Tetravalent Doping in Fluorite-Based Ferroelectric Oxides for Reduced Voltage Operations

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ABSTRACT: First-principles calculations show a reduced energy barrier for polarization switching via a bulk phase transition by doping of hafnium-zirconium oxide (HZO). The tetragonal $P4_2/nmc$ phase serves as a transition state for polarization switching of the polar orthorhombic Pca2₁ phase. Due to the high symmetry of the tetragonal phase, dopants can form more energetically favorable local oxygen bonding configurations in the tetragonal phase versus the orthorhombic phase. Significant bond strain is observed in the orthorhombic phase due to the low symmetry of the host crystal structure which decreases the relative stability of the doped orthorhombic phase compared to the doped tetragonal phase, thereby significantly lowering the barrier for switching but slightly affecting the polarization of the orthorhombic phase. Si is a



promising dopant for an efficient ferroelectric device with minimal disturbance in the electronic structure parameters. Ge doping is suitable for stabilizing the tetragonal phase which shows a high k value.

KEYWORDS: density functional theory, ferroelectric device, operation voltage, tetravalent doping, hafnium oxide

INTRODUCTION

Fluorite-based binary ferroelectric (FE) oxides such as hafnia (HfO₂), zirconia (ZrO₂), and their alloys (Hf_xZr_{1-x}O₂, HZO) offer great promises for in-memory compute and nonvolatile memory applications along with their CMOS-compatible processing.¹ Thanks to the robust ferroelectricity, scalability and CMOS compatibility, FE field-effect transistors (FEFETs) based on HZO thin film as gate oxide have been investigated extensively. However, they require operation voltages of at least ± 1.5 V, challenging efficient device operation. Lower coercive voltage directly indicates less energy dissipation during the device operation. Furthermore, lower read/write voltages applied to the gate oxide would induce less leakage and field-induced stresses, which are beneficial to improved endurance.

The advantage of doping Zr in HfO_2 is that the doped Zr can stabilize independently the FE orthorhombic phase while the additional dopants substitute at the Hf or Zr sites. Experimentally, while pure HfO_2 and ZrO_2 tend to form the paraelectric monoclinic phase and the antiferroelectric (AFE) tetragonal phase, respectively, the FE orthorhombic phase is favored in the mixture, that is, HZO.² Hf and Zr ions are of similar size and have similar bonding, thus they have similar oxide polymorphs as shown by the previous DFT calculations;³ therefore, the composition-dependent phase stability is determined by the kinetic factors such as annealing temperature, grain size, and interfacial free energy. Note, due to the

similarity between Hf and Zr, the extra tetravalent dopants introduced during the growth process would substitute at either the Hf or Zr sites, but the effects of doping would not be dependent on the dopant site, that is, Hf or Zr. Instead, the overall doping concentration and the phase of the parent HZO material would be the significant factors affecting the phase stability and switching characteristics.

Switching mechanisms of the polarization states, i.e., up and down, for HfO_2 have been investigated previously by using density functional theory (DFT) calculations. Clima et al. claimed that the polar orthorhombic Pca2₁ phases change the polarization states through *Pbcm* phase with a barrier height of 100 meV per HfO_2 formula unit (meV/fu).⁴ Huan et al. suggested the pathway through the antiferroelectric tetragonal $P4_2/nmc$ phase which is about 90 meV/fu higher in energy than the polar orthorhombic Pca2₁ phase, but the calculated barrier was overestimated due to the extra crystal rotation.⁵ Later, Barabash et al. showed the lower energy pathway is through antiferroelectric tetragonal $P4_2/nmc$ phase with the barrier of 90 meV/fu.⁶ Recently, Choe et al. proposed an

