelectric phase in hafnium oxide based films: impact of oxygen and zirconium. *Jpn. J. Appl. Phys.* 58, SL0801 (2019).
- 27. Schroeder, U. et al. Lanthanum-doped hafnium oxide: a robust ferroelectric material. *Inorg. Chem.* **57**, 2752–2765 (2018).
- Zarubin, S. et al. Fully ALD-grown TiN/Hf_{0.5}Zr_{0.5}O₂/TiN stacks: ferroelectric and structural properties. *Appl. Phys. Lett.* **109**, 192903 (2016).
- 29. Kim, K. M., Jang, J. S., Yoon, S. G., Yun, J. Y. & Chung, N. K. Structural, optical and electrical properties of HfO2 thin films deposited at low-temperature using plasma-enhanced atomic layer deposition. *Materials* **13**, 2008 (2020).
- Luo, Q. et al. Composition-dependent ferroelectric properties in sputtered Hf_xZr_{1-x}O₂ thin films. *IEEE Electron Device Lett.* 40, 570–573 (2019).
- Mittmann, T. et al. Origin of ferroelectric phase in undoped HfO₂ films deposited by sputtering. Adv. Mater. Interfaces 6, 1900042 (2019).
- Hsain, H. A. et al. Many routes to ferroelectric HfO₂: a review of current deposition methods. *J. Vac. Sci. Technol. A* 40, 010803 (2022).
- Hyuk Park, M. et al. Evolution of phases and ferroelectric properties of thin Hf_{0.5}Zr_{0.5}O₂ films according to the thickness and annealing temperature. *Appl. Phys. Lett.* **102**, 242905 (2013).
- Lomenzo, P. D., Takmeel, Q., Moghaddam, S. & Nishida, T. Annealing behavior of ferroelectric Si-doped HfO₂ thin films. *Thin* Solid Films 615, 139–144 (2016).
- 35. Hoffmann, M. et al. Stabilizing the ferroelectric phase in doped hafnium oxide. J. Appl. Phys. **118**, 072006 (2015).
- 36. Kim, S. J. et al. A comprehensive study on the effect of TiN top and bottom electrodes on atomic layer deposited ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ thin films. *Materials* **13**, 2968 (2020).
- Lin, Y.-J. et al. Role of electrode-induced oxygen vacancies in regulating polarization wake-up in ferroelectric capacitors. *Appl. Surf. Sci.* 528, 147014 (2020).
- Shimizu, T. et al. Contribution of oxygen vacancies to the ferroelectric behavior of Hf_{0.5}Zr_{0.5}O₂ thin films. *Appl. Phys. Lett.* **106**, 112904 (2015).
- Hsain, H. A. et al. Role of oxygen source on buried interfaces in atomic-layer-deposited ferroelectric hafnia–zirconia thin films. ACS Appl. Mater. Interfaces 14, 42232–42244 (2022).

- Kim, S. J. et al. Effect of film thickness on the ferroelectric and dielectric properties of low-temperature (400 °C) Hf_{0.5}Zr_{0.5}O₂ films. *Appl. Phys. Lett.* **112**, 172902 (2018).
- Mimura, T., Shimizu, T., Katsuya, Y., Sakata, O. & Funakubo, H. Thickness- and orientation-dependences of Curie temperature in ferroelectric epitaxial Y doped HfO₂ films. *Jpn. J. Appl. Phys.* 59, SGGB04 (2020).
- 42. Alcala, R. et al. The electrode-ferroelectric interface as the primary constraint on endurance and retention in HZO-based ferroelectric capacitors. *Adv. Funct. Mater.* **33**, 2303261 (2023).
- 43. Lee, D. H. et al. Domains and domain dynamics in fluorite-structured ferroelectrics. *Appl. Phys. Rev.* **8**, 021312 (2021).
- 44. Bhattacharya, K. & Ravichandran, G. Ferroelectric perovskites for electromechanical actuation. *Acta Mater.* **51**, 5941–5960 (2003).
- Zheng, T., Wu, J., Xiao, D. & Zhu, J. Recent development in lead-free perovskite piezoelectric bulk materials. *Prog. Mater. Sci.* 98, 552–624 (2018).
- Shimizu, T. et al. Ferroelectricity mediated by ferroelastic domain switching in HfO₂-based epitaxial thin films. *Appl. Phys. Lett.* **113**, 212901 (2018).
- Lederer, M. et al. Local crystallographic phase detection and texture mapping in ferroelectric Zr doped HfO₂ films by transmission-EBSD. Appl. Phys. Lett. **115**, 222902 (2019).
- Shimizu, T. et al. The demonstration of significant ferroelectricity in epitaxial Y-doped HfO₂ film. Sci. Rep. 6, 32931 (2016).
- Katayama, K. et al. Growth of (111)-oriented epitaxial and textured ferroelectric Y-doped HfO₂ films for downscaled devices. *Appl. Phys. Lett.* **109**, 112901 (2016).
- Mimura, T. et al. Effects of heat treatment and in situ hightemperature X-ray diffraction study on the formation of ferroelectric epitaxial Y-doped HfO₂ film. *Jpn. J. Appl. Phys.* 58, SBBB09 (2019).
- Mimura, T., Shimizu, T., Uchida, H., Sakata, O. & Funakubo, H. Thickness-dependent crystal structure and electric properties of epitaxial ferroelectric Y₂O₃-HfO₂ films. *Appl. Phys. Lett.* **113**, 102901 (2018).
- Shimura, R. et al. Preparation of near-1-µm-thick {100}-oriented epitaxial Y-doped HfO₂ ferroelectric films on (100)Si substrates by a radio-frequency magnetron sputtering method. *J. Ceram. Soc. Jpn.* **128**, 539–543 (2020).
- Shiraishi, T. et al. Fabrication of ferroelectric Fe doped HfO₂ epitaxial thin films by ion-beam sputtering method and their characterization. Jpn. J. Appl. Phys. 57, 11UFO2 (2018).
- Shiraishi, T. et al. Formation of the orthorhombic phase in CeO₂-HfO₂ solid solution epitaxial thin films and their ferroelectric properties. *Appl. Phys. Lett.* **114**, 232902 (2019).
- Li, T. et al. Epitaxial ferroelectric Hf_{0.5}Zr_{0.5}O₂ thin film on a buffered YSZ substrate through interface reaction. *J. Mater. Chem. C.* 6, 9224–9231 (2018).
- Lyu, J., Fina, I., Solanas, R., Fontcuberta, J. & Sánchez, F. Robust ferroelectricity in epitaxial Hf_{1/2}Zr_{1/2}O₂ thin films. *Appl. Phys. Lett.* 113, 082902 (2018).
- Lyu, J. et al. Enhanced ferroelectricity in epitaxial Hf_{0.5}Zr_{0.5}O₂ thin films integrated with Si(001) using SrTiO₃ templates. *Appl. Phys. Lett.* **114**, 222901 (2019).
- 58. Li, X. et al. Ferroelectric properties and polarization fatigue of La:HfO₂ thin-film capacitors. *Phys. Status Solidi RRL* **15**, 2000481 (2021).
- Li, T. et al. Origin of ferroelectricity in epitaxial Si-doped HfO₂ films. ACS Appl. Mater. Interfaces 11, 4139–4144 (2019).
- 60. Lee, Y. et al. The influence of crystallographic texture on structural and electrical properties in ferroelectric $Hf_{0.5}Zr_{0.5}O_2$. J. Appl. Phys. **132**, 244103 (2022).
- Lombardo, S. F. et al. Local epitaxial-like templating effects and grain size distribution in atomic layer deposited Hf_{0.5}Zr_{0.5}O₂ thin film ferroelectric capacitors. *Appl. Phys. Lett.* **119**, 092901 (2021).

