Ferroelectrics are materials with spontaneous electric polarization that can be switched by the application of an external electric field. This property makes ferroelectrics useful for a wide range of practical applications, such as non–volatile memory devices [1], field effect transistors [2], and tunable capacitors [3, 4]. However, most conventional ferroelectrics, such as BaTiO$_3$ or PbTiO$_3$, are not suitable for nanoscale devices, because of the depolarization field effect, which suppresses the ferroelectricity and becomes more significant as the thickness of the film decreases [5–7]. HfO$_2$–based materials are exceptions; the Al [8], Gd [9], Sr [10], Y [11–12] doped HfO$_2$ and Hf$_{0.5}$Zr$_{0.5}$O$_2$ alloy [13] can sustain ferroelectricity in films thinner than 20 nm. Furthermore, HfO$_2$–based materials can be integrated with silicon processing, and indeed are currently used as gate dielectrics [1] [14] [15].

HfO$_2$ adopts various polymorphs [10] (Fig. 1). The ferroelectricity in thin films has generally been attributed to the formation of the orthorhombic Pca$_2$1 phase (oIII–phase) [17,19]. The formation of the Pca$_2$1 phase is affected by various extrinsic factors, such as pressure [10], strain [20, 21], dopants [22–26], oxygen vacancies [27], surface energies [28–30] and electric fields [20, 31, 32]. This attribution does not preclude the existence of other competing ferroelectric phases [16]. For example, a ferroelectric phase different from oIII has been experimentally observed in (111)–oriented Hf$_{0.5}$Zr$_{0.5}$O$_2$ thin films [33]. This (111)–oriented ferroelectric film has a distinctive field–cycling behavior; wake–up cyclings [10, 12] are not required for acquiring a steady P–E hysteresis loop. This intriguing observation invites a definitive identification of this novel phase, which should also provide a natural explanation for the lack of wake–up behavior and may be of great significance for practical applications of hafnia–based materials.

In this study, we carry out density–functional theory (DFT) based first–principles calculations on different polymorphs of HfO$_2$, with a particular focus on the ferroelectric orthorhombic Pnm2$_1$ phase (oIV–phase). Although this oIV–phase is energetically less favorable in its conventional pseudocubic form [15], we provide evidence that it can be stabilized in epitaxial films with (111)–orientation via a transition from the tetragonal $P4_2/nmc$ phase (t–phase), which has compatible lattice parameters for (111)–oriented crystals. In fact, in the epitaxial geometry corresponding to a SrTiO$_3$ (001) substrate, the nonpolar t–phase is no longer locally stable, and collapses into a distorted version of the ferroelectric oIV phase, with a robust ferroelectric polarization ($P = 0.41\ \text{C/m}^2$). Our simulated x–ray diffraction (XRD) for this phase is consistent with the one for the polar phase of Hf$_{0.5}$Zr$_{0.5}$O$_2$ experimentally reported in Ref. [33], suggesting new ferroelectric functionality for (111) films.

We performed first–principles calculations of the energies, structural parameters and polarization of various phases of HfO$_2$ using the QUANTUM–ESPRESSO [34] plane–wave DFT code within the local density approximation (LDA). To check the dynamical, elastic, and mechanical stability of the structures studied, we performed additional DFT calculations using the Projector Augmented Wave (PAW) method [35] as implemented in the VASP software [36–38]. The numerical details along with the crystallographic information for the structures studied are provided in the supplemental material (SM) [39]. To understand the relationship between the tetragonal and the oIV phase, we start with the bulk t–phase of HfO$_2$ oriented along the (111) direction, with in–plane lattice parameters $a = 6.95\ \text{Å}, b = 6.91\ \text{Å}$, and cell angle $\gamma = 120^\circ$. We then apply an epitaxial strain of ~1\% on the in–plane lattice constants to match those of the (111)–oriented oIV phase ($a = b = 7.01\ \text{Å}, \gamma = 120^\circ$), and compute the potential energy profile as a function of the cell angle $\gamma$. We vary $\gamma$ in range $[110^\circ, 132^\circ]$, completely relax the distorted structures while fixing their in–plane lattice parameters ($a, b, \gamma$), corresponding to epitaxial constraint on a SrTiO$_3$ substrate, as explained in more detail below.
In Table I we list the pseudocubic lattice parameters and relative energies for several widely reported phases of HfO$_2$. A schematic representation of the phase transitions among these phases is shown in Fig. 1(a). The bulk HfO$_2$ adopts a highly–symmetric Fm$ar{3}$m cubic fluorite structure (c–phase) at high temperatures ($T > 2773$ K), and transforms to the t–phase as temperature decreases ($2073$ K < $T < 2773$ K). As the temperature drops below $2073$ K, bulk HfO$_2$ transforms to a $P2_1/c$ monoclinic phase (m–phase) [40]. Our DFT calculations show that among these three phases, the c–phase has the highest energy and the m–phase has the lowest energy (see Table I), which is consistent with the experimental observations [40] and previous calculations. Doping is a well-known technique for stabilizing the t–phase in bulk [41]. In thin films, the large surface energy of the m–phase makes it less favorable [28–30]. As the thickness of the film decreases, the t–phase to m–phase transition temperature is suppressed, and in thin-enough films, the structure remains tetragonal at room temperature [42–44].

