**Stability of Ferroelectric and Antiferroelectric Hafnium-Zirconium Oxide Thin Films**

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**Abstract**

Hafnium-zirconium oxide (HZO) thin films are of interest due to their ability to form ferroelectric (FE) and antiferroelectric (AFE) oxides. Density functional theory is employed to elucidate the stabilization mechanisms of the FE HZO thin films and the stabilization mechanisms for ZrO2 AFE films. The FE orthorhombic phase is primarily stabilized by in-plane tensile strain, which spontaneously occurs during the synthesis process, and this is more effective for HZO than HfO2. Stack models of the polymorphs of the HZO and ZrO2 reveal that the electrostatic component of interfacial free energy can play a critical role to understand prevalent formation of ZrO2 AFE tetragonal phase and the “wake-up” effect for FE HZO.

**Introduction**

The demonstration of ferroelectricity shown in hafnium oxide (HfO2)-base thin films such as Hf0.5Zr0.5O2 (HZO) and doped HfO2 [1], [2] has triggered intense research efforts because they may be a key component for next-generation electronic devices such as negative capacitance field effect transistors [3] and ferroelectric (FE) memories [4]. HZO films show large band gaps, high dielectric constants, and robust ferroelectric behavior in films with a thickness of ~10 nm [1], [2]. HZO is considered especially promising compared to doped HfO2 since there is a broad process window that induces FE behavior in HZO [5].

It is generally accepted that an orthorhombic Pca21 phase is responsible for the observed ferroelectricity in HZO thin films [1], [2]. It is a metastable phase in bulk films since the formation energy is ~70 meV per formula unit (fu) higher than the ground state of monoclinic P21/c phase according to density functional theory (DFT) calculations (see Figure 1). A number of factors have been suggested to stabilize the ferroelectricity of the HZO film in thin films such as thickness and composition of the film as well as the top/bottom electrode materials [1], [2], [6]–[8]. Thinner films with a composition close to 50% Hf and 50% Zr tend to favor ferroelectricity [6]. In addition, ferroelectricity is favored for HZO films grown on specific electrode materials. Titanium nitride (TiN) [6], [7] and tungsten (W) [9] are well-known to favor the ferroelectricity in HZO while Pt electrodes cannot form ferroelectric HZO [10]. In contrast to the inert Pt electrode, both TiN and W are known to form strong interfacial bonding with HZO, which is a key factor for inducing ferroelectricity in HZO.

While some of these factors are recognized as important by various research groups, most of the theoretical predictions based on DFT calculations argue that compressive strain be responsible for stabilization of the orthorhombic phase over the monoclinic phase [11], [12]. However, experimental studies often report the ferroelectric HZO {111} films have tensile stress [13]. For instance, Batra et al. show in their DFT calculations that compressive strain with external electric field can stabilize the orthorhombic phase both in hydrostatic and in-plane along (001) stress conditions [11]. Similarly, Liu and Hanrahan also show the effects of in-plane strains for {100}, {110} and {111}, arguing that ferroelectricity can be stabilized either by in-plane compression in those surfaces or by an external electric field [12]. These calculations are correct, but a separate mechanism must be present to explain the experimental results for {111} oriented films.

The tetragonal P42/nmc phase, assumed to be antiferroelectric (AFE), is often observed in pure ZrO2. The tetragonal ZrO2 phase has a formation energy which is ~70 meV/fu higher than the orthorhombic phase and ~140 meV/fu higher in energy than the ground state monoclinic phase as shown in Figure 1 and in other reports [14]. The observation of tetragonal ZrO2 likely results from interfacial free energy because ZrO2 tends to form nanocrystalline films due to its low crystallization temperature compared to the HfO2 [15]. In addition, nanocrystalline HfO2 and ZrO2 in a SiO­2 dielectric matrix are known to be tetragonal even in thick films (i.e., 200-700 nm) consistent again with favorable interfacial free energy [16], but such effects have not been validated by DFT calculations. Only a few DFT calculations can be found recently to take into the HZO with interfaces. For instance, Blaise has demonstrated a metal-ferroelectric-metal capacitor model of TiN/Si-doped HfO2/TiN in DFT calculations, and quantitatively estimated the depolarization field of 2.5 MV/cm [17], which agrees with experiments.