- Katayama, K. et al. Orientation control and domain structure analysis of {100}-oriented epitaxial ferroelectric orthorhombic HfO₂-based thin films. J. Appl. Phys. **119**, 134101 (2016).
- Hyuk Park, M., Joon Kim, H., Jin Kim, Y., Moon, T. & Seong Hwang, C. The effects of crystallographic orientation and strain of thin Hf_{0.5}Zr_{0.5}O₂ film on its ferroelectricity. *Appl. Phys. Lett.* **104**, 072901 (2014).
- Chen, D. et al. Correlation between crystal phase composition, wake-up effect, and endurance performance in ferroelectric Hf_xZr_{1-x}O₂ thin films. *Appl. Phys. Lett.* **122**, 212903 (2023).

Acknowledgements

This work was supported by National Key R&D Program of China (2022YFB3608400 [X.L.], 2024YFF0508500 [Y.C.], 2022YFA1403000 [Y.C.]), Shanghai Science and Technology Innovation Action Plan (24JD1401900 [X.L.]), National Natural Science Foundation of China (62274109 [X.L.], 62374043 [W.L.], 62450003 [X.L.], 52350195 [M.S.], 12304035 [Z.W.]), and Shanghai Pilot Program for Basic Research—Shanghai Jiao Tong University (21TQ1400212 [M.S.]). We thank the Shanghai Synchrotron Radiation Facility of BL02U2 (https://cstr.cn/31124.02.SSRF.BL02U2) and Dr. Yuanhe Sun and Dr. Xu Zheng for the assistance with GIXRD measurements. We also thank Xin Zhang from the Analytical and Testing Center of Hunan University for his support with the in-situ TEM experiments, and the Aberration-Corrected Microscopy Laboratory at the same center for instrumental support. We also thank Living Wu from the Center of Advanced Electronic Materials and Devices (AEMD) of Shanghai Jiao Tong University for supporting the atomic layer deposition of HZO films.

Author contributions

Y.C., Z.W., W.L., and X.L. conceived the idea and supervised the experiments and analysis. Y.F., S.Z., and J.Z. performed the device fabrication. Y.F. and Z.X. performed and participated in the GIXRD measurement and analysis. Z.W. performed the S/HRTEM measurement and analysis. Y.F., Y.D., and D.C. performed and participated in the electrical measurement. J.L., M.S., C.L., W.L., and J.C. provide critical suggestions. X.L. and Y.F. co-wrote the manuscript, and all authors commented on it.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information The online version contains supplementary material available at https://doi.org/10.1038/s41467-025-59519-2.

Correspondence and requests for materials should be addressed to Wenwu Li, Yanwei Cao, Zhen Wang or Xiuyan Li.

Peer review information *Nature Communications* thanks Ignasi Fina, Jan-Chi Yang, and the other, anonymous, reviewer(s) for their contribution to the peer review of this work. A peer review file is available.

Reprints and permissions information is available at http://www.nature.com/reprints

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http:// creativecommons.org/licenses/by-nc-nd/4.0/.

© The Author(s) 2025