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Figure 1. Energy landscape and polarization changes in pristine and doped HZO during the polarization switching through the P4₂/nmc phase. (a) The energy landscape changes due to the tetravalent doping. The polarization switching energy barrier (E_b) and the difference in energy between Pca2₁ and P4₂/nmc phases (ΔE) are marked in the energy curve. (b) Local O arrangements are shown for the polar and transient states. Displaced O atoms in the polar states can be compared with the O atoms at neutral positions in the transient state, shown as blue dashed line. (c) Spontaneous polarizations for different dopants are shown during the polarization switching. (d) Scatter plot of E_b and ΔE are shown for 3% doped HZO as well as pure HZO.

efficient pathway of polarization switching by domain wall motion.⁷ It is noted that, up to date, polarization switching via bulk phase transition with the tetragonal phase as a transient state is the most widely accepted polarization switching mechanism.

Several DFT studies reported the change in relative phase stability due to tetravalent⁸ and aliovalent^{9,10} doping in HfO₂. Clima et al. reported the reduced polarization switching energy barrier in Si-doped HfO₂, but the polarization switching pathway was via the *Pbcm* phase instead of the *P*4₂/*nmc* phase.⁴ Yang et al. reported the effects of Si doping in HfO₂ on the polarization switching energy barrier via a paraelectric monoclinic *P*2₁/*c* phase¹¹ and an AFE tetragonal *P*4₂/*nmc* phase.¹² However, the polarization switching energy barrier for HZO, which is the most common composition for FE thin films,² has not been studied to the best of our knowledge. An important insight from the previous reports is that the energy barrier for polarization switching scales with the energy difference between the phases (to be discussed below).¹²

Experimentally, Si doping was used to stabilize both FE and AFE phases in HfO₂. The first FE HfO₂ thin films reported in 2011 were Si-doped HfO₂,^{13,14} and they were followed by many others, reporting that Si doping can tune the characteristics and functionalities of the fabricated films.^{15–17} Si doping in HfO₂ was shown to favor the FE orthorhombic phase at a low concentration and to favor the AFE tetragonal phase for higher Si content.^{16,17}

Compared with the perovskite-based ferroelectrics (BaTiO₃), for which the polarization switching barrier is about 10 meV/fu, fluorite-based FE HZO show a much large switching barrier of about 100 meV/fu.¹⁸ This is partly due to the intrinsically high energy difference between the polar orthorhombic phase and the intermediate tetragonal phase, which ranges 80–100 meV/fu depending on the composition of HZO.³ Accordingly, it is hypothesized that introducing

tetravalent dopant would effectively change the energy landscape to lower the polarization switching barrier by distorting the local bonding configurations of the dopants. The tetravalent dopants have advantages over the aliovalent dopants such as La and Y with a trivalent charge state in that they do not require additional charge-compensating defects such as oxygen vacancies.⁹

Here, DFT calculations are conducted to investigate the effects of tetravalent doping in HZO on the relative phase stability and polarization switching behavior. HZO model is used in this work because HZO thin films are much more widely used for FE device applications than pristine HfO₂ thin films which tend to form a paraelectric monoclinic $P2_1/c$ phase.² Various tetravalent dopants (Si, Ge, Ti, and Ce) of technological importance are used to substitute the Hf sites in both the orthorhombic and tetragonal phases. Upon doping, the polarization switching barrier is decreased significantly due to the reduced energy difference between the orthorhombic phase and the tetragonal phase. The orthorhombic phase becomes relatively destabilized compared to the tetragonal phase because the dopant site cannot have favorable bonds with the neighboring O atoms due to the low crystal symmetry. The effects on relative phase stability are most significant for small ions such as Si and Ge. Si seems a promising dopant in HZO for efficient FE device applications due to the absence of dopant states in the band gap. Ge doping, however, should not be used for FE device applications due to the formation of deep trap state. Conversely, Ge does not form a gap state in the tetragonal phase and might be employed to stabilize the tetragonal phase for high k dielectric applications.

