**Structural Polymorphism Kinetics Promoted by Charged Oxygen Vacancy in HfO$_2$**

Li-Yang Ma$^{1,2}$ and Shi Liu$^{2,3,*}$

$^1$Fudan University, Shanghai 200433, China

$^2$Key Laboratory for Quantum Materials of Zhejiang Province, Department of Physics, Westlake University, Hangzhou, Zhejiang 310024, China

$^3$Institute of Natural Sciences, Westlake Institute for Advanced Study, Hangzhou, Zhejiang 310024, China

(Dated: April 22, 2022)

**Abstract**

Defects such as oxygen vacancy are widely considered to be critical for the performance of HfO$_2$-based devices, and yet atomistic mechanisms underlying various exotic effects such as wake-up and fluid imprint remain elusive. Here, guided by a lattice-mode-matching criterion, we systematically study the phase transitions between different polymorphs of hafnia under the influences of neutral and positively charged oxygen vacancies by mapping out the minimum energy pathways using a first-principles-based variable-cell nudged elastic band technique. We find that the positively charged oxygen vacancy can substantially promote the transition of various nonpolar phases to the polar phase kinetically, enabled by a transient high-energy tetragonal phase and extreme charge-carrier-inert ferroelectricity of the polar $Pca_{21}$ phase. The intricate coupling between structural polymorphism kinetics and the charge state of the oxygen vacancy has important implications for the origin of ferroelectricity in HfO$_2$-based thin films as well as wake-up, fluid imprint, and inertial switching.

*liushi@westlake.edu.cn*
Ferroelectric memory has long been considered as a competitive non-volatile information storage technology because of various merits such as fast switching rate, low power consumption, and high endurance [1–3]. However, conventional perovskite ferroelectrics have complex compositions and poor compatibility with the modern complementary metal oxide semiconductor (CMOS) technology, severely limiting the scalability of ferroelectric memory [4]. The discovery of ferroelectricity in silicon doped thin films of hafnium oxide in 2011 [5] has quickly made HfO$_2$ a leading candidate material for incorporating ferroelectric functionalities into integrated circuits. Thanks to its robust electric dipoles at the nanoscale [6], simple composition, and the CMOS compatibility, HfO$_2$-based ferroelectrics have already been implemented in several memory devices [7, 8].

The commercialization of ferroelectric HfO$_2$-based devices is mainly hindered by the device reliability issues associated with the profound wake-up effect, strong imprint, and limited endurance [9, 10]. For example, the imprint effect, manifested as the shift of a hysteresis loop along the voltage axis with time, will destabilize one of the polarization states and cause retention loss [11]. It is now widely accepted that the polar orthorhombic (PO) $Pca2_1$ phase of HfO$_2$ is responsible for the ferroelectricity [12–16], despite being higher in energy than the nonpolar monoclinic (M) $P2_1/c$ phase. The origin of the stabilization of the PO phase in thin films remains debated, and has been attributed to the concerted effects of a wide range of extrinsic factors such as finite size and surface/interface effects of grains [12, 16–20], clamping stress [21–23], defects [24–30], and electric fields [22]. The as-prepared HfO$_2$-based thin film often contains high volume factions of nonpolar M phase and tetragonal (T) $P4_2/nmc$ phase [26, 31, 32]. Several models have been proposed to explain the performance instability of ferroelectric HfO$_2$-based devices during electrical cycling, and they can be categorized into two groups: (i) defects and their evolution; (2) electric field-induced structural polymorphism that may originate from defects [33]. In this work, we discover an intricate coupling between structural polymorphism kinetics and the charge state of the oxygen vacancy that has important implications for the origin of ferroelectricity and several device reliability issues in HfO$_2$-based thin films.

We start by emphasizing two unique features of the ferroelectric PO phase that are different from perovskite ferroelectrics. First, the $X_7^-$ lattice mode characterized by antiparallel $x$-displacements of neighboring oxygen atoms in the $yz$ plane (Fig. 1a) plays an important
role in structural polymorphism of HfO$_2$. Though phase transitions between different polymorphs of HfO$_2$ have been investigated with density functional theory (DFT) calculations previously [23], the importance of the X$_2^-$ mode matching was not appreciated. There could be multiple pathways connecting two phases depending on the choice of atom-to-atom mapping. We find that an atomic mapping that conserves the sign of the X$_2^-$ mode gives a lower enthalpy barrier than a mapping that reverses the X$_2^-$ mode. Taking the phase transition of T→PO as an example (Fig. 1a), the X$_2^-$-sign-conserving pathway has an enthalpy barrier of 2.5 meV per formula unit (f.u.), much lower than the pathway with the X$_2^-$ mode reversed (47.5 meV/f.u.). It is noted that recent DFT studies also found that the polarization switching in the PO phase during which the X$_2^-$ mode is revered has to overcome a large barrier [34]. The small enthalpy barrier of T→PO already hints at the importance of nonpolar-polar structural polymorphism in HfO$_2$-based devices.