| phase          | $a$  | $b$  | $c$  | $\alpha$ | $\beta$ | $\gamma$ | $\Delta E$ |
|----------------|------|------|------|-----------|---------|----------|------------|
| Fm$3\bar{m}$ (c) | 4.89 | 4.89 | 4.89 | 90.0      | 90.0    | 90.0     | 105.0      |
| P4$_2$/nmc (t)  | 4.89 | 4.89 | 4.93 | 90.0      | 90.0    | 90.0     | 80.2       |
| Pca$_{21}$ (oIII) | 4.88 | 4.87 | 5.07 | 90.0      | 90.0    | 90.0     | 49.8       |
| P$_2_1$/c (m)   | 5.06 | 4.93 | 5.05 | 90.0      | 90.0    | 90.0     | 0          |
| P$n m 2_1$ (oIV) | 4.95 | 4.95 | 4.96 | 90.0      | 90.0    | 90.0     | 83.9       |

TABLE I. Lattice parameters and relative energies ($\Delta E$) of different HfO$_2$ phases in their pseudocubic structures, corresponding to the conventional fcc cell of the Fm$3\bar{m}$ structure. Details of the cell transformations between the primitive cells and pseudocubic cells are provided in the SM. All length, angle, and energy units are in Å, degrees, and meV/f.u., respectively.

Recent experimental work demonstrates that the oIII ferroelectric phase forms as a compromise state resulting from the competition among bulk energy, surface, and doping energies [12,13,14], as shown in Fig. 1(a) and (b). Since the t– and oIII– phases have approximately identical in–plane lattice parameters (Table I), careful selection of film thickness, doping concentration and growth conditions is needed to stabilize this phase. For example, Bölscke et al. proposed that depositing a top electrode before annealing can impose a mechanical confinement and promote the oIII–phase formation [17,18].

Next, we consider the oIV–phase, which was proposed theoretically and investigated in previous work [16,19], but has not yet been experimentally observed. The oIV–phase is also ferroelectric, being related to the tetragonal structure by the same polar distortion as the oIV–phase except along the (110) direction of the primitive tetragonal cell rather than the (100) direction. Our first–principles calculations based on the Berry’s phase method [17] reveal that this phase has a 0.59 C/m$^2$ polar–

FIG. 1. (a) Structures and transitions of the c, t, m, oIII, and oIV phases; (b) Schematic plot of the HfO$_2$ phase diagram under the influence of temperature and the joint–effect of doping and film thickness. We should emphasize that the stabilization of the ferroelectric Pca$_{21}$ phase should be a joint–effect of doping and finite thickness; Only doping or decreasing the film thickness can hardly lead to ferroelectricity. Besides, increasing the doping concentration does not guarantee the enhancement of ferroelectricity, because over–doping leads to the formation of the non–polar t–phase; (c) Schematic plot of phase diagram of the (111)–oriented HfO$_2$–based films under the influence of temperature and in–plane shear. Both enlarging or reducing the $\gamma$ angle can induce the t–phase to oIV–phase transition.
ization along the [011] direction. The calculated phonon spectrum reveals that there are no unstable phonon modes in the oIV–phase, confirming the dynamical stability of this structure. Moreover, this structure is elastically and mechanically stable (see SM).

