

Role of local cation environment on the formation energy of oxygen vacancies in ferroelectric $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$

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Oxygen vacancies play a critical role in stabilizing the ferroelectric phase of hafnia-zirconia thin films, yet their interplay with zirconium doping is less well understood. In this work, we employ Density Functional Theory to uncover how local cation environments caused by zirconium doping, and charge states ($q = -2$ to $+2$), shape the oxygen vacancy landscape in ferroelectric hafnia-zirconia ($\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$; $x = 0.25, 0.50, 0.75$). We reveal the crucial role of the local cation environment in facilitating the formation of oxygen vacancies in ferroelectric hafnia-zirconia compared to hafnia, extending the analysis to nine unique environments. The environment comprised of four zirconium cations was found to have the lowest formation energy out of the set of local cation environments for neutral oxygen vacancy formation. The charge transition to positively charged vacancies ($q = +2$) dramatically increases the number of available sites, suggesting that electric field-induced charge transitions can facilitate vacancy diffusion. We find that the concentration of zirconium doping surprisingly did not impact the formation energies of oxygen vacancies, instead acting as a lever controlling the population of available sites for oxygen vacancy formation. Bonding analysis reveals that zirconium content weakens the cation-oxygen bond by introducing occupied antibonding states, further stabilizing defect formation. These findings reveal how doping and charge state modulate the defect landscape, offering a blueprint for tuning oxygen vacancy behavior and, by extension, the performance of next-generation ferroelectric devices.

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I. INTRODUCTION

Ferroelectric materials have become a promising platform for developing energy-efficient electronics. A key discovery was the unexpected observation of ferroelectricity in silicon-doped hafnia (HfO_2) by Böske *et al.* [1], which was followed by the discovery of ferroelectricity in undoped hafnia [2] and related binary oxides such as zirconia (ZrO_2) [3]. These findings represent a potentially revolutionary technological advance due to the compatibility between HfO_2 and current complementary metal-oxide semiconductor technology.

In its bulk form, HfO_2 adopts a monoclinic structure ($P2_1/c$) at low temperature. At high temperatures above 2000 K it undergoes a martensitic phase transition into a tetragonal phase ($P4_2/nmc$) [4]. Ferroelectric HfO_2 has only been observed in thin films and is attributed to a different metastable orthorhombic phase ($Pca2_1$). Interestingly, polar

HfO_2 thin films exhibit robust ferroelectricity at thicknesses below approximately 10 nm, in contrast to classical ferroelectrics where polarization typically diminishes at reduced scales. We note that a ferroelectric rhombohedral phase stabilized by strain and surface energy effects has also been reported in HfO_2 thin films [5,6].

It is widely accepted that a complex interplay between dopants [7–10], oxygen defects [11–13], surface energy [14,15], and strain [16,17] governs the stabilization of the ferroelectric phase in the thin films. Of these, recent studies have particularly emphasized the critical role of oxygen defects, particularly oxygen vacancies, and dopants.

Oxygen vacancies have been found to modulate both the stability and polarization value of the polar phase [11,12,18–22]. Some works have linked ferroelectric polarization to the redistribution of oxygen vacancies at local and global scales within films [23–26], leading to the proposal of a “ferroionic” state hypothesis to explain nanoscale ferroelectricity [27,28]. Hill *et al.* [29] demonstrated the existence of intrinsic polar states originating from broken inversion symmetry and asymmetric lattice distortions. They showed that electrochemical changes related to defect redistribution occurred simultaneously to ferroelectric switching under applied bias, suggesting that such extrinsic mechanisms contribute but do not fully explain the absence of ferroelectric degradation at ultrathin dimensions.

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In the case of dopants, zirconium shows the most success in stabilizing ferroelectricity in HfO_2 . Lanthanide contraction causes the radii of the metal cations ($\text{Hf}^{+4}, \text{Zr}^{+4}$) in HfO_2 and ZrO_2 to be very close in size, making these two oxides isostructural, facilitating mixing [30]. The solid solution of hafnia-zirconia ($\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$) supports ferroelectricity over a broad range of compositions, exhibiting enhanced ferroelectric behavior compared to pristine HfO_2 thin films, with maximum ferroelectric phase content typically observed at $x = 0.50$ [9,10]. To rationalize some of these observations, first-principles density functional theory (DFT) studies by Pavoni *et al.* [31] and Lee *et al.* [32] have shown that zirconium doping reduces the free-energy difference between the ferroelectric and the nonferroelectric bulk phases. However, even in these studies, the nonferroelectric monoclinic phase remains the most stable. Wei *et al.* [13] show that zirconium doping helps stabilize ferroelectric HfO_2 by interacting with oxygen defects. In undoped tetragonal HfO_2 (the typical seed for polar phase growth) oxygen interstitials form spontaneously, causing large structural distortions that push the material toward the monoclinic ground state. Zirconium doping suppresses the formation of these defects and their distortions, promoting the crystallization of the ferroelectric phase.