COMPUTATIONAL DETAILS

Density functional theory (DFT) was employed to elucidate the effects of tetravalent doping in bulk HZO on the polarization switching. All the DFT calculations were

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Figure 2. Energy landscape in doped HZO during the polarization switching through P4₂/nmc phase. Total energy during the polarization switching as a function of (a) Si, (b) Ge, (c) Ti, and (d) Ce content in HZO calculated by the CI-NEB method. (e) ΔE is summarized for all the dopants as a function of doping content. $\Delta E = 0$, shown as dashed line, refers to a morphotropic phase boundary condition, above (below) which Pca2₁ (P4₂/nmc) phase is stabilized.

performed by using Vienna ab initio Software Package.^{19,20} Tetravalent dopants (Si, Ge, Ti, and Ce) were assumed to substitute in the Hf sites. Since Hf and Zr ions have very similar valence charge and ionic size, it is hypothesized that the doping effects are not site-specific, so that the only Hf sites were considered for simplicity. The tetragonal $(P4_2/nmc)$ phase was assumed as an intermediate state for polarization switching between the bistable polar states (i.e., polarization up and down) in orthorhombic (Pca2₁) phase.^{5,6} Supercells of $2 \times$ 2×2 containing 32 (Hf/Zr)O₂ formula units (or 96 atoms) were used to model 3% (1/32 Hf/Zr site) and 6% (2/32 Hf/ Zr site) substitutional doping. For Si, $3 \times 2 \times 2$ supercells containing 48 (Hf/Zr)O₂ formula units (or 144 atoms) were used to model 2% (1/48 Hf/Zr site) doping. For Ge, $3 \times 1 \times 1$ and $2 \times 1 \times 1$ supercells were used for 8% (1/12 Hf/Zr sites) and 12.5% (1/8 Hf/Zr sites) doping. Total energy and intermediate atomic positions during the polarization switching process were interpolated by using climb image nudged elastic band (CI-NEB) method.²¹⁻²³ The energies of the images during switching were interpolated by using a cubic spline as implemented in SciPy.²⁴ Spontaneous polarizations in crystalline solids were calculated based on the Berry phase of the Bloch wave functions as described in the modern theory of polarization.²⁵

To represent electron wave functions, plane-wave basis set were used with a kinetic energy cutoff of 500 eV, and the pseudopotential core part was described by the projector augmented wave method.²⁸ Perdew-Burke-Ernzerhof²⁹ exchange-correlation functional was used to construct the Kohn-Sham Hamiltonian. For Brillouin zone sampling, Monkhorst-Pack³⁰ scheme was used on a $6 \times 6 \times 6$ grid for the unit cell of HZO, and was adjusted for supercells accordingly. The Kohn-Sham eigenvalues were regarded selfconsistent with the energy difference less than 10^{-5} meV. Both ions and lattice parameters for pristine systems were relaxed with the force criteria of 1 meV/Å. For doped systems, ionic relaxation was conducted in a fixed cell with the force criteria of 10 meV/Å, and the same force criteria was used for NEB calculations. Hybrid DFT calculations with a mixing parameter of 0.2 were used to correct the underestimated band gap values of the HfO_2 and ZrO_2 .

RESULTS AND DISCUSSION

Figure 1a shows the energy landscape during the polarization switching process of the orthorhombic Pca2₁ phase via the tetragonal $P4_2/nmc$ phase in pristine and 3% doped HZO. The energy barrier for polarization switching (E_b) is about 80 meV/ formula unit (meV/fu) for pristine HZO, consistent with previous calculations in HfO₂.^{6,7,31,32} The barrier decreases in the doped HZO, but the amount of reduction in the $E_{\rm h}$ varies with the type of dopant. The reduction is most significant for Si doping, followed by Ge, Ti, and Ce. O atomic positions as illustrated in Figure 1b are responsible for the energy landscape. The displaced O atoms relative to the metal ions (Hf or Zr) are shown in the polar states, whereas the O atoms are located at the symmetric position in the nonpolar state as indicated by the blue dashed line. Macroscopic polarizations, calculated by using the modern theory of polarization,²⁵ change during the polarization switching process are shown in Figure 1c. In orthorhombic phase of pristine HZO, the polarization of 51.9 μ C/cm² is in agreement with the previous results.^{5–7,31–33} Unlike the reduction in the $E_{\rm b}$, polarizations are nearly unchanged by doping as seen in Supporting Information (SI) Figure S1. Note that it does not mean that the macroscopic polarization does not change with doping because tetravalent doping can increase the fraction of nonpolar phases (e.g., monoclinic and tetragonal phases).^{15–17}