Our DFT results show that the relaxed bulk energy of the oIV–phase in (001)–oriented crystals is relatively high, as shown in Table I, the oIV–phase has the highest energy among the other studied phases. Besides, compared with the t–phase, which is the parent phase of other low–temperature phases, this ferroelectric phase has a more than 1% mismatch in the in–plane (a and b) lattices, and a difference of about 6° in the γ angle, making the t–phase to oIV–phase transition even more unfavorable for a square lattice epitaxial constraint in this plane.

However, the situation improves for the oIV–phase in (111)–oriented films. In Table II, we list the lattice parameters of (111)–oriented crystals of different HfO$_2$ phases. Among the low–temperature phases, the oIV–phase has the b lattice parameter closest to that of the t–phase. Besides, the difference in the angle γ decreases to less than 4°, which further increases the possibility of t–phase to oIV–phase transition. We also note that the major difference between the t– and oIV phases is in their γ angles, which inspires the investigation of whether a t–phase to oIV phase transition can be induced by modulating γ with a epitaxial shear strain.

| phase             | a    | b    | c    | α   | β   | γ     |
|-------------------|------|------|------|-----|-----|-------|
| Fm$ar{3}$m      | 6.91 | 6.91 | 8.46 | 90.0| 90.0| 120.0 |
| P4$_2$/nmc        | 6.95 | 6.95 | 8.49 | 89.6| 90.4| 120.3 |
| Pca$_2_1$        | 6.89 | 7.03 | 8.56 | 91.8| 90.1| 119.4 |
| P2$_1$/c         | 7.06 | 7.15 | 9.14 | 93.6| 87.5| 125.9 |
| Pnm$_2_1$        | 7.01 | 7.01 | 8.89 | 89.7| 92.4| 123.7 |

TABLE II. Lattice parameters of different HfO$_2$ phases in their (111)–oriented structures. We note that there are similar structures whose epitaxial planes are (-111), (-11-1) and so on; for simplicity, these are not included in the list. Detailed lattice parameters and atomic positions are given in the SM [39]. All length and angles units are in Å and degrees, respectively.

To explore the possible reaction path, we start with the t–phase and γ = 120° [Fig. 2(c)], since the t–phase is the parent phase of the low temperature phases. We then apply a ~1% epitaxial strain on the in–plane lattices to match those of the (111)–oriented oIV phase (a ≈ b = 7.01 Å, γ = 120°). Next, the γ angle is increased/decreased to 130°/110° with 1° steps. The energy and out–of–plane polarization are plotted as functions of γ in Fig. 2(a). We can see that as γ increases, a first–order phase transition occurs at γ = 128°, associated with a jump in the polarization [Fig 2(a), indicated by the black arrow]. The polar structure at γ = 129° is shown in Fig 2(d). Then we carry out a variable–cell relaxation about the polar structure, and find that the optimized structure is exactly the (111)–oriented oIV–structure. We also note that in the γ > 123° range, the distorted oIV–structure is energetically more favorable than the t–phase, indicating that the skew angle for triggering the phase transition can be as small as 3°. Meanwhile, decreasing γ to less than 114° also induces a first–order phase transition. The low–angle phase is also the oIV phase, but with a different epitaxial plane [(–11-1) oriented, Fig. 2(b)]. However, the polarization of this (-11-1)–oriented oIV structure lies in plane, which attracts less interest.

![Image](image_url)

FIG. 2. (a) Energy and out–of–plane polarization as a function with γ. (b) The structures in the oIV, t, and oIV phases for γ = 114°, 120° and 129° respectively.

We have demonstrated that for (111)–oriented films, a t–phase to oIV phase transition can be induced by a shear strain [the schematic phase diagram is shown in Fig. 1(c)]. Such transitions are not uncommon when the underlying substrate has a different symmetry than that of the mounted thin film above. Based on these results, we propose a new ferroelectric phase stabilization process. At first, a (111)–oriented thin film is deposited on the substrate at a high temperature (> 1000 K). At this stage, a cubic or tetragonal structure is more favorable due to the surface energy and thermal budget. However, because of the lattice mismatch, the substrate keeps imposing a shear strain upon the film. After annealing,
the t–phase loses its stability, and collapses into the oIV ferroelectric phase.