HfO_2 -based films suffer from two major reliability issues: “wake-up” and “fatigue.” These phenomena cause changes in the remanent polarization during device operation, making performance inconsistent. Although the mechanisms underlying wake-up [17,33–35] and fatigue [36,37] are distinct, both have been strongly linked to the behavior of oxygen vacancies. Given that zirconium (one the most common dopants) has been shown to influence the defect energetics [13,38], understanding the relationship between oxygen vacancies and zirconium doping in $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ is vital to addressing these reliability issues. In this work, we employ first-principles calculations to investigate this interplay, focusing on how the energetic stability of oxygen vacancies is modulated by their charge state and by the local cation environment introduced through zirconium doping. We further discuss the implications of these findings on the ferroelectric properties of zirconium-doped HfO_2 systems.

II. METHODS

We start by constructing structural models of $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$. The hafnium sublattice in HfO_2 has a single Wyckoff position (4e), and substitutional zirconium doping introduces cation disorder on this site. We build supercell models of the orthorhombic ($Pca2_1$) phase of $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$, containing 64 oxygen atoms and 32 metal cations, that explicitly include different cation arrangements with compositions $x = 0.25$, 0.5, and 0.75 (see Fig. 1).

We next introduce oxygen vacancies to $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$. Oxygen atoms occupy two distinct sublattices in the orthorhombic HfO_2 phase, leading to two inequivalent lattice sites: an O3 site coordinated by three cations and an O4 site by four (Fig. 1). The O3 sites break the centrosymmetry of the orthorhombic cell, creating a dipole moment. In $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$, we define the local cation environment of an oxygen site as the set of metal atoms within a sphere centered on the oxygen site, with a radius equal to the longest observed metal-oxygen

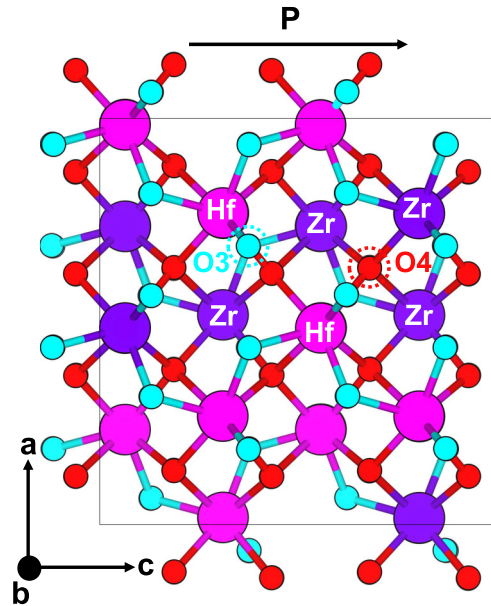


FIG. 1. Structure of $Pca2_1$ $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ depicted in a $2 \times 2 \times 2$ supercell. Hafnium atoms are colored pink, and zirconium atoms are purple. Oxygen at O3 sites is colored blue and O4 sites are red. The O3 site breaks the centrosymmetry of the crystal, inducing the polarization which is oriented along the c axis. The crystal structure is rendered using Visualization for Electronic and STructural Analysis (VESTA) [39].

bond length in the structure, $2.3 \text{ \AA}$, corresponding to the Zr-O bond. This results in nine distinct local cation configurations for oxygen sites: five types for O4 sites (4Hf, 3Hf1Zr, 2Hf2Zr, 1Hf3Zr, and 4Zr) and four types for O3 sites (3Hf, 2Hf1Zr, 1Hf2Zr, and 3Zr). For example, a 1Hf2Zr O3 site corresponds to an O3 site coordinated by one hafnium and two zirconium atoms, a configuration illustrated at the O3 site highlighted in Fig. 1. We introduce oxygen vacancies by removing oxygen atoms from the $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ structural models described above resulting in an oxygen vacancy concentration of 1.56% per simulation cell. Previous studies have only explored a subset of these environments, such as the 2Hf2Zr, 2Hf1Zr, and 1Hf2Zr configurations [38,40,41]. Our study thus extends the previous set of local cation environments relevant to zirconium-doped ferroelectric HfO_2 , allowing a comprehensive understanding of the role of cation disorder in defect formation.