During the polarization switching process, the intermediate tetragonal phase shows a very shallow energy well at the tetragonal phase (Figure 1a), so the energy barrier $E_{\rm b}$ and ΔE (= $E_{\rm tetra} - E_{\rm ortho}$) – the energy difference between the orthorhombic and tetragonal phases, are quite close to each other. Figure 1d shows a scatter plot of the $E_{\rm b}$ and the ΔE in various doped HZO, clearly displaying a nearly linear correlation. This indicates that the ΔE can serve as a good indicator of the $E_{\rm b}$. Note, for given doping concentration of 3%, the decrease in both $E_{\rm b}$ and ΔE is greater as the size of dopant ion decreases, that is, the decrease is greater for Si > Ge > (Ti \approx Ce), indicating the role of local oxygen bonding configurations of the dopants.

Figure 2 shows the polarization transition energy landscapes in the doped HZO with varying doping concentrations. Both



Figure 3. Local atomic configurations in pristine and doped HZO. (a,b) Hf/Zr, (c,g) Si, (d,h) Ge, (e, (i) Ti and (f, j) Ce sites are shown for both $P4_2/nmc$ and $Pca2_1$ phases. For dopants, the outline of (Hf/Zr)-O polyhedron is shown for a reference.

 $E_{\rm b}$ and ΔE decrease with an increasing doping concentration as mentioned above. The energy landscape is most sensitive for Si doping: the $E_{\rm b}$ varies from 80 meV/fu to 46 meV/fu (43% reduction) and 31 meV/fu (61% reduction) for 2% and 3% Si doping, respectively. For 6% Si doping, the tetragonal phase becomes more stable than the orthorhombic phase, so was not considered in this study. For Ge, the $E_{\rm b}$ is decreased to 53 meV/fu (34% reduction) and 33 meV/fu (59% reduction) for 3% and 6% Ge doping, respectively. For Ti and Ce doping, the amount of reduction in the energy landscape is smaller compared with Si and Ge.

The effect of doping in the relative phase stability (ΔE) is summarized in Figure 2e. The ΔE varies almost linearly with the doping content, and the reduction is significant for Si and Ge. The stabilization of the tetragonal phase relative to the other phases due to tetravalent dopants is in agreement with previous experimental¹⁶ and theoretical⁸ studies on doping of HfO₂. Conversely, polarization is nearly independent of the dopant type and concentration (see Figure 1c and SI Figure S1). For ~5% and ~10% Si- and Ge-doped HZO, respectively, there is an energetic crossover of the phase stability, after which the $P4_2/nmc$ phase becomes more stable than the Pca2₁ phase, and the films no longer show ferroelectric behavior. This is not desired for stable ferroelectric device operations. Therefore, the doping content must be precisely controlled to optimize the device performance.

Doping of Si and Ge changes the energy landscape of the HZO. The energy curve along the switching pathway is slightly different for 3% Si doping of HZO than the other concentrations as shown in Figure 2a; a slight shoulder is observed between the $Pca2_1$ and the $P4_2/nmc$ phase. (see SI Figure S2 for the spline fit of the data points.) For Ge doping, when the doping content is reached at 6%, the tetragonal phase shows a deeper energy minimum compared with other cases as in Figure 2b. This is because of the stronger covalency of Si and Ge, and the bonding energy is sensitive to the coordination number and bond angle. Due to the difference in oxygen bonding characteristics between Si/Ge and Hf/Zr, the energy landscape is significantly varied in these cases

compared with the pristine HZO. The effects are much weaker for Ti and Ce as shown in Figure 2c,d.