In this letter, the two key observations described above are given an atomistic mechanism using DFT models. First, by carefully examining the crystal structures of various polymorphs in HZO, two distinct planes of the monoclinic phase have been identified, one of which shows higher surface atomic density than the FE phase and is observed experimentally on common electrodes. Crystallization of amorphous HZO on a strongly bound the electrodes, generates tension due to the crystalline phases having a higher density than the amorphous phase. During post-deposition crystallization of amorphous HZO, the resulting tension will favor formation of FE orthorhombic HZO compared to the high density plane of the monoclinic phase. Second, stack models show that a polarization perpendicular to the dielectric-ferroelectric interface has a high interfacial free energy consistent with nanocrystalline ZrO2 spontaneous forming the tetragonal phase and HZO commonly required electrical cycling for observation of strong ferroelectric behavior.

**Computational Details**

DFT calculations are performed as implemented in Vienna *Ab initio* Software Package [18], [19] to determine the stabilization mechanisms of HZO thin films. The plane-wave basis set of pseudopotentials are expanded up to a kinetic energy cut off of 400 eV. The projector augmented wave method is used for core part [20]. The exchange-correlation functional of Perdew-Burke-Ernzerhof is employed [21]. Kohn-Sham energy eigenvalues are integrated in reciprocal space on even grids generated by a Monkhorst-Pack scheme with density of 0.25 2π Å-1 [22]. Electronic structure self-consistent field is iterated until changes in each of the eigenvalues and the total energy are less than 10-4 meV. Atomic positions and lattice parameters are optimized by conjugate gradient until the Hellmann−Feynman forces acting on each atom became smaller than 1 meV/ Å.

To impose in-plane strain along different orientations of the HZO such as {001}, {011} and {111}, the unit cell rotation was performed to orient one of the cell axis, i.e., c, along the planes of interest, which is similar to the previous study [12]. Isotropic change of the initial rotated cell area is imposed to generate in-plane strain. To model plane-stress condition, i.e., σ3=0, the cell parameter along that orientation is set free to relax while the other two cell parameters are fixed at their initial values.

To model HZO in 1x1x1 cell containing four HfO2 formula units, two of the metal sites are occupied by Hf, while the rest two sites are occupied by Zr. All the possible configurations of HZO alloys are determined to be energetically degenerated within sub meV/fu limit for 1x1x1 cell, and the difference in energy is less than 2 meV/fu for doubled cells. Therefore, the most energetically stable configuration of the ordered HZO alloy is chosen for all of the calculations below.

**Results and Discussion**

Figure 1(a) shows various polymorphs of HZO. Derived from a cubic parent phase (fluorite), all the polymorphs show similar atomic arrangements; the metal ions (Hf/Zr) form a face-centered cubic framework with the O atoms occupying all of the tetrahedra sites. Each of the O atoms are displaced from the cubic symmetric positions and the polymorphs are identified by the specific arrangement of the O atoms as shown in Figure 1(a). Note that the Pca21 phase (ortho FE) represents a non-centrosymmetric ferroelectric phase with spontaneous dipoles as marked by blue arrows in Figure 1(a). However, the ortho FE phase is a metastable phase in a pure bulk state with its formation energy higher by ~60-80 meV/fu (ZrO2 to HfO2) than the ground state P21/c phase (mono) as seen in Figure 1(b). The Pbca phase (ortho AFE) show similar atomic arrangement as the ortho FE, but the displacements of O atoms are switched in every unit cell of the ortho FE inducing centrosymmetric phase.

Figure 1(b) shows that the P42/mnc phase (tetra AFE) is ~65-93 meV/fu (ZrO2 to HfO2) higher in energy than the ortho FE in static DFT calculations (i.e., at 0 K), but it is known that the tetra AFE is the ground state at relatively high temperature [23], indicating that entropic contribution from phonons plays a role. Note that the tetra AFE does not show local dipole in contrast to the ortho AFE as shown in Figure 1(a), and it is known to experimentally exhibit paraelectric behavior for weak external electric fields [24], which is the middle part of the double hysteresis of the AFE. Once the external field is greater than the onset field, the tetragonal transforms into orthorhombic ferroelectric phase, as indicated by double hysteresis curve [24]. Understanding both unusual response to the external field and highly symmetric atomic arrangements similar to the ortho FE phase is the key to provide underlying mechanisms in this material system (to be discussed).