Using these structural models, we study the properties of $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ with oxygen vacancies using first-principles calculations and the “Vienna *ab initio* Simulation Package” (VASP) [42–46] (see Supplemental Material [47] for the computational methods). We start by fully relaxing the internal coordinates of each structural model. We next evaluate the formation energy E_f of an oxygen vacancy:

$$E_f = E_{V_0} - E_{\text{bulk}} + \mu + qE_{\text{Fermi}}^{(\text{VBM})} + \Delta E_{\text{cor}}, \quad (1)$$

where E_{V_0} is the total energy of the defect structure, E_{bulk} the total energy of the defect-free structure, μ is the chemical potential of oxygen, q is the charge of the oxygen vacancy, $E_{\text{Fermi}}^{(\text{VBM})}$ is the Fermi level referenced to the valence band maximum (VBM) of the bulk structure, and ΔE_{cor} is the finite-size

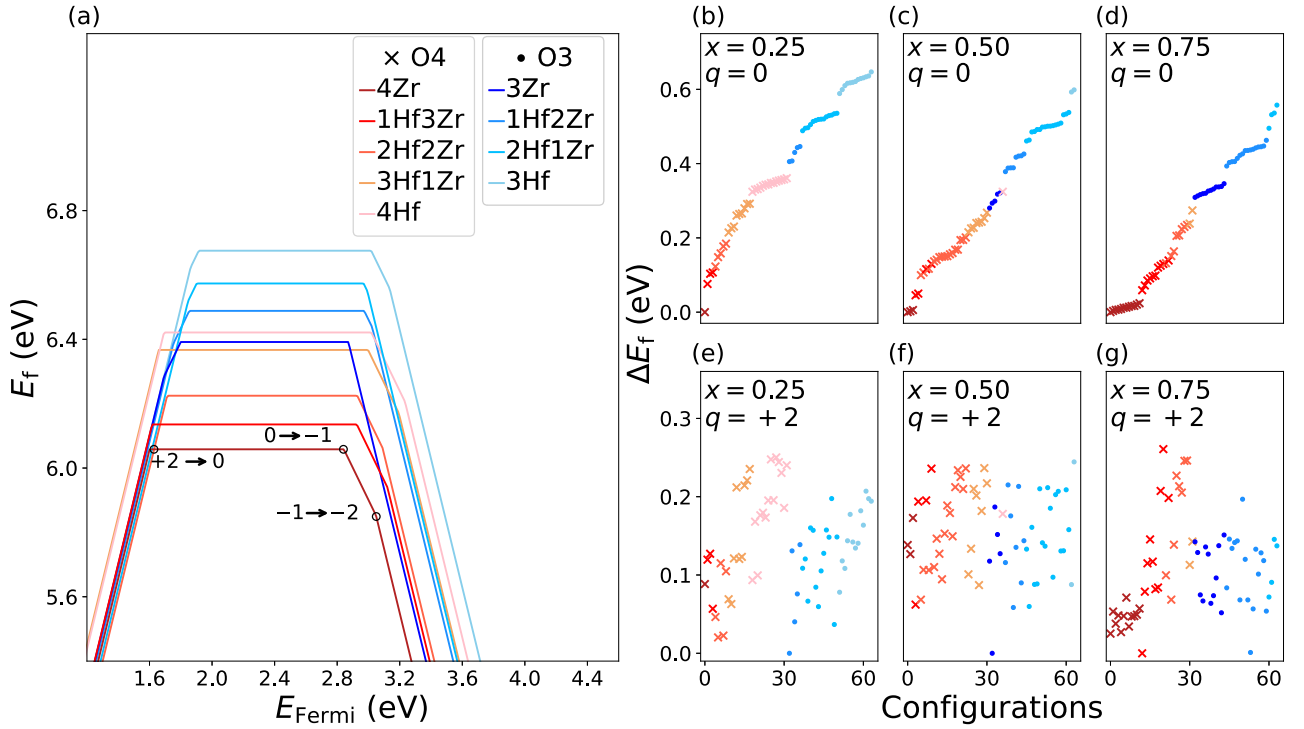


FIG. 2. The formation energies of oxygen vacancies in a $\text{Hf}_{x-1}\text{Zr}_x\text{O}_2$ $2 \times 2 \times 2$ supercell containing 64 oxygen atoms and 32 metal cations. The formation energies were calculated for oxygen-rich conditions. O3 sites are shown in blue and O4 sites are in red. The shade of the color represents the amount of hafnium in the local cation environment, with the darkest red and blue being the 4Zr and 3Zr local cation environments, respectively. (a) The formation energies of oxygen vacancies in the lowest-energy charge state $q = -2, -1, 0, +1, +2$ is determined for a given Fermi level for the set of local cation environments in $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$. The position of the Fermi level is relative to the valence band maximum. Open circles indicate the charge transition points, the first at $q = +2$ to $q = 0$ at $E_{\text{Fermi}} = 1.63$ eV, the second $q = 0$ to $q = -1$ at $E_{\text{Fermi}} = 2.84$ eV, and the third $q = -1$ to $q = -2$ at $E_{\text{Fermi}} = 3.04$ eV. (b)–(g) The O3 sites are plotted as blue dots and O4 sites as red crosses, with the shade of the color indicating the composition of local cation environment as in (a). (b)–(d) Relative formation energy of charge-neutral oxygen vacancies for each possible site in the $\text{Hf}_{x-1}\text{Zr}_x\text{O}_2$ structures where $x = 0.25, 0.50, 0.75$. (e), (f) Relative formation energy of $q = +2$ charged oxygen vacancies at $E_{\text{Fermi}} = 0.1$ eV for each possible site in the $\text{Hf}_{x-1}\text{Zr}_x\text{O}_2$ structures where $x = 0.25, 0.50, 0.75$.