Another intriguing feature is the extreme charge-carrier-inert ferroelectricity in the PO phase of HfO$_2$. We compute the polar atomic displacements in ferroelectric tetragonal BaTiO$_3$ and the PO phase of HfO$_2$ as a function of charge-carrier concentration obtained via the background-charge method [35]. Consistent with a recent study [36], both hole doping and electron doping quickly suppress the polar displacements in tetragonal BaTiO$_3$. In sharp contrast, the local atomic displacements of polar oxygen atoms in the PO phase of HfO$_2$ are rather insensitive to charge-carrier doping (Fig. 1b). Such feature, likely resulting from the improper nature of the ferroelectric transition of HfO$_2$ [37], suggests that the PO phase can support a substantial amount of charged defects while maintaining the polar structure. Since the charge injection to and entrapment from defects occur frequently during the electrical cycling, studying the impacts of charged defects on polymorphism kinetics thus becomes highly relevant.

In this work, we focus on neutral oxygen vacancy (V$_0^0$) and doubly positively charged oxygen vacancies (V$_0^{2+}$), as they are known prominent defects in HfO$_2$-based thin films [33, 38], particularly at the electrode/HfO$_2$ interface [39, 41]. Different from several previous DFT studies on oxygen-deficient HfO$_2$ where the assumed oxygen vacancy concentration reaches a rather high level (up to 12.5 f.u.% [42]), we focus on a relatively low oxygen vacancy concentration (3.125 f.u.%). First-principles DFT calculations are performed using Vienna Ab initio Simulation Package (VASP) with Perdew-Burke-Ernzerhof (PBE) density functional [43]. Structural parameters of unit cells of hafnia polymorphs are optimized using
a plane-wave cutoff of 600 eV, a $4 \times 4 \times 4$ Monkhorst-Pack $k$-point grid for Brillouin zone sampling, an energy convergence threshold of $10^{-6}$ eV, and a force convergence threshold of $10^{-3}$ eV/Å. All possible configurations of a supercell with an oxygen vacancy concentration of 3.125 f.u.% are explored to identify the lowest-energy configuration. The minimum energy pathway (MEP) connecting two polymorphs is identified with the variable-cell nudged elastic band (VCNEB) technique implemented in the USPEX code \[44\text{–}46\]. The main difference between conventional NEB and VCNEB is that VCNEB allows lattice constants to change during solid-solid transformations, thus capable of quantifying the intrinsic transition barrier between two phases possessing different lattice constants. More computational details can be found in Supplementary Materials (SM).

We first examine the intrinsic transition barriers in the absence of defects between different phases of HfO$_2$ including an “antiferroelectric-like” orthorhombic (AO) $Pbca$ phase and another polar orthorhombic $Pmn2_1$ phase. The $Pmn2_1$ phase has been suggested to be responsible for the ferroelectricity in (111)-oriented Hf$_{0.5}$Zr$_{0.5}$O$_2$ thin films \[47\text{–}48\]. All pathways have the sign of the $X_2^-$ mode conserved (see Fig. S1 in SM). Taking the lowest-energy M phase as the reference, the energy of T, AO, PO, and $Pmn2_1$ phase is 166, 73, 84, and 143 meV/f.u., respectively. As shown in Fig. 2a, the transitions of $T \rightarrow M$, $T \rightarrow PO$, and $T \rightarrow Pmn2_1$ are all kinetically fast with negligible enthalpy barriers (< 5 meV/f.u.). In comparison, the transition of $T \rightarrow AO$ needs to overcome a large kinetic barrier despite AO being the second most favored phase thermodynamically. By the meanwhile, the transitions from the polar $Pmn2_1$ phase to the M phase and $Pca2_1$ only needs to overcome a small barrier of 28 and 37 meV/f.u., respectively. We suggest that although the emergence of the $Pmn2_1$ phase from the T phase is effortless kinetically, it may quickly evolve to other phases such that its transient presence during crystallization is probably undetectable in experiments. Additionally, phase transitions of $Pca2_1$ to other nonpolar phases are all hindered by large barriers. Overall, the formation of the M phase is the most favored process both kinetically and thermodynamically in the absence of extrinsic effects. This explains why the most stable M phase dominates in bulk synthesis: since the transitions from T to $Pmn2_1$, PO, and M are all fast, the volume fractions of different phases will be determined mostly by their relative stability and follow the Boltzmann distribution. Moreover, the rather large intrinsic barrier of $M \rightarrow PO$ (169 meV/f.u.) seems to suggest it is unlikely to drive such nonpolar-polar phase transition with an electric field alone. This is inconsistent with ex-
experimentally observed structural changes upon field cycling that a substantial amount of M phase is transformed to the PO phase in the woken-up thin films of HfO$_2$ [15, 49, 50]. As we will discuss in below, the presence of charged oxygen vacancies resolves this puzzle.