Unlike the orthogonal phases, the mono phase has non-equivalent planes with (hkl) and (hk-l) indices where h, k and l are integers. The mono (01-1) show higher surface atom density than the mono (011) as shown in Figure 1(c). Similarly, mono (11-1) and mono (111) show higher and lower surface atom densities, respectively, than both tetra (111) and ortho FE (111) as in Figure 1(d). This is in agreement with splitting of the x-ray diffraction peaks (2θ) corresponding to tetra (111) or ortho (111) at ~30° into two separate peaks at ~28° and ~32° [23]. Note that the peak at ~28° corresponds to greater interplanar spacing (d) as well as higher surface atomic density according to the Bragg’s law (e.g., nλ=2dsinθ). Experimentally, it is known that mono (11-1) peak is more favored in thinner HZO films [25] on the reactive TiN electrodes, where the interface effects are expected to play a significant role. This is consistent with the concept that the reactive extrude tightly bond oxygen thereby favoring the more dense crystal plane of mono (11-1).

The experimental procedures to obtain ferroelectric HZO thin films elucidates the stabilization mechanism for ferroelectricity. In general, as-deposited HZO grown by thermal atomic layer deposition (ALD) forms an amorphous film, which is subsequently crystalized during thermal annealing over 400°C [1], [2], [25], [26]. It is hypothesized that reactive metal electrodes such as TiN and W, also help stabilize the FE films [10], which result in in-plane tension during the crystallization as the film is densified while maintaining strong bonding at the interfaces. It has been previously shown that FE HZO film sandwiched by TiN electrodes after annealing is under tension [13]. Therefore, identifying the distinct planes with different densities and taking into account the strong bond formations at the interface play a crucial role to explain properly the experimental observations that in-plane tension generated during the post-deposition annealing might stabilize the ortho FE phase.

Figure 2 shows the energy of HZO polymorphs with varying compositions (i.e., HfO2, Hf0.5Zr0.5O2 and ZrO2) with in-plane strain perpendicular to the {111} orientation which is the preferred growth direction when HZO is deposited on TiN or W [1], [2], [25], [26]. Here, only the high density plane of the monoclinic phase, or (11-1), is shown since it should be preferred on reactive electrodes and since it is observed experimentally [25]. The curve for amorphous phase, generated by melt-quench in *ab* *initio* molecular dynamics, is shown in all cases, confirming higher energy and surface area than the crystalline phases due to the disordered atomic arrangements. When the amorphous phase is crystallized with the strong bonds formed at the interface, it is hypothesized that the volume reduction due to the crystallization will result in in-plane tension, favoring the ortho AFE over the m phase first, and then the ortho FE phase with further strain. This is consistent with experimental observations that in-plane tension promotes the ferroelectricity, but is in contrast with previous computational results, in which the high density monoclinic planes have not been discussed [11], [12]. Note that the main difference with previous theoretical results is not a calculational difference but a difference in the choice of the monoclinic {111} orientation in accordance with the experimental data.

The quantitative effect of tension is compared versus oxide composition. For pure HfO2, the ortho FE phase becomes more stable than the mono phase when 4.2% of in-plane tension is applied with respect to the minimum of the ortho FE, while the required strains to stabilize the ortho FE phase are as small as 2.9% and 2.7% for HZO and ZrO2, respectively. The lower amount of in-plane tension is required for the HZO than pure HfO2 to stabilize the ortho FE phase over the mono phase is consistent with experimental results showing that the ferroelectricity is the most stable for HZO [6].

While the pure ZrO2 shows the least amount of in-plane tension needed to stabilize the ferroelectricity, it is known that amorphous formation is hindered for ZrO2 since it grows in a nanocrystalline phase instead of in a purely amorphous phase due to the low crystallization temperature [15]. It has been shown that inserting interfacial HfO2 layers between the electrode and ZrO2, which would direct the growth of ZrO2 into a greater crystal size, enhances the ferroelectricity [27]. As shown in the Figure 1(b), the tetragonal phase is relatively more stable for ZrO2 (65 meV above the minimum of the ortho FE) than either HZO or HfO2 (74 and 93 meV/fu) which is consistent the easier formation of tetragonal phase over orthorhombic FE.

In the absence of external field, the amount of tension needed to stabilize the orthorhombic FE phase over the orthorhombic AFE phase seems similar for all the compositions (5.3-5.5%). However, it has been theoretically shown that external electric field can further stabilize the orthorhombic FE over the orthorhombic AFE [11], [12]. This suggests that the necessity of external field cycling on the as-annealed films to invoke the ferroelectricity which is known as “wake-up” process since ortho AFE will become unstable in the presence of external field.