electrostatic correction term based on the work of Freysoldt, Neugebauer, and Van de Walle (FNV) [48]. The FNV correction accounts for spurious electrostatic interactions between periodically repeated charged defects and the compensating background charge in the finite simulation cell by separating the long-range Coulomb contribution from the short-range defect potential. While finite-size corrections are required for all charged defect calculations, they are particularly critical in composition-dependent studies such as the present one, where electrostatic finite-size errors do not cancel uniformly due to differences in local dielectric screening associated with distinct local chemical environments. Details of the FNV correction implementation are provided in the Supplemental Material [47].

III. RESULTS

We define a relative formation energy ΔE_f as

$$\Delta E_f = E_f - E_{f \min}, \quad (2)$$

where $E_{f \min}$ is the minimum oxygen vacancy formation energy among all structures considered.

We consider one of the stochastically generated $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ structures exhibiting all of the possible local cation environments. For this model, we calculate the

formation energy of an oxygen vacancy at each possible site and for different charge states $q = +2, +1, 0, -1, -2$. As shown in Fig. 2(a), the lowest-energy charge state is determined for a given Fermi level. Here, the neutral case $q = 0$ corresponds to two electrons localized at the vacancy site, while the $q = +2$ state represents the removal of those two electrons. In the charge-neutral case [Fig. 2(a)], the impact of the local cation environment is most pronounced, with an energy range spanning 617 meV. The 4Zr local cation environment is the most energetically favourable site for oxygen vacancy formation ($q = 0$), with a formation energy 77.3 meV lower than the next most favorable environment, 1Hf3Zr. The formation energy increases with the number of hafnium atoms in the local environment, with the 3Hf environment requiring the largest formation energy. In both oxygen-rich and oxygen-poor conditions (see Supplemental Material Fig. S1 [47]) charge neutral oxygen vacancies have positive formation energies and so $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ is stable with respect to their formation. For neutral oxygen vacancies in undoped HfO_2 , we calculate that the O4 site has a 256 meV energy advantage over the O3 site, consistent with previous DFT results [12]. Comparing the formation energies at the two sites in HfO_2 to the formation energies of the local cation environments in $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$, we find that