The decrease in the ΔE is attributed to the local bond distortion in the vicinity of the dopant site. The tetravalent dopants differ in size and bonding character; therefore, local oxygen coordination structures are changed compared with the host Hf or Zr atoms. In the pristine HZO, the tetragonal $P4_2/$ *nmc* phase shows a distorted cubic local configuration with a coordination number (CN) of 8 (Figure 3a), while the orthorhombic Pca2₁ phase shows further distorted structure with a CN of 7 (Figure 3b). The reduction in the CN in transitioning from the tetragonal phase to the orthorhombic phase, is due to the displaced O atoms, accompanying oxygen-metal bond breaking, which are responsible for the macroscopic polarizations (see Figure 1b). The detailed analysis of bond distance distribution in difference phases and dopants in HZO is provided in SI Figure S3.

When Si, Ge, and Ti are doped in the tetragonal $P4_2/nmc$ phase, the local structure of the HZO is substantially changed to form the tetrahedral local structure as shown in Figure 3ce. Note that this is particularly favored for Si and Ge, of which the local structures of the intrinsic oxides (i.e., SiO_2 and GeO_2) are tetrahedral. Conversely, the tetrahedral local structure near the Ti is less favored due to the Ti being stabilized in an octahedral local structure in TiO2. This explains the more dramatic reduction in the ΔE by the Si and Ge doping as shown in Figure 2e. Note that the tetrahedral coordinates are formed by systematic relaxations in the tetragonal phase; half of the O are attracted toward the dopant site, while the other half of the O are pushed away from the dopant site. This can be confirmed by increased splitting of the bond distance distribution due to the doping of Si, Ge, and Ti as in Figure S2b-d. Short bonding distances of SiO₄, GeO₄, and TiO₆ local structures are close to the bulk phase bonding distances in SiO_{2} , GeO_{2} , and TiO_{2} . Such a concerted local relaxation is enabled by the high crystal symmetry of the tetragonal phase. Ce, however, binds with 8 O atoms as in the pristine HZO as seen in Figure 3f.

In contrast, crystal symmetry of the orthorhombic phase is relatively low, and the oxygen atoms at the dopant site cannot

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Figure 4. Density of states in pristine and doped HZO. (a,f) Pristine, (b,g) Si-, (c,h) Ge-, (d, (i) Ti-, and (e, j) Ce-doped HZO with a concentration of 3%. Energy of 0 eV corresponds to the VBM.

freely relax to the ground state due to the constraints from the surrounding atomic structures. Larger residual bond strains, especially for Si and Ge, can be seen in Figure S2g,h. The local structures end up being a distorted octahedron with a varying CN as shown in Figure 3g–i. Trends in the local structures of Si, Ge, and Ti doping in HZO are consistent with previous calculations⁸ on Si doping of HfO₂: tetrahedral Si–O bonding network in the tetragonal HZO and distorted octahedral Si–O bonding network in the orthorhombic HZO. (Si may show octahedron with CN of six depending on the cutoff value of Si–O bond distance. In this study, Si–O bond cutoff of 2.0 Å is used, while the sixth Si–O bond distance is about 2.14 Å; see SI Figure S3g.) The local structures of Ce in HZO are less sensitive to the phase, showing similar structures to the Hf local structure in the pristine HZO as seen in Figure 3f.j.

