

Tetravalent doping in hafnium-zirconium oxides to lower polarization switching voltage

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Abstract—Effects of tetravalent doping (Si, Ge, Ti, Ce) are investigated in hafnium-zirconium oxide (HZO). Density functional theory is employed to demonstrate: 1) relative stability change, 2) polarization switching energy barrier, and 3) electronic structures in doped HZO. Si and Ge induce large local bond distortions and have more significant effects on stabilizing the tetragonal phase and lowering the polarization switching voltage than Ti and Ce. They also do not introduce any midgap states rendering great promise for memory applications.

I. INTRODUCTION

Low switching voltage in ferroelectric (FE) devices such as FeFET and FeRAM is crucial for efficient device operation. Functional response was shown to vary with a Si doping concentration in HfO₂[1] indicating the dependence of phase stability on doping. Fig. 1 shows the characteristic double-well potential energy landscape of FE materials with a varying polarization switching energy barrier height. In hafnium-zirconium oxide (HZO), the orthorhombic *Pca2*₁ and tetragonal *P4*₂/*nmc* phases are generally accepted as the polar and non-polar phases, respectively. Thus, polarization switching energy can be tuned by engineering relative stability. Doping is a viable option to engineer the properties of the HZO thin films, and some dopants have been studied in HZO thin films. For example, enhanced FE behaviors were shown in Gd-doped HfO₂[2] while Y-doped doping ZrO₂ is known to stabilize the cubic phase.

II. COMPUTATIONAL DETAILS

First-principles calculations based on density functional theory (DFT) were performed to study the effects of tetravalent dopants such as Si, Ge, Ti and Ce in orthorhombic and tetragonal HZO. It is hypothesized that the metal site

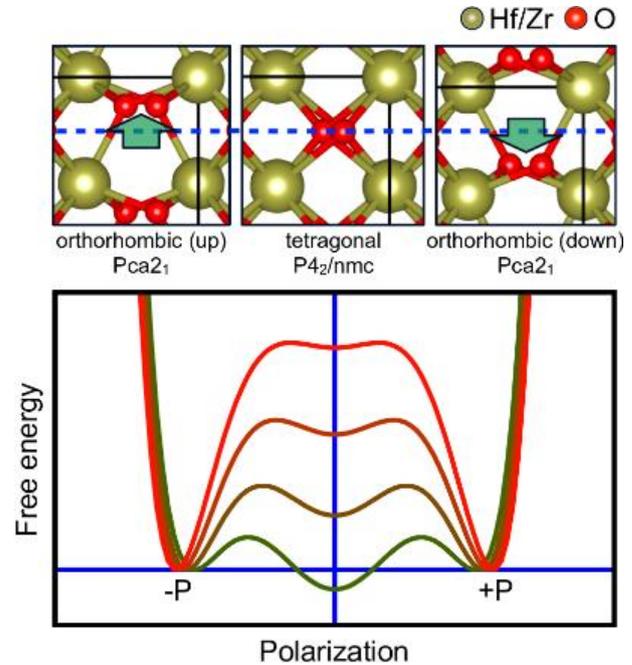


Fig. 1. Double-well free energy landscape of a FE material during polarization switching. The energy barrier height for the polarization switching qualitatively scales with the energy difference between the polar and non-polar states. In HZO, orthorhombic *Pca2*₁ and tetragonal *P4*₂/*nmc* phases are responsible for polar and non-polar states. (top) The displacements of the O atoms in the orthorhombic phase with respect to the symmetric positions in the tetragonal phase indicated by dashed line. (bottom) Energy barrier height for polarization switching can vary by the relative energy difference between *Pca2*₁ and *P4*₂/*nmc* phases.