the O3 and O4 sites (HfO_2) match the required formation energy for oxygen vacancies at the 3Hf and 4Hf local cation environments. Neutral oxygen vacancy formation is therefore more favorable in $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ than HfO_2 due to zirconium doping. For both $q = -1$ and $q = -2$ charge states ($x = 0.50$) the 4Zr cation environment remains the most energetically favorable for oxygen vacancy formation [Fig. 2(a)]. The charge transition [Fig. 2(a), open circles] from $q = -1$ to $q = -2$ occurs at $E_{\text{Fermi}} = 3.04$ eV and the transition from $q = 0$ to $q = -1$ occurs at $E_{\text{Fermi}} = 2.84$ eV. We find the charge transition from $q = 0$ to $q = +1$ to never be energetically favorable. Instead the $q = 0$ charge state transitions straight to $q = +2$ [Fig. 2(a), first open circle on the left] when $E_{\text{Fermi}} = 1.63$ eV. The $q = +2$ to $q = 0$ charge transition is accompanied by a change in the preferred vacancy site. For the $q = +2$ charge state the energetic ordering of local cation environments observed in the neutral charge state ($q = 0$) is lost. Along with this loss of energetic ordering due to the local cation environment, the difference in formation energy between the type of oxygen site O3 or O4 is found to vanish. The difference in the formation energy between the most energetically favorable O4 2Hf2Zr local environment and the next most energetically favorable O3 2Hf1Zr environment is 26.5 meV, making the formation of oxygen vacancies in these environments thermally degenerate at room temperature. In both oxygen-poor and intermediate conditions (see Supplemental Material Fig. S1 [47]), the $q = -2$ charge state has negative formation energies for a range of values of E_{Fermi} . This suggests that oxygen vacancy formation could be induced by Fermi-level engineering.

Next, we consider the impact of changing the concentration of zirconium on the defect formation energies for $x = 0.25, 0.50, 0.75$ [Figs. 2(b)–2(g)]. Motivated by the preceding discussion, we focus on the $q = 0, +2$ charge states as illustrative. In the charge-neutral case [$q = 0$; Figs. 2(b)–2(d)], vacancy formation energies remain positive in all zirconium concentrations, indicating that the material is thermodynamically stable against spontaneous vacancy formation. Varying the concentration of zirconium does not noticeably impact the formation energy of oxygen vacancies, with the 4Zr local cation environment consistently exhibiting the lowest formation energy across zirconium doping concentrations. The energetic ordering of the different local cation environments is also preserved across the doping range, indicating the impact of zirconium doping is secondary. Moving to the $q = +2$ state in Figs. 2(e)–2(g), across the doping range for $q = +2$ charged vacancies, the formation energies are spread over a range of 250 meV [Figs. 2(e)–2(g)], which is lower than the energy range for neutral vacancy formation. Similar to the case of a neutral vacancy, the level of zirconium doping has no significant effect on the ordering of formation energies across local cation environments for a $q = +2$ vacancy. For completeness, we note that the relative differences in formation energies between local cation environments are preserved across all Fermi-level values for a given charge state, so Figs. 2(b)–2(g) present the relative formation energies at an arbitrary Fermi level where the relevant charge state is the most stable for the considered doping concentration.

The level of zirconium doping has no discernible impact on the formation energies; however, it does impact the distribu-

tion of local cation environments. For example, at zirconium doping concentrations of $x = 0.25$ and $x = 0.75$, some local environments are absent due to statistical improbability. At $x = 0.25$, the 3Zr environment is missing [Figs. 2(b) and 2(e)], while at $x = 0.75$, 3Hf and 4Hf environments are absent [Figs. 2(d) and 2(g)]. To quantify this, we sampled the local cation environment from 10 000 stochastically generated structures. The frequency of occurrence of these absent sites was below 0.6% in all cases (see Supplemental Material Fig. S5 [47]). The frequency at which the most probable sites for oxygen vacancy formation occurs gives an indication of the impact that the level of zirconium doping has on the oxygen vacancy density. In the charge-neutral case ($q = 0$) the 4Zr local cation environment was the most energetically favorable; the frequency with which this local cation environment occurred in $x = 0.75$ is approximately 6 times higher than at $x = 0.50$, and approximately 155 times higher than at $x = 0.25$. This suggests that higher levels of zirconium doping would have a larger density of oxygen vacancies due to the increased number of energetically favorable sites.