The reduction in both ΔE and E_b as observed in Figure 2e can be understood by the local structures shown in Figure 3. The doping only modestly affects the tetragonal phase, while destabilizing the orthorhombic phase thereby decreasing ΔE , which is most significant for Si and Ge, whereas the effect is much weaker for Ti and Ce. Si and Ge in the tetragonal HZO can have the favorable tetrahedral local structure as in Figure 3c,d. Conversely, in orthorhombic HZO, the local bonds are constrained due to the surrounding atoms, so that Si and Ge have very unstable local structures as seen in Figure 3g,h. Due to the smaller size and stronger covalent bonding of Si than Ge, Si doping shows greater effects in reducing the ΔE as shown in Figure 2e, consistent with the limited doping concentration as mentioned above.

Due to the difference in size and chemistry between the dopant and the host ions (Hf/Zr), the relative phase stability between the relevant phases (orthorhombic vs tetragonal phases) changes significantly. The high-symmetry tetragonal phase can accommodate different ions by symmetric relations as shown in Figure 3, resulting in relatively stable structures. Conversely, tetravalent structures cannot be stabilized in the low-symmetry orthorhombic phase. This raises the energy of the orthorhombic phase relative to the tetragonal phase, reducing both the energy difference (ΔE) and the energy barrier (E_b).

The different amount of ΔE reduction can be supported by the ground state local bonding structures of those materials in their oxide forms: SiO₂, GeO₂, TiO₂, and CeO₂ being tetrahedral, tetrahedral, octahedron, and cubic, respectively. When those tetravalent species are doped in HZO, they form different local structures depending on the size of the atoms and host crystal structure.⁸ Smaller ions such as Si and Ge form stronger bonds to the O atoms and are more sensitive to the bond strain; therefore, there is a stronger tendency for the smaller ions to destabilize the orthorhombic phase relative to the tetragonal phase.

Figure 4 shows density of states (DOS) calculated in pristine and doped HZO. As an ionic solid, the pristine HZO has valence and the conduction bands composed of O p states and Hf and Zr d states, respectively (Figure 4a,f). When doped with Si, HZO shows a clean, wide band gap without any midgap states associated with the doped Si, similar to the pristine HZO, as can be seen in Figure 4b,g. Si states in the valence band are well-hybridized with the host Hf states. For Ge doping, no midgap states are observed in the tetragonal phase (Figure 4c) similar to Si. However, a highly localized midgap state mainly composed of the doped Ge appears near the conduction band minimum in the orthorhombic phase (Figure 4h). The phase-dependent occurrence of the midgap state is attributed to local bond strains in the orthorhombic phase. The dopant states become more pronounced for Ti and Ce, decreasing size of the bandgap (Figure 4d,e,i,j). Moreover, these midgap states due to the substitutional dopants would not be desired and should be avoided because they could act as trap states, degrading the device performance.

The presence of dopant states in the bandgap is related to intrinsic size of the band gap of the bulk oxides of dopants. While the bandgap of HZO from the DFT calculations is 3.8 eV, the sizes of the DFT band gaps for SiO₂, GeO₂, TiO₂, and CeO₂ in their ground state structures are 5.9 eV, 3.3 eV, 2.7 eV, and 1.9 eV, respectively. (These DFT band gap values are \sim 50% smaller than experimental band gap values, but the overall trend is consistent enough to provide a meaningful interpretation in the current analysis. The experimental bandgaps are summarized in the SI Table S1.) The band gaps of HfO₂ and ZrO₂ in the tetragonal phase calculated from hybrid DFT calculations are 6.16 and 5.46 eV, consistent with the experimental bandgaps of 5.8 and 5.5 eV, respectively. The calculated band gap values are consistent with the other post-DFT calculations as listed in the SI Table S2. Note that SiO₂ has a larger bandgap than HZO, while the sizes of the bandgaps for GeO₂, TiO₂, and CeO₂ are smaller. The bonding-antibonding split in the oxide bond states is a critical factor because the valence and the conduction bands of oxides are mainly composed of O p and cation states, respectively, determining the size of the bandgap of the doped HZO. Consequently, the positions of the dopant states in the band gap might be located inside or outside of the HZO bandgap depending on the relative bond strengths with respect to the HZO.