The oxygen vacancy has long been postulated to play an important role in the stabilization of the PO phase. It has been demonstrated that a low oxygen content during the deposition favors the stabilization of the T and PO phases whereas a high oxygen content tends to stabilize the M phase [51, 52]. However, results from DFT calculations showed that even at a high $V^0_O$ concentration of $\approx$12.5 f.u.%, the M phase remains much more stable thermodynamically than the PO phase [53]. Rushchanskii et al. proposed that oxygen vacancies tend to be arranged in the form of two-dimensional extended defects, thus affecting the phase transition properties, and the lowest-energy configuration tends to transform into the ferroelectric PO phase [42]. However, the oxygen vacancy concentration in their model reached 12.5 f.u.%, much higher than typical experimental values of 2–3 f.u.% [30, 52]. We further investigate the impact of $V^0_O$ on polymorphism kinetics at a relatively low concentration of 3.125 f.u.%. Compared with the intrinsic defect-free cases, the presence of $V^0_O$ has little impact on the relative stability between M and PO phases, nor does it substantially affect the kinetics of phase transitions (Fig. 2b). We conclude that at experimentally relevant concentrations, charge neutral oxygen vacancies alone cannot explain the substantial impacts of O$_2$ partial pressures on the ferroelectric properties of HfO$_2$-based thin films.

Recently, He et al. reported that the presence of $V^{2+}_O$ beyond some critical concentration will make the PO phase more stable than the M phase [54]. At a low $V^{2+}_O$ concentration of 3.125 f.u.% studied here, we carefully examine the energetics of different configurations containing $V^{2+}_O$ and find that the M phase remains to be most stable thermodynamically (See Table S2 in SM). Interestingly, the relative stability between two representative configurations of the T phase, denoted as T$_a$ and T$_c$ (Fig. 3a), depends sensitively on the charge state of oxygen vacancy. Specifically, T$_a$ and T$_c$ has the vacancy pair aligned along the long axis a and the short axis c, respectively. The energies of T$_a$ and T$_c$ are comparable when the oxygen vacancy is charge neutral. But once the charge state of oxygen vacancy turns to +2, T$_c$ becomes rather unstable relative to T$_a$, higher in energy by $\approx$0.5 eV per vacancy pair (Fig. 3b and Table S3 in SM). We attribute the drastic stability change upon $V^0_O \rightarrow V^{2+}_O$ to the X$_2^-$ mode. Locally, the X$_2^-$ mode breaks the inversion symmetry along the a axis but not along the c axis. As illustrated in Fig. 3a, for the oxygen atom between two $V^{2+}_O$’s in the
configuration, it experiences forces of the same magnitude but opposite directions, thus becoming almost immobile and less effective in screening ionically the electrostatic interactions between charged vacancies. In contrast, for the oxygen atom separating two charged vacancies in the $T_a$ configuration, it endures asymmetric interactions along $a$ and is more adaptable for ionic screening. Therefore, $T_a$ has a lower energy than $T_c$. The MEPs connecting $T_a$ ($T_c$) to the most stable configurations of M and PO phases containing $V^{2+}$ are shown in Fig. 3c. We find that $T_c \to PO$ with a barrier of 24 meV/f.u. is kinetically favored over $T_c \to M$ with a barrier of 54 meV/f.u., while M and PO remain well separated by a large kinetic barrier. Therefore, $V^{2+}$ promotes $T_c \to PO$ but suppresses $T_c \to M$. In addition, as $T_a$ is more difficult to undergo phase transitions (Fig. 3c), it explains why as-prepared thin films of HfO$_2$ often exhibits a high volume fraction of nonpolar T phase.

The $V^{2+}$-promoted nonpolar-polar structural polymorphism, $T_c \to PO$, likely plays an important role for the emergence of the metastable PO phase in thin films. A capping electrode was often required to induce the ferroelectricity in Si-doped HfO$_2$ thin films [55, 56]. This could be due to the fact that the formation of $V^{2+}$ becomes much more feasible at the metal/HfO$_2$ interface as the two electrons may fall to the metal Fermi level [39]. Since raising the temperature often causes an increase in the intrinsic charge-carrier concentration, we propose that during the high-temperature annealing treatment of thin films, the formation of $V^{2+}$ at the metal/HfO$_2$ interface is facilitated such that the occurrence of $T_c \to PO$ becomes substantial. Similarly, the difficulty to obtain the PO phase of HfO$_2$ through bulk synthesis may be attributed to a low concentration of $V^{2+}$ in bulk crystals; previous DFT calculations reported that the formation energy of oxygen vacancy in bulk HfO$_2$ is rather large (6.38 eV) [57]. Moreover, the necessity of $V^{2+}$ for $T_c \to PO$ is consistent with a large body of experimental data that nearly all cation dopants that can induce ferroelectricity in HfO$_2$-based thin films are of $p$-type because the substitution of Hf$^{4+}$ with acceptor dopants such as La$^{3+}$ and Al$^{3+}$ naturally promotes the formation of $V^{2+}$ in order to maintain charge neutrality. For the same reason, the emergence of ferroelectricity in N-doped HfO$_2$ [29] could be arising from $V^{2+}$ that compensates $N^{-}$ [58].