This indicates a hierarchical influence on defect energetics, led by charge state, followed by vacancy site type, and finally the local cation environment. Zirconium content only indirectly affects defect energetics by controlling the probability of the occurrence of local cation environments and thus the total number of expected sites for oxygen vacancy formation, implying that zirconium doping can be used as a lever to control the density of oxygen vacancies in $\text{Hf}_{x-1}\text{Zr}_x\text{O}_2$.

Using the frequency of occurrence and the formation energies, the Boltzmann probabilities (P_i) for the occupation of a local cation environment with an oxygen vacancy can be calculated, and from this the expected number of sites can be obtained (See Supplemental Material [47] for details of the calculation). For the charge transition $q = 0$ to $q = +2$ we find that the expected number of available sites for oxygen vacancy formation increases for all doping levels. This increase in the available sites for oxygen vacancy formation results in an increased probability of an energetically favorable percolation pathway to exist for oxygen vacancy diffusion. We find that as the concentration of zirconium doping increases, the percentage change in the number of expected sites due to the charge transition $q = 0$ to $q = +2$ decreases from 45.6% ($x = 0.25$), down to 28.3% ($x = 0.50$), to 12.3% ($x = 0.75$). Doping concentrations of $x = 0.25$ would therefore have the highest likelihood of a percolation pathway existing but also the lowest initial density of oxygen vacancies; the opposite is true for $x = 0.75$ having the highest initial density of oxygen vacancies but the lowest likelihood of a percolation pathway existing. The value $x = 0.50$ therefore sits in a “goldilocks” zone for oxygen vacancy diffusion. Oxygen vacancies are needed to stabilize the ferroelectric phase; however, larger concentrations can cause disordered dipoles and high leakage currents, degrading the measured polarization. This provides an explanation for why films with $x = 0.50$ exhibit the best ferroelectric properties; having enough oxygen vacancies for maximal phase stability while also being optimal for oxygen vacancy diffusion.

During the $q = 0$ to $q = +2$ charge transition, the two electrons localized at the charge-neutral oxygen vacancy must