(Hf/Zr) is replaced by the extrinsic dopants. Doping concentration was varied either by incorporating the different number of dopant atoms and using different supercell sizes. The climb-image nudged elastic band method was used to

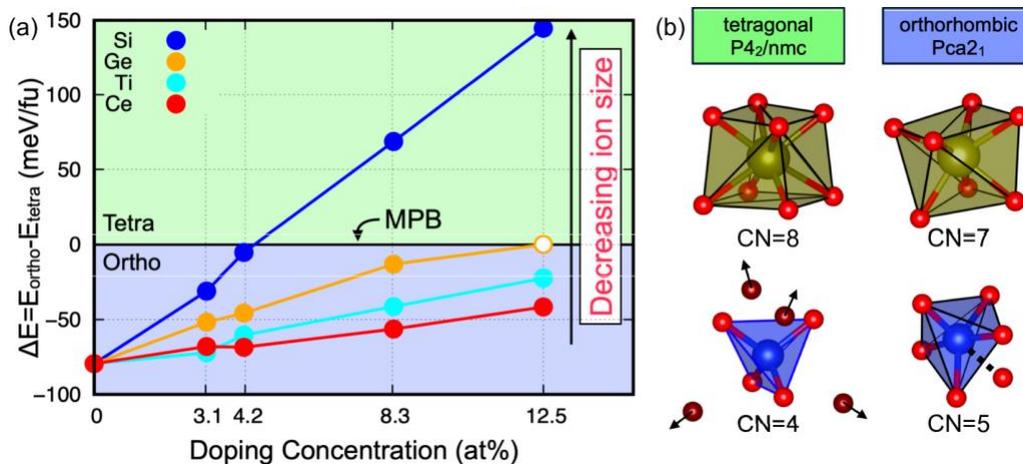


Fig. 2. Relative stability and local structures due to isovalent doping. (a) Energy difference (ΔE) between orthorhombic and tetragonal phase as a function of doping concentration and isovalent dopant. In all the cases, doping stabilizes the tetragonal phase, and is most significant as dopant size decreases. Morphotropic phase boundary (MPB) condition refers to the two phases in energetic degeneracy, i.e., $\Delta E=0$. (b) Local structures of the M-O and Si-O complexes in Si-doped HZO. In tetragonal phase, Si can easily form desirable tetrahedral local geometry by repelling 4 of the O atoms (dark red), while significant bond strain is induced adjacent to the Si site in orthorhombic phase due to its low symmetry.

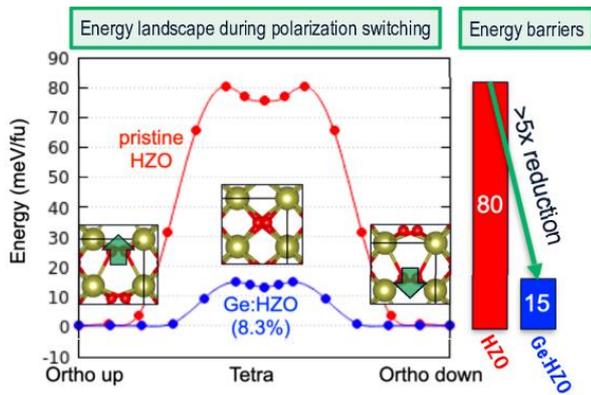


Fig. 3. Energy landscape during the polarization switching process. Nudged elastic band method was used to compute the variation in the energy during the polarization switching process. In pristine HZO, the energy barrier is 80 meV/fu, which is similar to the ΔE of 75 meV/fu. When Ge is doped at 8.3% in HZO, ΔE decreases significantly, thereby the energy barrier for polarization switching is reduced by more than 5x.

compute the energy barrier height for polarization switching. DFT calculations were performed as implemented in Vienna *ab initio* Simulation Package.[3] Exchange-correlation functional of Perdew-Burke-Ernzerhof[4] was implemented to build the Kohn-Sham Hamiltonian, and the projector augmented wave method was used for the core part of the wave functions.[5] The plane waves were expanded up to a kinetic energy cutoff of 450 eV, and the k -points were uniformly sampled within Brillouin zone at a minimum of 0.032 \AA^{-1} by using Monkhorst-Pack scheme.[6] The stopping criteria for DFT self-consistent field and conjugate gradient ionic relaxation were 10^{-5} meV and 10 meV/\AA , respectively.