The finding that $V^{2+}$ can strongly modulate the relative configurational stability is not unique to the T phase. We discover a configuration of oxygen-deficient M phase, denoted as $M_h$, that is stable when the oxygen vacancy is charge neutral but becomes highly unstable upon the charge entrapment from $V^{0}_O$. This $M_h$ configuration may evolve to the most stable
configuration of the M phase via $V_{O}^{2+}$ diffusion, but this process needs to overcome a high barrier of $\approx 1.30$ eV. It is more feasible kinetically for $M_h$ to transform to $T_c/T_a$ and PO ($< 29$ meV/f.u.). These results demonstrate that $V_{O}^{2+}$ can enable a previously forbidden transition of $M \rightarrow$ PO. In addition, we identify a configuration of PO phase, $PO_h$, which will be destabilized by $V_{O}^{2+}$ and can easily transform to nonpolar T and M phases. The phase transition network involving multiple polymorphs containing $V_{O}^{2+}$ depicted in Fig. 3c: highlight that $V_{O}^{2+}$ can enable facile transitions among nonpolar M and T phases and the polar PO phase, the kinetic barriers of which are lower than the polarization switching barrier of the PO phase ($\approx 85$ meV/f.u.).

The intricate coupling between $V_{O}^{2+}$ and structural polymorphism kinetics are expected to contribute to performance instability issues including wake-up and imprint. In a pristine ferroelectric HfO$_2$-based capacitor at room temperatures, $V_{O}^{0}$ is the dominant type of oxygen vacancy, as supported by recent DFT calculations [59] and experiments [40]. Therefore, $V_{O}^{0}$ may distribute at the metal-ferroelectric interface in the matrix of M, T, and PO phases at room temperatures (Fig. 4a). Upon the application of a voltage, electrons of $V_{O}^{0}$ tend to detrapping to the adjacent electrode (top electrode in Fig. 4b), leading to the formation of $V_{O}^{2+}$ and the activation of $M_h \rightarrow$ PO and $T_c \rightarrow$ PO (Fig. 4c). The diffusion of $V_{O}^{2+}$, recently observed in experiments [60], may further help the nonpolar-polar phase transitions in regions away from the electrode. Similar processes will occur near another electrode after reversing the bias. The overall result is the reduction of the M and T phases and the increase in the volume fraction of the PO phase after field cycling, leading to the wake-up effect [50].

Finally, the low phase transition barriers of $M_h \rightarrow$ PO and $T_c \rightarrow$ PO ($< 29$ meV/f.u.) could to some extent explain recently observed “fluid imprint” in ferroelectric La-doped HfO$_2$ capacitors that the imprint is easily changeable and has a strong dependence on the switching prehistory [11]. As illustrated in Fig. 4d, after the application of a preset pulse that polarize an woken-up capacitor (that still has residual nonpolar phases), the electron entrapment occurs more easily near the negative bound charge side. The presence of $V_{O}^{2+}$ creates a local electric field that aligns with the bulk polarization; this could be the source of imprint field ($E_i$). Even in the absence of additional bias, the $V_{O}^{2+}$-promoted nonpolar-polar phase transitions, due to their low kinetic barriers, can still occur driven by $E_i$, leading to continued polarization switching toward the same direction as the previously applied field, similar to the inertial switching observed in experiments [11]. Consequently, the fluid imprint is associated
with an evolving microstructure with a changing volume fraction of the PO phase.

In summary, the robust ferroelectricity against charge doping in the Pca21 phase of HfO2 highlights the importance to quantify the effects of charged defects on the ferroelectric properties of HfO2-based devices. We demonstrate that the positively charged oxygen vacancy can drastically modulate the relative configurational stability of the same phase, the origin of which can be traced back to the X2− mode. The V2+O−-promoted nonpolar-polar structural polymorphism is likely an overlooked yet important mechanism for the emergence of polar Pca21 phase in HfO2-based thin films, which offers a new perspective to experimentally observed electrode and doping effects. Generic mechanisms based on the coupling between V2+O− and structural polymorphism kinetics are proposed to explain performance instability issues. Future studies focusing on the coupling between structural polymorphism kinetics and other extrinsic effects such as strain are important for a complete understanding of HfO2-based ferroelectrics.