Next, we consider the wake–up effect, which is the need for electric field cycling to establish the full value of switching polarization in as-grown thin films [10,12]. This wake–up effect has a variety of origins, including internal bias fields [48–50], migration of oxygen vacancies [45,51], structural change at the interface [10,45,52]. An important intrinsic factor that can lead to a wake–up effect is an electric field induced non–polar to polar phase transition [111]-[110] STO and [010] crystalline axes. The dashed lines correspond to the [100] STO geometry employed in Ref. [33], and (b) orientations of the crystalline axes with the experimental information [111] STO // [001] LSMO, [1-10] HZO // [1-10] STO, and [11-2] HZO // [110] STO. For $l = 1/2 (a_{HZO} + a_{LSMO}) = 4.47 \text{ Å}$, we have in–plane lattice parameters of the (111)–oriented films as $l_a = l_b = 7.07 \text{ Å}$ and $\gamma = 127^\circ$, which is a remarkable match with our DFT predicted results.

To estimate the shear strain imposed by the La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) substrate, we begin with analyzing the film–substrate geometry as shown in Fig. 3(a). Between the (001)–oriented LSMO substrate and (111)–oriented HZO thin film, there are several interfacial t–phase layers. Both LSMO and tetragonal HZO have a pseudocubic structure. However, their in–plane lattices are quite different ($a_{HZO} = 5.06 \text{ Å}$ and $a_{LSMO} = 3.88 \text{ Å}$) [29,57], and we do not expect a coherent strain. Here, we make the assumption that the effective lattice $l$ is the average of $a_{HZO}$ and $a_{LSMO}$. In Fig. 3(b), we plot the orientations of the crystalline axes with the experimental information [111] STO // [001] LSMO, [1-10] HZO // [1-10] STO, and [11-2] HZO // [110] STO. For $l = 1/2 (a_{HZO} + a_{LSMO}) = 4.47 \text{ Å}$, we have in–plane lattice parameters of the (111)–oriented films as $l_a = l_b = 7.07 \text{ Å}$ and $\gamma = 127^\circ$, which is a remarkable match with our DFT predicted results.

In Fig. 4, we plot the simulated XRD patterns of the oIII and (111)–oriented oIV structures. Some XRD reflection peaks in the (111)–oriented oIV phase practically overlap.

Further, this work suggests a structure for the experimentally reported ferroelectric phase in (111)–oriented Hf$_{0.5}$Zr$_{0.5}$O$_2$ (HZO) films distinct from the rhombohedral structure previously proposed [33,50]. In experiments, the deposition temperature is $T = 800^\circ\text{C}$, which favors the non–polar t–phase. After annealing, thin films with robust polarization (0.34 C/m$^2$ for 5 nm and 0.18 C/m$^2$ for 9 nm) were obtained. This ferroelectricity can be attributed to the oIV phase. In our DFT calculation, the out–of plane polarization of (111)–oriented oIV phase is 0.41 C/m$^2$. It is not surprising that this value is somewhat larger than the experimentally reported result [33]. Since we consider a perfect polar oIV–phase in our calculations while the actual thin–films in experiments may contain some or a mixture of the nonpolar crystallites in a part, such as the m–phase. The size of the nonpolar crystallites grows with increasing film thickness, reducing the net polarization in the thicker films. The substitution of Hf by Zr may also contribute to a reduction in the polarization.

In Fig. 4, we plot the simulated XRD patterns of the oIII and (111)–oriented oIV structures. Some XRD reflection peaks in the (111)–oriented oIV phase practically overlap.
peak around 17.5° is also much weaker. A closer examination of the selected-area electron diffraction pattern, shown in Fig. 3a of Ref. [32], reveals a distinct splitting of the diffraction peaks, which can be attributed to slight breaking of $C_3$ lattice symmetry ($\gamma \neq 120^\circ$) by the (111)–oriented oIV phase. All these results demonstrate that attributing the ferroelectricity in (111)–oriented HfO$_2$ thin films to the formation of the oIV phase is highly plausible.

In this study, we predict a non–polar to polar phase transition in (111)–oriented HfO$_2$ from first-principles calculations. Under an in–plane shear strain which enlarges the $\gamma$ angle, the nonpolar $P4_2/nmc$ t–phase transforms to a polar phase which is a distortion of the ferroelectric $Pnm_2$, oIV–phase. This ferroelectric phase is metastable and has a robust polarization. We also propose that by a proper selection of the substrate, the wake–up effect, which is undesirable for technological applications, can be reduced or eliminated, so that as–grown films would be ferroelectric. Our work also opens a new avenue to explaining the recent experimentally reported ferroelectricity in (111)–oriented Hf$_{0.5}$Zr$_{0.5}$O$_2$ thin films.

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