

Stress-induced ferroelectricity in hafnia core-shell nanoparticles

Anna N. Morozovska^{1,*} Eugene A. Eliseev² Richard (Yu) Liu³ Sergei V. Kalinin^{3,†} and Dean R. Evans^{4,‡}¹*Institute of Physics of the National Academy of Sciences of Ukraine,
46, Nauky Avenue, 03028, Kyiv, Ukraine*²*Frantsevich Institute for Problems in Materials Science of the National Academy of Sciences of Ukraine,
3, Street Omeliana Pritsaka, 03142, Kyiv, Ukraine*³*Department of Materials Science and Engineering, University of Tennessee,
Knoxville, Tennessee, 37996, USA*⁴*Zone 5 Technologies, Special Projects, San Luis Obispo, California 93401, USA*

(Received 25 February 2026; revised 14 July 2026; accepted 29 September 2026; published 22 October 2026)

In contrast to hafnia (HfO_2) thin films, where the appearance of switchable ferroelectric polarization can be induced by strain or defect engineering, reliable methods for controlling ferroelectricity in HfO_2 nanoparticles are absent. Direct experimental observations of ferroelectric hysteresis and ferroelectric domains in these nanoparticles have also not been reported. To the best of our knowledge, stress-induced ferroelectric states in the HfO_2 nanoparticles have not been explored. In this work, we study the influence of chemical stress on phase diagrams, dielectric properties, and polar properties of spherical HfO_2 core-shell nanoparticles using a Landau-Ginzburg-Devonshire free energy functional that includes trilinear and biquadratic couplings involving polar, antipolar, and nonpolar order parameters. The ferroelectric phase exhibits reentrant behavior as a function of nanoparticle size, such that the spontaneous polarization exists only within a limited range of core radii R_c , namely $R_{\text{cr}}^{\text{min}} < R_c < R_{\text{cr}}^{\text{max}}$. The minimal critical radius $R_{\text{cr}}^{\text{min}}$ is primarily determined by the size dependence of the depolarization field and correlation effects, whereas the maximal critical radius $R_{\text{cr}}^{\text{max}}$ is governed mainly by the size dependence of chemical stresses induced by the elastic defects in the shell. Thus, this work identifies a stress-driven mechanism for reentrant ferroelectricity stabilization in nanoscale hafnia systems, arising from the competition between depolarization field-induced suppression of ferroelectricity and its stabilization by shell-induced chemical stress. We revealed that relatively large compressive chemical strains are necessary to induce the ferroelectric phase in the HfO_2 nanoparticles. Successful chemical strain engineering opens the way for significant enhancement of nanoscale HfO_2 polar properties for applications in advanced memory cells and logic devices.

DOI: 10.1103/yktz-f1hv

I. INTRODUCTION

Thin films of hafnia-zirconia ($\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$) are among the most promising silicon-compatible ferroelectric materials for advanced electronic memories [1–4]. At the same time, they are one of the more enigmatic ferroelectric systems, since the physical mechanisms responsible for the emergence of ferroelectric and/or antiferroelectric behavior remain under active debate [5,6]. The transition from the bulk nonpolar monoclinic m-phase (space group

$P2_1/c$) to the ferroelectric (FE) orthorhombic o-phase (space group $Pca2_1$) can occur in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ films when the thickness h decreases below a critical value $h_{\text{cr}} \cong 20\text{--}30\text{ nm}$ [7], whereas in more typical ferroelectric materials the FE phase becomes stable at larger thicknesses, $h > h_{\text{cr}}$. According to direct experimental observations [8] and *ab initio* calculations [9,10], the switching path of spontaneous polarization $\vec{P}_s$ in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films is indirect, in that the transition from $+\vec{P}_s$ to $-\vec{P}_s$ states proceeds via the nonpolar tetragonal t-phase.

The existence of ferroelectricity and the mechanism of polarization switching are much more complicated in small $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles with $x \geq 0.5$ and sizes $10\text{--}30\text{ nm}$. Because of their small sizes, it is difficult to distinguish between the t-phase (space group $P4_2/nmc$) and the o-phases (space groups $Pbca$, $Pbcm$, and ferroelectric $Pca2_1$) using x-ray diffraction (XRD) analysis, since the corresponding peaks are very close and broadened [11].

*Contact author: anna.n.morozovska@gmail.com

†Contact author: sergei2@utk.edu

‡Contact author: deanevans@zone5tech.com

In contrast to $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films, where switchable ferroelectric polarization can be induced by strain or defect engineering [12–16], reliable methods of controlling ferroelectricity are absent in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles. Furthermore, direct experimental evidence of ferroelectric hysteresis and/or ferroelectric domains in the nanoparticles has not been reported. Since the coupling between polar and nonpolar modes enhanced by large compressive strains can induce robust ferroelectricity in HfO_2 thin films and nanoislands [17], it is therefore plausible that similar effects may also occur in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles. However, a theoretical framework describing stress-induced ferroelectric states in nanoparticles has not yet been developed.