ACKNOWLEDGMENTS

L.M. and S.L. acknowledge the supports from National Key R&D Program of China (2021YFA1202100), National Natural Science Foundation of China (12074319), and Westlake Education Foundation. The computational resource is provided by Westlake HPC Center. We thank Dr. Yichun Zhou and Jiangheng Yang for useful discussions inspired by which we discovered the importance of the X2− mode for phase transitions.

[1] J. F. Scott, Applications of modern ferroelectrics, Science 315, 954 (2007).
[2] W. Huang, W. Zhao, Z. Luo, Y. Yin, Y. Lin, C. Hou, B. Tian, C.-G. Duan, and X.-G. Li, A high-speed and low-power multistate memory based on multiferroic tunnel junctions, Adv. Electron. Mater. 4, 1700560 (2018).
[3] T. Mikolajick, U. Schroeder, and S. Slesazeck, The past, the present, and the future of ferroelectric memories, IEEE Trans. Electron Devices 67, 1434 (2020).
[4] C.-U. Pinnow and T. Mikolajick, Material aspects in emerging nonvolatile memories, J. Electrochem. Soc. 151, K13 (2004)
[5] T. S. Böcke, J. Müller, D. Bräuhaus, U. Schröder, and U. Böttger, Ferroelectricity in hafnium oxide thin films, Appl. Phys. Lett. 99, 102903 (2011).

[6] H.-J. Lee, M. Lee, K. Lee, J. Jo, H. Yang, Y. Kim, S. C. Chae, U. Waghmare, and J. H. Lee, Scale-free ferroelectricity induced by flat phonon bands in HfO$_2$, Science 369, 1343 (2020).

[7] Q. Luo, Y. Cheng, J. Yang, R. Cao, H. Ma, Y. Yang, R. Huang, W. Wei, Y. Zheng, T. Gong, J. Yu, X. Xu, P. Yuan, X. Li, L. Tai, H. Yu, D. Shang, Q. Liu, B. Yu, Q. Ren, H. Lv, and M. Liu, A highly CMOS compatible hafnia-based ferroelectric diode, Nat. Commun. 11, 1391 (2020).

[8] M.-K. Kim, I.-J. Kim, and J.-S. Lee, CMOS-compatible ferroelectric NAND flash memory for high-density, low-power, and high-speed three-dimensional memory, Science Advances 7, eabe1341 (2021).

[9] H. Mulaosmanovic, P. D. Lomenzo, U. Schroeder, S. Slesazeck, T. Mikolajick, and B. Max, Reliability aspects of ferroelectric hafnium oxide for application in non-volatile memories, 2021 IEEE International Reliability Physics Symposium (IRPS).

[10] S. Mueller, J. Muller, U. Schroeder, and T. Mikolajick, Reliability characteristics of ferroelectric Si:HfO$_2$ thin films for memory applications, IEEE Trans. Electron Devices 13, 93 (2013).

[11] P. Buragohain, A. Erickson, P. Kariuki, T. Mittmann, C. Richter, P. D. Lomenzo, H. Lu, T. Schenk, T. Mikolajick, U. Schroeder, and A. Gruverman, Fluid imprint and inertial switching in ferroelectric La:HfO$_2$ capacitors, ACS Appl. Mater. Interfaces 11, 35115 (2019).

[12] M. H. Park, Y. H. Lee, H. J. Kim, Y. J. Kim, T. Moon, K. D. Kim, J. Müller, A. Kersch, U. Schroeder, T. Mikolajick, and C. S. Hwang, Ferroelectricity and antiferroelectricity of doped thin HfO$_2$-based films, Adv. Mater. 27, 1811 (2015).

[13] T. D. Huan, V. Sharma, G. A. Rossetti, and R. Ramprasad, Pathways towards ferroelectricity in hafnia, Phys. Rev. B 90, 064111 (2014).

[14] S. E. Reyes-Lillo, K. F. Garrity, and K. M. Rabe, Antiferroelectricity in thin-film zro$_2$ from first principles, Phys. Rev. B 90, 140103 (2014).

[15] X. Sang, E. D. Grimley, T. Schenk, U. Schroeder, and J. M. LeBeau, On the structural origins of ferroelectricity in HfO$_2$ thin films, Appl. Phys. Lett. 106, 162905 (2015).