Figure 3 shows the energy-area curves for biaxial strain perpendicular to the {011} orientation. According to the hypothesis that strong bonding formed at the electrode interface favors the high density planes, the high density plane, i.e., (01-1), of the monoclinic phase is shown in Figure 1(b). It is noted that proper choice of substrate for epitaxial growth by molecular beam epitaxy technique can also be used to favor (01-1), of the monoclinic phase. In this case, the ortho FE phase is the most stable at its minimum for all the compositions, indicating no in-plane strain is necessary to stabilize the ferroelectricity. This implies that ferroelectric films can be prepared by different methods than thermal ALD and annealing. In fact, Shimizu et al. have demonstrated the ferroelectricity in epitaxially grown (011) yttrium- (Y-) doped HfO2 on top of Y-stabilized ZrO2 (YSZ) by using pulsed laser deposition (PLD) [28], which is consistent with the present DFT calculations in Figure 3. The amount of tension to stabilize the ortho FE over ortho AFE ranges 3.2-3.8%, which is even smaller than that for {111} orientation. This indicates that the “wake-up” process can be reduced compared to the {111} growth.

In contrast to {111} and {011}, the HZO films along {001} cannot be stabilized either by mechanical strain or epitaxial growth since the monoclinic phase always shows lower energy than the orthorhombic ferroelectric phase in a wide range of in-plane strain as seen in Figure S1. Shimizu *et al*. have grown an epitaxial film of (001) Y-doped HfO2 on (001) YSZ by using PLD, of which the phase is progressively varied with Y content from monoclinic to orthorhombic to tetragonal [29]. As lattice parameters of Y-doped HfO2 and YSZ are sufficiently close to each other, the tetragonal/orthorhombic phases in these films are stabilized by other mechanisms than mechanical strain.

To further elucidate the observed FE behavior of HZO and the AFE behavior of nanocrystalline ZrO2 films, stack models with domain boundaries of the tetra and ortho FE phases are constructed for ZrO2 in Figures 4(a-d) and other compositions in Figure S2. Atomically sharp domain boundaries without a defect within a single grain are built based on the recent experimental report [30]. Each model is constructed based on the dipole orientations in ortho FE layers with a varying thickness, and the volume of each phase is set at the bulk ortho FE phase. The interface free energy (*Einter*) is calculated by

where *Estack* is the total energy of the stack. *Etetra* and *Eortho* are energies in bulk state for tetragonal AFE and orthorhombic FE phases, respectively, with the unit cell volume fixed at ortho FE. The *n* and *A* are tetra/ortho layer thickness and cross-sectional area, respectively. Figure 4(e) shows that the *Einter* converges with increasing *n* in all cases. Moreover, the stack with dipole direction perpendicular to the interface (i.e., along z) shows the highest *Einter*, which is expected to be due to the electrostatic interactions. This is consistent with the negative capacitance models of Khan *et al*. showing that perpendicular polarization is destabilized by having a paraelectric in series with ferroelectric HZO [31]. The field due to the spontaneous polarization in the ferroelectric orthorhombic region induces the neighboring dielectric layer polarized, which will increase the energy of the system. It is observed that unconstrained stack models spontaneously transform into other phases or change its polarization direction from perpendicular to parallel to the interface.

Based on a kinetic model proposed previously [26], the tetra phase would form first during the thermal annealing, which is subsequently transformed into the ortho FE phase. By using internal energy change (*ΔU*=*Etetra* – *Eortho*) and interfacial free energies (*ES*) obtained from the stack models as shown in Figure 4(e), the energy of ortho-tetra phase transition within a 3D tetra matrix (*ΔE*) is estimated as a function of the orthorhombic nanocrystal size (*m*) which is depicted in Figure 4(f):

where the subscript *S* in the second term runs all six interfaces. Here, *m* x *m* x *m* orthorhombic nanocrystal is assumed to form within the tetragonal matrix for simplicity although asymmetric precipitates are known to form within cubic/tetragonal matrix consistent with the anisotropic *Einter* [32]. Figure 4(g) shows that the interfacial energy dominates for small-sized crystals, indicated by negative *ΔE*, while the *ΔU* term starts to dominate for large crystals when *m* (the length of the nanocrystallytes) reaches ~10, which corresponds to crystal with a length of 5 nm and a volume of 125 nm3. The results show that the orthorhombic ferroelectric grains below 5 nm in length will transform to tetragonal due to high surface free energy, while grains larger than 5 nm will remain in the orthorhombic phase inside the tetragonal matrix due to the higher bulk thermodynamic stability of the orthorhombic phase.