III. RESULTS AND DISCUSSION

Doping the tetravalent atoms favors the tetragonal phase with respect to the orthorhombic phase, and the stabilization effect is increased as the size of dopant decreases as seen in Fig 2a. The increased effects for these small-sized ions are attributed to the significant local strains caused by the substitution, and the local distortion is significantly different depending on the phase of the HZO matrix.

In tetragonal HZO, where metals are octahedrally coordinated (coordination number, CN=8), the dopant atom can easily have a preferred tetrahedral configuration (CN=4) by repelling the 4 out of the 8 O atoms as illustrated in Fig 2b. In contrast, such a concerted motion is hindered in the orthorhombic phase due to the low symmetry thereby raising the energy of the orthorhombic phase. Si and Ge, favoring tetrahedral configuration, induce higher energy cost when doped into the orthorhombic phase due to the significant bond strains in the orthorhombic HZO (Fig 2b) which will lower the switching barrier by decreasing the energy difference between the tetragonal and orthorhombic phases.

Ti and Ce induce only mild local strain effects because the Ti-O and Ce-O complexes show octahedral (CN=6) and cubic (CN=8) geometries, respectively. Therefore, the energy difference in both the orthorhombic and tetragonal phases due to the incorporation of Ti and Ce is not as significant as Si and Ge.

Fig 3 shows that the polarization switching barrier is reduced by over 5x due to 8.3% Ge doping. It should be noted that a finite energy barrier is still needed for robust FE stability, otherwise unwanted phase transition might occur

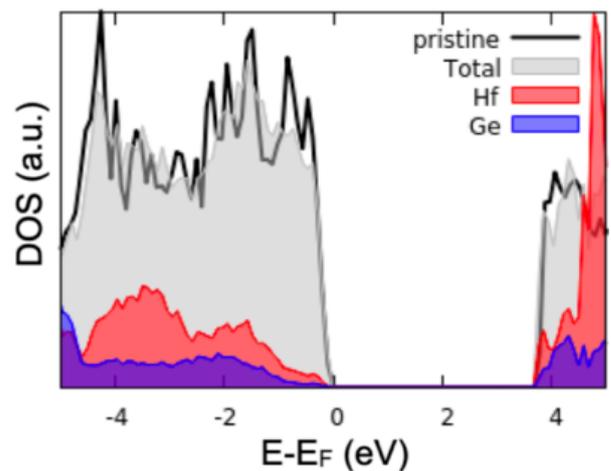


Fig. 4. Density of states (DOS) for pristine and Ge-doped HZO. Both pristine and Ge-doped HZO show a sizable bandgap (~ 3.6 eV), indicating that size of the bandgap is unchanged due to doping. For Ti- and Ce-doped HZO, however, size of the bandgap is reduced significantly due to the d and f states of Ti and Ce, respectively, forming the conduction band. It is found that bandgap in the oxide form (TO_2 , T=Si, Ge, Ti and Ce) is a relevant parameter.

from the FE to non-FE phases. This indicates that doping level has been optimized for stable yet low voltage FE device operation.

Density of states in Fig. 4 shows that the bandgap size does not change with the Ge doping. A DFT bandgap of 3.6 eV in the pristine HZO is retained after doping. This is advantageous due to the minimum dielectric leakage, which is critical for memory applications. Similarly, Si doping does not reduce the bandgap, whereas the incorporation of Ti and Ce significantly reduces the bandgap.[7] This is consistent with the bandgap sizes in the oxide form, i.e., $\text{SiO}_2 > \text{GeO}_2 > \text{HZO} > \text{TiO}_2 > \text{CeO}_2$. In brief, doping small-sized tetravalent species of Si and Ge is promising to lower switching voltage in FE HZO.

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