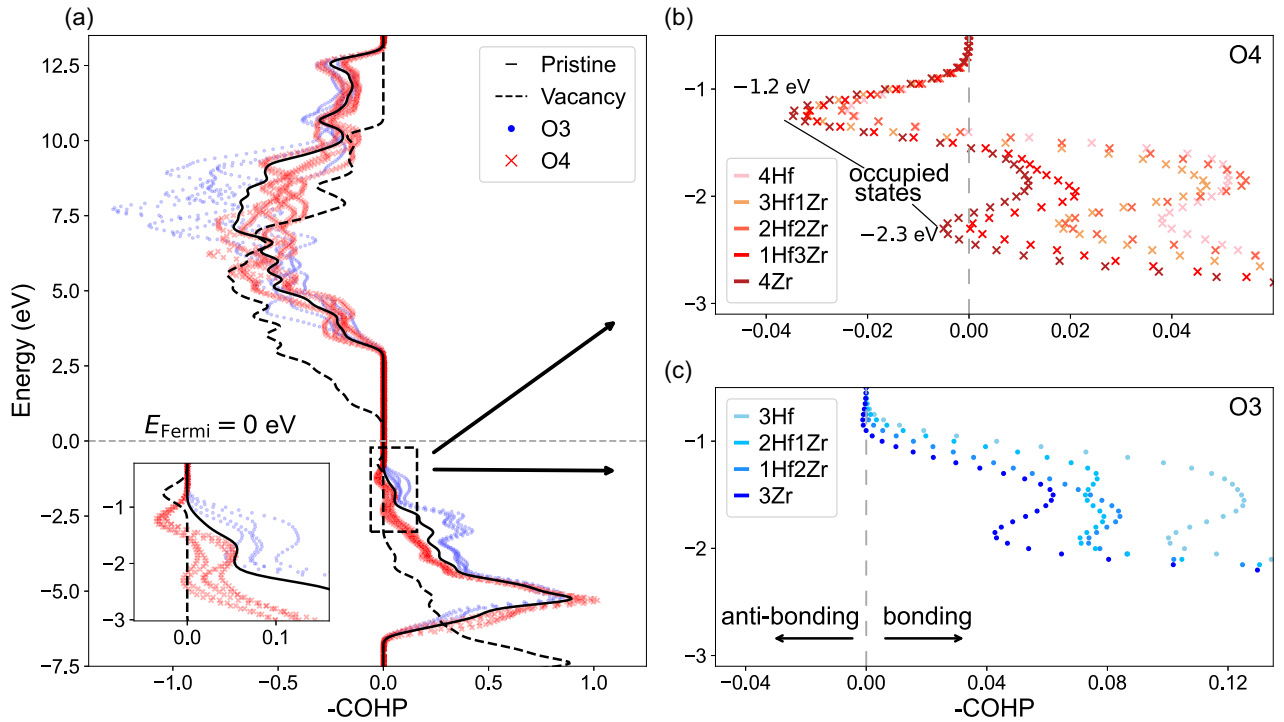


FIG. 3. The negative of the Crystal Orbital Hamiltonian Population (COHP) is plotted so that bonding states take on positive values and antibonding states are negative. The Fermi level is set to 0 eV. (a) Total average $-\text{COHP}$ for oxygen vacancy containing (dashed black line) and defect-free pristine (solid black line) ferroelectric $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ with partial $-\text{COHP}$ defect-free O3 (blue dots) and O4 (red crosses) local cation environments. (b) Region of interest for the partial $-\text{COHP}$ for the five different types of O4 site (4Zr, 3Zr1Hf, 2Zr2Hf, 1Zr3Hf, 4Hf). (c) Region of interest for the partial COHP for the four different types of O3 site (3Zr, 2Zr1Hf, 1Zr2Hf, 3Hf). The dashed line in (b) and (c) is the zero line.

overcome a transition barrier to be promoted to the conduction band. In real ferroelectric devices with metal electrodes, these electrons may instead transfer to the Fermi level of the electrodes, where the effective barrier is typically lower than the full band gap due to band alignment and Schottky effects at the interface. Experimentally, external electric fields are applied to switch the polarization, with typical values around 2 MV/cm as reported by Jan *et al.* [49]. To induce the charge transition, the applied bias must be greater than or equal to the transition barrier. We calculate this barrier (see Supplemental Material Fig. S6 [47]) to be 1.47 MV/cm for a 5 nm film, indicating that the experimentally applied bias is sufficient to trigger the transition. Once a defect transitions to the $q = +2$ charge state, it becomes energetically favorable for the oxygen vacancy to migrate from a 4Zr site. Previous calculations [22] have shown that the kinetic energy barrier for migration is significantly lower in the $q = +2$ state (< 1 eV) than in the $q = 0$ (> 2.3 eV). Additionally, the charge transition results in a 28.3% ($x = 0.50$) increase in the number of expected sites for oxygen vacancy formation. This increase enhances the diffusion gradient and improves the likelihood that a continuous percolation pathway exists. Thus, the $q = 0$ to $q = +2$ charge transition acts as a catalyst for oxygen vacancy motion in $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$, driving vacancies toward more stable sites under applied bias. This migration could lead to an increase in the measured value of spontaneous polarization [41], with defects migrating away from O4 sites that are typically located at domain walls [50] providing another link between oxygen

vacancy motion and the increase in polarization seen during the wake-up process.

To gain a deeper insight into the formation of oxygen vacancies in relation to the local cation environments, we calculate the crystal orbital Hamiltonian population [51–55] (COHP; the negative of the COHP is plotted so that bonding states take on positive values and antibonding states are negative) for all cation-to-oxygen bonds in both the defect-free and oxygen vacancy-containing structures. We also calculate the partial $-\text{COHP}$ for the set of nine local cation environments in the defect-free structure (See Supplemental Material [47] for details of the calculation). The solid black line in Fig. 3(a) shows the total average $-\text{COHP}$, which includes all metal-oxygen bonds in the structure. Upon formation of a charge-neutral ($q = 0$) oxygen vacancy in $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$, an occupied antibonding state appears in this average $-\text{COHP}$ (highlighted by the dashed black line), relative to the defect-free case. This feature consistently emerges regardless of which oxygen site is removed, and the associated electrons are strongly localized near the vacancy site and its nearest-neighbor cations (see Supplemental Material Figs. S7 and S8 [47]). To better understand the local contributions to this average signal, we also show partial $-\text{COHP}$ s (red and blue lines) for the set of nine local cation environments. These local $-\text{COHP}$ s do not sum to the total average $-\text{COHP}$ because they only account for a subset of the 64 metal-oxygen bonding environments in the supercell. Instead, they serve to illustrate how specific local configurations contribute