These results can explain kinetics of crystallization of the film during the cooling process. Starting from the high temperature where each of the grains is tetragonal, only small nanocrystalline grains of orthorhombic would be formed in a rapid cooling process; the present DFT calculations show that these small orthorhombic FE crystallites are transformed to tetragonal AFE films due to interfacial electrostatic free energy effects. For a slow cooling rate, however, orthorhombic nanocrystals with sizes greater than the critical size can be formed and grow to take up the tetragonal phase. The results are shown for HZO but similar values are observed for all three oxides. Note that effects of point defects are not taken into account in this study, but they are known to play an important role as well [33]–[35], which is beyond the scope of the study. These results also do not take into account tension which will stabilize both the tetragonal and orthorhombic phases against relaxation to the monoclinic phase. However, the results show that formation of tetragonal films can be favored for ZrO2 if film formation is initiated by nanocrystal formation.

To model the experimentally observed formation of the AFE tetragonal ZrO2 ­in a paraelectric matrix [15], [16], the interface effects are explicitly taken into account in three-dimensional (3D) DFT models of ferroelectric orthorhombic and tetragonal cores embedded within cubic matrix as illustrated in Figure 5(a). The cubic phase is employed as the matrix due to its high symmetry, and it serves as a paraelectric medium. Note in a real materials, this could be amorphous ZrO2 or SiO2 in grain boundaries and amorphous interlayers on the electrode surfaces [15], [16]. Unlike the stack models in Figure 4, in which interface is made along one direction, the dipole in the ferroelectric core is always pointing to the interfaces in the 3D models. Therefore, the unfavorable interactions at the FE/DE interface cannot be avoided; therefore, the core of orthorhombic ferroelectric is transformed into the tetragonal phase despite its higher *ΔU* as seen in Figure 1(b). All the O atoms in the 3D models were fixed at their ideal positions of the corresponding phases to prevent the models in Figure 5 from converting to a single phase.

Figure 5(b) shows that the tetragonal cores are significantly lower in energy compared to the orthorhombic core due to the interfacial free energy. Mechanical strain did not influence significantly in this case as shown in Figure S3. The effect of having a AFE tetragonal vs FE orthorhombic core is profound; the AFE tetragonal core is more stable than the FE orthorhombic core by ~195-210 meV/fu despite the bulk AFE tetragonal phase being less stable than the FE orthorhombic phase by 60-90 meV/fu as seen in Figure 1(b). The *ΔE* is the lowest for the pure ZrO2 partly due to the smaller energy difference compared to HfO2 and HZO between the orthorhombic and tetragonal phases as in Figure 1(b), which is consistent with the experiments that tetragonal phase is most prevalent in pure ZrO2 films [15], [16], together with the low crystallization temperature to form nanocrystals. It has been shown that ZrO2 films with large grain sizes favor the orthorhombic phase [27], confirming the interfacial effects.

Lastly, the role of field cycling, also known as “wake-up”, is related to the stability of the antiferroelectric vs ferroelectric phases. Experimentally, the HZO film is grown along {111}; therefore, as described by Blaise *et al*. there will always be a dipole component pointing to the interface [17]. The results shown in this study indicate that AFE tetragonal phase or the AFE orthorhombic phase would be favored due to the unfavorable electrostatic interactions. In addition, grain boundaries are often observed in the films after post-deposition annealing, where paraelectric oxide is likely to form; this could further promote AFE formation over the orthorhombic ferroelectric. In the presence of external field, however, the ferroelectric phase would be stabilized compared to the non-polar phases as shown previously [11], [12]. This field-aided stabilization of the ferroelectric phase is consistent with the FE HZO film synthesis in general that “wake-up” is necessary to obtain FE behavior.

**Conclusions**

Density functional theory calculations were employed to address two major questions on the phase stabilizations for hafnium-zirconium oxide thin films. First, stabilization of the ferroelectric orthorhombic phase is enabled by in-plane tensile strain if the amorphous film is deposited on top of the reactive metal electrodes, and is subsequently crystallized by post-deposition annealing. Second, interfacial free energy plays a crucial role to stabilize antiferroelectric tetragonal phase and is consistent with the need for electrical cycling for observation of ferroelectric behavior.