[16] R. Materlik, C. Künmeth, and A. Kersch, The origin of ferroelectricity in Hf$_{1-x}$Zr$_x$O$_2$: A computational investigation and a surface energy model, J. Appl. Phys. 117, 134109 (2015).
[17] P. Polakowski and J. Müller, Ferroelectricity in undoped hafnium oxide, Appl. Phys. Lett. 106, 232905 (2015)

[18] R. Batra, H. D. Tran, and R. Ramprasad, Stabilization of metastable phases in hafnia owing to surface energy effects, Appl. Phys. Lett. 108, 172902 (2016)

[19] C. Künnett, R. Materlik, and A. Kersch, Modeling ferroelectric film properties and size effects from tetragonal interlayer in Hf$_{1-x}$Zr$_x$O$_2$ grains, J. Appl. Phys. 121, 205304 (2017).

[20] M. H. Park, Y. H. Lee, H. J. Kim, T. Schenk, W. Lee, K. D. Kim, F. P. G. Fengler, T. Mikolajick, U. Schroeder, and C. S. Hwang, Surface and grain boundary energy as the key enabler of ferroelectricity in nanoscale hafnia-zirconia: A comparison of model and experiment, Nanoscale 9, 9973 (2017)

[21] T. Shiraishi, K. Katayama, T. Yokouchi, T. Shimizu, T. Oikawa, O. Sakata, H. Uchida, Y. Inai, T. Kiguchi, T. J. Konno, and H. Funakubo, Impact of mechanical stress on ferroelectricity in Hf$_{0.5}$Zr$_{0.5}$O$_2$ thin films, Appl. Phys. Lett. 108, 262904 (2016).

[22] R. Batra, T. D. Huan, J. L. Jones, G. Rossetti, and R. Ramprasad, Factors favoring ferroelectricity in hafnia: A first-principles computational study, J. Phys. Chem. C 121, 4139 (2017)

[23] S. Liu and B. M. Hanrahan, Effects of growth orientations and epitaxial strains on phase stability of HfO$_2$ thin films, Phys. Rev. Mater. 3, 054404 (2019)

[24] U. Schroeder, E. Yurchuk, J. Müller, D. Martin, T. Schenk, P. Polakowski, C. Adelmann, M. I. Popovici, S. V. Kalinin, and T. Mikolajick, Impact of different dopants on the switching properties of ferroelectric hafnium oxide, Jpn. J. Appl. Phys. 53, 08LE02 (2014)

[25] S. Starschich and U. Boettger, An extensive study of the influence of dopants on the ferroelectric properties of HfO$_2$, J. Mater. Chem. C 5, 333 (2017).

[26] M. H. Park, T. Schenk, C. M. Fancher, E. D. Grimley, C. Zhou, C. Richter, J. M. LeBeau, J. L. Jones, T. Mikolajick, and U. Schroeder, A comprehensive study on the structural evolution of HfO$_2$ thin films doped with various dopants, J. Mater. Chem. C 5, 4677 (2017).

[27] L. Xu, T. Nishimura, S. Shibayama, T. Yajima, S. Migita, and A. Toriumi, Kinetic pathway of the ferroelectric phase formation in doped HfO$_2$ films, J. Appl. Phys. 122, 124104 (2017)

[28] R. Batra, T. D. Huan, G. A. Rossetti, and R. Ramprasad, Dopants promoting ferroelectricity in hafnia: Insights from a comprehensive chemical space exploration, Chem. Mater. 29, 9102 (2017)
[29] L. Xu, T. Nishimura, S. Shibayama, T. Yajima, S. Migita, and A. Toriumi, Ferroelectric phase stabilization of HfO\textsubscript{2} by nitrogen doping, Appl. Phys. Express \textbf{9}, 091501 (2016).

[30] A. Pal, V. K. Narasimhan, S. Weeks, K. Littau, D. Pramanik, and T. Chiang, Enhancing ferroelectricity in dopant-free hafnium oxide, Appl. Phys. Lett. \textbf{110}, 022903 (2017).

[31] E. D. Grimley, T. Schenk, T. Mikolajick, U. Schroeder, and J. M. LeBeau, Atomic structure of domain and interphase boundaries in ferroelectric HfO\textsubscript{2}, ACS Appl. Mater. Interfaces \textbf{5}, 1701258 (2018).

[32] C. Richter, T. Schenk, M. H. Park, F. A. Tscharntke, E. D. Grimley, J. M. LeBeau, C. Zhou, C. M. Fancher, J. L. Jones, T. Mikolajick, and U. Schroeder, Si doped hafnium oxide—a “fragile” ferroelectric system, Adv. Electron. Mater. \textbf{3}, 1700131 (2017).

[33] A. Chouprik, D. Negrov, E. Y. Tsymbal, and A. Zenkevich, Defects in ferroelectric HfO\textsubscript{2}, Nanoscale \textbf{13}, 11635 (2021).