Ge-doped HZO in the orthorhombic phase shows distorted octahedral local structures in the Ge site (see Figure 4h), inducing a midgap state. Conversely, Ge has a tetrahedral local configuration when doped in the tetragonal HZO (Figure 3d), pushing the Ge state above the conduction band minimum (Figure 4c). This is consistent with the larger bandgap shown in the GeO₂ with the tetrahedral local structure (space group of $P3_121$) than that of the octahedral local structure ($P4_2/mnm$, Arguite): 3.3 eV vs 1.9 eV. The electronic structures of Ge in the tetragonal phase remain intact in a relatively high doping concentration of 12.5% (SI Figure 2e).

To quantify the Ge gap state in the orthorhombic phase during device operation conditions, relative formation energy $(\Delta E_{\rm f})$ of 3% Ge-doped HZO depending on various charge states is calculated as

$$\Delta E_{\rm f} = \Delta E_{\rm tot} + q(E_{\rm VBM} + \mu_{\rm e}) \tag{1}$$

where ΔE_{tot} is the total energy difference between charged and neutral 3% Ge-doped HZO systems, *q* is additional charge in the system, E_{VBM} is the energy of the valence band maximum (VBM), and μ_{e} is the electronic chemical potential which is 0 eV at the VBM. The ΔE_{f} in Figure 5 shows a charge transition



Figure 5. Relative formation energy of 3% Ge doping in HZO as a function of electronic chemical potential (μ_e). Energy of 0 eV corresponds to the VBM. Charge transition level (CTL) between 0 and -2 charge states are located at 2.2 eV above the VBM.

level (CTL) of 0/-2 charge state at 2.2 eV above the VBM. This indicates that the Ge gap state (Figure 4h) remains empty until the μ_e is reached at 2.2 eV, and is doubly occupied with electrons with the μ_e higher than 2.2 eV. DOS with a variable charge state is shown in SI Figure S5.

The findings in this study can be extended to a guideline for a novel dopant for device applications based on the HZO to engineer the intrinsic properties of the film. (1) Change of the energy landscape sensitively depends on the local structures of the dopant and the host materials. (2) Both intrinsic bond strength to oxygen atoms and residual bond strains are critical to determine the presence of the dopant states in the bandgap.

CONCLUSIONS

Density functional theory is employed to elucidate the effects of doping in fluorite-based ferroelectric oxides to lower intrinsic polarization switching barrier. Si and Ge are shown to significantly reduce the switching barrier due to the selective destabilization of the orthorhombic phase relative to the transition state tetragonal phase. The local bonding structures of the dopant with the O atoms and the crystal symmetry of the host material are revealed to play a critical role in destabilizing orthorhombic phase because doping of the orthorhombic phase is less favorable than doping the tetragonal phase due to the low orthorhombic phase symmetry. Sufficiently strong intrinsic bond strength is primarily critical to ensure the large band gap without forming a dopant state in the bandgap, while low residual stress in the local structures is also important. Behavior of the Ge gap state, only present when doped in the orthorhombic phase near the conduction band, is documented, while the Ge doping of the tetragonal phase leaves a defect-free band gap suggesting that Ge is promising for stabilizing the tetragonal phase. The findings in this study can provide an effective method for the practical fabrication of emerging electronic devices based on ferroelectric oxide thin films.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c05886.

Polarization changes in pristine and doped HZO during the polarization switching through $P4_2/nmc$ phase. Polarization switching energy landscape for 3% Sidoped HZO. Bond distance distribution analysis. Density of states in 12.5% Ge-doped HZO in $P4_2/nmc$ phase. Density of states in 3% Ge-doped HZO in Pca2₁ phase with a varying charge state. Experimental band gap values of various oxides Post-DFT band gap values of various oxides (PDF)

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Notes

The authors declare no competing financial interest.

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