characteristic bonding features to the total average. Examination of the defect-free partial average $-\text{COHPs}$ within the energy range corresponding to this antibonding state [Fig. 3(a), inset] provides insight into the site-dependent variation in vacancy formation energies. The nature of the local cation environment strongly influences the bonding characteristics in this region. In both O3 and O4 coordination environments, an increasing zirconium concentration systematically reduces bonding contributions, as observed in the partial $-\text{COHPs}$ for the 3Zr [Fig. 3(c), darkest blue dots] and 4Zr [Fig. 3(b), darkest red crosses] configurations. A critical distinction lies in the presence of preexisting antibonding states: all O4-type environments exhibit an occupied antibonding state at approximately -1.2 eV [Fig. 3(b)], while in the 4Zr configuration, an additional antibonding state is present at -2.30 eV. Consequently, the formation of a vacancy at an O3 site results in the removal of bonding states and the creation of a new occupied antibonding state [Fig. 3(a), dashed black line], leading to a significant increase in the total energy. In contrast, vacancy formation at an O4 site primarily removes bonding states without generating additional antibonding states, resulting in a comparatively smaller energy increase. Furthermore, in the 4Zr O4 environment, the removal of the oxygen atom also eliminates the antibonding state at -2.30 eV, which further lowers the total energy of the system. This mechanism accounts for the lower formation energies of charge-neutral oxygen vacancies at O4 sites and explains their favorable energetics in pure HfO_2 relative to O3 sites. In the case of a doubly positively charged vacancy ($q = +2$), the antibonding state associated with vacancy formation shifts above the Fermi level and remains unoccupied (see Supplemental Material Fig. S9 [47]). As a result, the destabilizing effect of the occupied antibonding state observed in the charge-neutral case is absent, thereby mitigating the energy penalty typically associated with oxygen vacancy formation. This explains why the energetic ordering of the local cation environment is lost in the $q = +2$ charge state.

IV. CONCLUSION

Our results also align with several robust experimental trends in $\text{Hf}_{x-1}\text{Zr}_x\text{O}_2$ ferroelectrics. Films with Zr concentrations near $x \approx 0.5$ consistently exhibit the highest fraction of orthorhombic phase and therefore the strongest ferroelectric response, but also show pronounced wake-up behavior [2,9,10]. In our calculations, this composition simultaneously optimizes the density of low-energy vacancy environments and the increase in accessible sites triggered by the $q = 0$ to $+2$ charge transition, providing a microscopic route for enhanced defect mobility under bias. Experimental studies further show that oxygen-rich to oxygen-poor processing conditions shift the structural balance from monoclinic toward orthorhombic and ultimately tetragonal phases [11].

This trend is mirrored in our finding that Zr content primarily modifies the availability of favorable vacancy environments rather than their individual formation energies. Finally, the experimentally observed link between wake-up and vacancy redistribution [33–35] is consistent with our result that charged vacancies not only lower migration barriers [22] but also expand the percolation network of accessible sites. While a detailed mapping to specific measurements lies beyond the scope of this work, the overall consistency indicates that local cation environments and charge state-dependent defect energetics provide a microscopic framework that complements the main experimental observations across Zr doping and processing conditions.

This work elucidates the role of zirconium content on oxygen vacancy formation in ferroelectric $\text{Hf}_{x-1}\text{Zr}_x\text{O}_2$ across doping levels $x = 0.25, 0.50, 0.75$ and charge states. Zirconium disrupts the binary vacancy formation energy landscape of pure HfO_2 , producing a distribution governed by nine distinct local cation environments. For charge-neutral vacancies ($q = 0$), the 4Zr environment exhibits the lowest formation energy, attributed to the removal of a preexisting antibonding state. Increasing zirconium content enhances the density of such favorable sites without significantly altering individual formation energies. In the $q = +2$ state, vacancy-induced antibonding states shift above the Fermi level, reducing the energetic cost and increasing the number of available sites. These results suggest that electric field-driven charge-state transitions can facilitate vacancy mobility in $\text{Hf}_{x-1}\text{Zr}_x\text{O}_2$ films, with implications for ferroelectric reliability and switching behavior.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [56].

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