[34] Y. Qi, S. Singh, and K. M. Rabe, Polarization switching mechanism in HfO\textsubscript{2} from first-principles lattice mode analysis, arXiv preprint arXiv:2108.12538 (2021).

[35] Vasp the guide, \url{https://www.vasp.at/wiki/index.php/The_VASP_Manual}, accessed April 15, 2022.

[36] V. F. Michel, T. Esswein, and N. A. Spaldin, Interplay between ferroelectricity and metallicity in BaTiO\textsubscript{3}, J. Mater. Chem. C \textbf{9}, 8640 (2021).

[37] F. Delodovici, P. Barone, and S. Picozzi, Trilinear-coupling-driven ferroelectricity in HfO\textsubscript{2}, Phys. Rev. Materials \textbf{5}, 064405 (2021).

[38] S. Guha and V. Narayanan, Oxygen vacancies in high dielectric constant oxide-semiconductor films, Phys. Rev. Lett. \textbf{98}, 196101 (2007).

[39] E. Cho, B. Lee, C.-K. Lee, S. Han, S. H. Jeon, B. H. Park, and Y.-S. Kim, Segregation of oxygen vacancy at metal-HfO\textsubscript{2} interfaces, Appl. Phys. Lett. \textbf{92}, 233118 (2008).

[40] W. Hamouda, C. Lubin, S. Ueda, Y. Yamashita, O. Renault, F. Mehmood, T. Mikolajick, U. Schroeder, R. Negrea, and N. Barrett, Interface chemistry of pristine TiN/La: Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} capacitors, Appl. Phys. Lett. \textbf{116}, 252903 (2020).

[41] F. P. G. Fengler, R. Nigon, P. Murlat, E. D. Grimley, X. Sang, V. Sessi, R. Hentschel, J. M. LeBeau, T. Mikolajick, and U. Schroeder, Analysis of performance instabilities of hafnia-based ferroelectrics using modulus spectroscopy and thermally stimulated depolarization currents, Adv. Electron. Mater. \textbf{4}, 1700547 (2018).
[42] K. Z. Rushchanskii, S. Blügel, and M. Ležaić, Ordering of oxygen vacancies and related ferroelectric properties in HfO$_2$–δ, Phys. Rev. Lett. **127**, 087602 (2021).

[43] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. **77**, 3865 (1996).

[44] A. R. Oganov and C. W. Glass, Crystal structure prediction using ab initio evolutionary techniques: Principles and applications, J. Chem. Phys. **124**, 244704 (2006).

[45] A. O. Lyakhov, A. R. Oganov, H. T. Stokes, and Q. Zhu, New developments in evolutionary structure prediction algorithm USPEX, Comput. Phys. Commun. **184**, 1172 (2013).

[46] A. R. Oganov, A. O. Lyakhov, and M. Valle, How evolutionary crystal structure prediction works—and why, Acc. Chem. Res. **44**, 227 (2011).

[47] Y. Wei, P. Nukala, S. Salverda, S. Matzen, H. J. Zhao, J. Momand, A. S. Everhardt, G. Agnus, G. R. Blake, P. Lecoeur, B. J. Kooi, J. Íñiguez, B. Dkhil, and B. Noheda, A rhombohedral ferroelectric phase in epitaxially strained Hf$_{0.5}$Zr$_{0.5}$O$_2$ thin films, Nat. Mater. **17**, 1095–1100 (2018).

[48] Y. Qi, S. Singh, C. Lau, F.-T. Huang, X. Xu, F. J. Walker, C. H. Ahn, S.-W. Cheong, and K. M. Rabe, Stabilization of competing ferroelectric phases of HfO$_2$ under epitaxial strain, Phys. Rev. Lett. **125**, 257603 (2020).

[49] M. Hoffmann, U. Schroeder, T. Schenk, T. Shimizu, H. Funakubo, O. Sakata, D. Pohl, M. Drescher, C. Adelmann, R. Materlik, A. Kersch, and T. Mikolajick, Stabilizing the ferroelectric phase in doped hafnium oxide, J. Appl. Phys. **118**, 072006 (2015).

[50] E. D. Grimley, T. Schenk, X. Sang, M. Pešić, U. Schroeder, T. Mikolajick, and J. M. LeBeau, Structural changes underlying field-cycling phenomena in ferroelectric HfO$_2$ thin films, Adv. Electron. Mater. **2**, 1600173 (2016).

[51] L. Baumgarten, T. Szyjka, T. Mittmann, M. Materano, Y. Matveyev, C. Schlueter, T. Mikolajick, U. Schroeder, and M. Müller, Impact of vacancies and impurities on ferroelectricity in PVD- and ALD-grown HfO$_2$ films, Appl. Phys. Lett. **118**, 032903 (2021).