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**Figure 1 Atomic structures of HZO polymorphs:** (a) Unit cells of the polymorphs for antiferroelectric tetragonal P42/nmc, paraelectric monoclinic P21/c, ferroelectric orthorhombic Pca21 and antiferroelectric orthorhombic Pbca. The blue arrows indicate displaced O atoms. (b) Relative energies of the HfO­2, HZO and ZrO2 polymorphs with respect to the ground state of paraelectric monoclinic P21/c phase in meV/fu. (c) Rotated supercells to apply biaxial strains along {011}. (d) Rotated supercells to apply biaxial strains along {111}. Note that the monoclinic P21/c phase shows non-equivalent planes for both {011} and {111} with different area per formula unit (Å2/fu) for each configuration. O atoms are omitted for clarity.



**Figure 2 Energy vs Surface Area per Formula Unit along {111}.** Energy-area curves for polymorphs of (a) HfO2, (b) HZO and (c) ZrO2 along {111}. For m phase, only the high density plane (11-1) is displayed. Bottom panels show the energies of the polymorphs relative to the ortho FE phase of (a) HfO2, (b) HZO and (c) ZrO2. The crossover strain values with the ortho AFE and FE being more stable than monoclinic are marked.



**Figure 3** **Energy vs Surface Area per Formula Unit along {011}.** Energy-area curves for polymorphs of (a) HfO2, (b) HZO and (c) ZrO2 along {011}. For m phase, only the high density plane (01-1) is displayed. Bottom panels show the energies of the polymorphs relative to the ortho FE phase of (a) HfO2, (b) HZO and (c) ZrO2. The crossover strain values with the ortho AFE and FE being more stable than monoclinic are marked.



**Figure 4 Transformation of Ferroelectric Crystallites to Tetragonal Films.** ZrO2 stack models for tetra-ortho domain boundaries in which each layer is four unit cell thick with polarization orientation along (a) x, (b) y and (c) z, marked by yellow arrow. (d) Stack model of polarization along z with a thickness of six unit cells. The O atoms in the two unit cells in the middle of each layer are fixed to prevent phase transition. (e) Interfacial free energy (*Einter*) of each model with varying polarization direction and layer thickness. (f) Three-dimensional (3D) models of the orthorhombic ferroelectric (blue) nanocrystal embedded within tetragonal antiferroelectric (light blue) matrix. The data shown here is for ZrO2 but similar values are observed for HZO and HfO2. (g) Thermodynamic model for the orthorhombic nanocrystal formation within a 3D tetra matrix as a function of nanocrystal length based on the changes of internal energy (*ΔU*) and interfacial free energy (*ES*). When *ΔE* is positive, the FE core in the tetragonal matrix is stable. This model takes into account the internal energies from bulk calculations and the interfacial energies in all three directions from (e). The negative interfacial free energy, *ES,* dominates for small-sized crystals, while the *ΔU* term starts to dominate when *m* is reached at ~10, which corresponds to about 5 nm length and 125 nm3 in volume. The results show that the orthorhombic ferroelectric grains below 5 nm in length will transform to tetragonal due to high surface free energy while grains larger than 5 nm will remain in the orthorhombic phase inside the tetragonal matrix. The data shown here is for ZrO2 but similar values are observed for HfO2 and HZO.



**Figure 5 Three-Dimensional Core-Matrix Models.** Schematic models of the 3D model with 3x3x3 cubic (yellow) matrix embedding (a) 2x2x2 cores orthorhombic ferroelectric (blue) and 2x2x2 cores tetragonal antiferroelectric (light blue) phases, respectively. The cubic phase in the matrix serves as paraelectric layer. (b) Difference in energy of the 3D models with tetragonal and orthorhombic cores embedded within cubic matrix were calculated with a varying core size: energy differences for a 2x2x2 matrix with orthorhombic FE vs tetragonal AFE 1x1x1 cores and 3x3x3 matrix with orthorhombic FE vs tetragonal AFE 2x2x2 cores. The negative values mean the tetragonal core is more stable than the orthorhombic core due to the presence of the paraelectric matrix. This is in contrast to bulk case where the orthorhombic FE is 60-90 meV/fu more stable than the tetragonal AFE as shown in Figure 1(b).

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