[52] T. Mittmann, M. Materano, P. D. Lomenzo, M. H. Park, I. Stolichnov, M. Cavalieri, C. Zhou, C.-C. Chung, J. L. Jones, T. Szyjka, M. Müller, A. Kersch, T. Mikolajick, and U. Schroeder, Origin of ferroelectric phase in undoped HfO$_2$ films deposited by sputtering, Adv. Mater. Interfaces , 1900042 (2019).

[53] Y. Zhou, Y. Zhang, Q. Yang, J. Jiang, P. Fan, M. Liao, and Y. Zhou, The effects of oxygen va-
cancies on ferroelectric phase transition of HfO₂-based thin film from first-principle, Comput. Mater. Sci. 167, 143 (2019)

[54] R. He, H. Wu, S. Liu, H. Liu, and Z. Zhong, Ferroelectric structural transition in hafnium oxide induced by charged oxygen vacancies, Phys. Rev. B 104, L180102 (2021)

[55] S. J. Kim, D. Narayan, J.-G. Lee, J. Mohan, J. S. Lee, J. Lee, H. S. Kim, Y.-C. Byun, A. T. Lucero, C. D. Young, S. R. Summerfelt, T. San, L. Colombo, and J. Kim, Large ferroelectric polarization of TiN/Hf₀.5Zr₀.5O₂/TiN capacitors due to stress-induced crystallization at low thermal budget, Appl. Phys. Lett. 111, 242901 (2017).

[56] J. Wan, X. Chen, L. Ji, Z. Tu, H. Wu, and C. Liu, Ferroelectricity of Hf₀.5Zr₀.5O₂ thin films free from the influence of electrodes by using Al₂O₃ capping layers, IEEE Trans. Electron Devices 69, 1805 (2022).

[57] J. Robertson, O. Sharia, and A. A. Demkov, Fermi level pinning by defects in HfO₂-metal gate stacks, Appl. Phys. Lett. 91, 132912 (2007).

[58] N. Umezawa, K. Shiraishi, T. Ohno, H. Watanabe, T. Chikyow, K. Torii, K. Yamabe, K. Yamada, H. Kitajima, and T. Arikado, First-principles studies of the intrinsic effect of nitrogen atoms on reduction in gate leakage current through hf-based high-k dielectrics, Appl. Phys. Lett. 86, 143507 (2005).

[59] J. Wei, L. Jiang, M. Huang, Y. Wu, and S. Chen, Intrinsic defect limit to the growth of orthorhombic HfO₂ and (Hf, Zr)O₂ with strong ferroelectricity: First-principles insights, Adv. Funct. Mater. 31, 2104913 (2021).

[60] P. Nukala, M. Ahmadi, Y. Wei, S. de Graaf, E. Stylianidis, T. Chakrabortty, S. Matzen, H. W. Zandbergen, A. Björling, D. Mannix, D. Carbone, B. Kooi, and B. Noheda, Reversible oxygen migration and phase transitions in hafnia-based ferroelectric devices, Science 372, 630 (2021)
FIG. 1. (a) Schematic illustration of $X_2^-$ mode in the tetragonal phase of HfO$_2$. The tetragonal unit cell has the long axis along $x$. The closer and further Hf atoms are colored in dark and light grey; outward and inward displaced oxygen atoms are colored in blue and red, respectively. The generic phase space coordinate is denoted as $\lambda$. (b) Polar atomic displacement ($d_z$) as a function of charge-carrier concentration for the PO phase of HfO$_2$ and tetragonal BaTiO$_3$. The insets illustrate the definitions of $d_z$ in HfO$_2$ and BaTiO$_3$. 
FIG. 2. (a) Minimum energy pathways connecting different polymorphs of HfO$_2$ obtained with VCNEB. (b) Comparison of transition pathways between M, T, and PO phases at the pristine state (solid lines) and those in the presence of V$_O^0$ at a concentration of 3.125 % (dashed lines). The energy of the M phase is chosen as the energy zero point.
FIG. 3. (a) Schematics of two different configurations of T phase containing a pair of V$_{O}^{2+}$. Back arrows represent the induced forces at the instance of V$_{O}^{2+}$ pair creation. (b) Change in the relative stability between T$_{a}$ and T$_{c}$ upon V$_{O}^{0}$ → V$_{O}^{2+}$. (c) Transition pathways in the presence of V$_{O}^{2+}$ at a concentration of 3.125%. (d) Phase transition network involving multiple polymorphs of HfO$_{2}$ containing V$_{O}^{2+}$. The color of the arrow scales with the magnitude of the transition barrier (see values in Table S5).
FIG. 4. Schematics of wake-up and inertial switching enabled by $V_{O}^{2+}$-promoted nonpolar-polar structural polymorphisms. Oxygen vacancies in the right schematics are not shown in (c) and (d) for clarity.