Several experimental [18,19] and theoretical [20,21] studies have revealed a leading role of oxygen vacancies [22,23] in the emergence and stabilization of the FE o-phase in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films. Thermodynamic considerations [24] based on the Landau-Ginzburg-Devonshire (LGD) approach predict that ferro-ionic states can be stable in small $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles due to a high degree of screening provided by ionic-electronic charges. The prediction was later supported experimentally by the observation that small (size 8–10 nm) oxygen-deficient $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles, which contain a large fraction of indistinguishable o-phases due to the annealing in a reducing $\text{CO} + \text{CO}_2$ atmosphere [25,26], can exhibit ferroelectriclike properties, such as a colossal dielectric response over a wide frequency range [27], as well as demonstrate resistive switching and pronounced temperature-dependent charge accumulation [28,29]. Since the defect formation energy is much lower near the oxide surface compared with the bulk [30], the reducing $\text{CO} + \text{CO}_2$ atmosphere creates the high concentration of oxygen vacancies near the surface of the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles. As a result, the oxygen-deficient $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles may acquire a “core-shell” type structure, in which oxygen vacancies are predominantly localized within the surface layer (shell), and the central part of the particle (core) is almost free of vacancies. However, the diffraction peaks for the different o-phases could not be resolved by XRD in the $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles due to proximity and broadening of corresponding peaks, making it impossible to identify the *Pca21* o-phase and/or determine its fraction. Since oxygen vacancies inevitably produce Vegard strain and chemical stress [24,31], it is likely that they can induce the desired *Pca21* o-phase when their concentration increases.

In this work, we investigate stress-induced stabilization of ferroelectricity in spherical HfO_2 core-shell nanoparticles. We use a thermodynamic LGD model to obtain analytical expressions for the critical radii that define a stable range of spontaneous polarization. Calculations indicate that a reentrant ferroelectric behavior results from the competition between depolarization effects and shell-induced chemical stress. This interplay provides a

mechanism for ferroelectric state stabilization in nanoscale HfO_2 core-shell systems. We note that dense nanocomposites and nanogained ceramics consisting of FE core-shell HfO_2 nanoparticles with large spontaneous polarization and minimal misorientation of crystallographic axes can be prepared by tape casting or cold pressing of the core-shell HfO_2 nanoparticles in a large orienting electric field, or by reactive templated grain growth (see, e.g., Ref. [32] and refs. therein). Such nanomaterials may overcome the principal thickness limitation of FE HfO_2 films (less than 20–30 nm [17–19]) and thus can be significant for hafnia-based high-performance piezoelectric actuators, pyroelectric sensors, and electrocaloric devices with a minimal risk of electric breakdown.

II. PROBLEM GEOMETRY AND MAIN ASSUMPTIONS

We consider a spherical HfO_2 core-shell nanoparticle with a single-domain core characterized by a spontaneous polarization $\vec{P}_3$ directed along the polar axis “3.” The core is considered as defect-free, crystalline, and insulating. The core is covered with a thin shell, whose thickness ΔR is much smaller than the core radius. The core radius is R_c , and the outer radius is $R_s = \Delta R + R_c$. Because of the well-established fact that the defect formation energy is much lower near the oxide surface compared with the bulk [30], we assume that the reducing $\text{CO} + \text{CO}_2$ atmosphere promotes the formation of oxygen vacancies primarily in the shell rather than in the HfO_2 core. Therefore, the shell is assumed to be semiconducting and nonferroelectric due to the high concentration of free ionic-electronic charges and elastic defects, primarily oxygen vacancies. We assume that the effective screening length in the shell, λ_{eff} , is smaller than the critical value λ_{cr} . For $\lambda_{\text{eff}} < \lambda_{\text{cr}}$, the free charges in the shell provide effective screening of the bound charges associated with the spontaneous polarization in the core, thereby preventing domain formation and ensuring that the single-domain approximation is self-consistent. The critical value λ_{cr} depends on R_c , W_s , and T . As a rule, λ_{cr} is about 0.1–0.5 nm at room temperature, $R_c \geq 5$ nm, and $\Delta R \sim 1$ nm. For $\lambda_{\text{eff}} \geq \lambda_{\text{cr}}$, insufficient screening leads to a strong depolarization field that destabilizes the single-domain state in the core and favors the formation of a multidomain state. Under these conditions, the single-domain approximation is no longer applicable, and the finite element method (FEM) [33,34] or the phase-field approach [35] should be used to account for possible domain formation in the nanoparticle.

We also assume that the elastic defects (e.g., oxygen vacancies) in the shell induce strong chemical strains, denoted as w_{ij}^s . The chemical strains are regarded as isotropic, $w_{ij}^s = \delta_{ij}w_s$, where δ_{ij} is the Kronecker-delta symbol and w_s is the magnitude of the strains. These strains, which originate from, e.g., oxygen vacancies

and/or elastic dipoles, are proportional to the product of the Vegard strain tensor W_s and the defect concentration n , such that $w_s \cong W_s n$. The magnitude of W_s is about $(1-3) \times 10^{-29} \text{ m}^3$ in oxide ferroelectrics [36,37]. Assuming an atomic concentration $n_0 \cong 10^{29} \text{ m}^{-3}$, we estimated the defect concentration as $n \approx (1-5) \times 10^{27} \text{ m}^{-3}$. This value of n is consistent with many experiments [38–40], which show that the defect concentration can exceed 2%–5% near the surface of various oxides. Hence, the range of chemical strains w_s can be taken as about 1%–5% for the purpose of this work. We should note that Vegard strains larger than several % can induce structural relaxation, defect clustering, and/or lattice instability, which cannot be considered within the continuum LGD approach. To justify the feasibility of such large strains, we refer to the experiments for oxides [30,38–40], as well as *ab initio* calculations [15,16] corroborated by experiments [12,13], where very large mismatch strains were applied to induce the ferroelectricity in thin $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ films.

Because of the elastic mismatch at the core-shell interface, the chemical strains induce elastic stress in the core. In addition to defect-induced chemical strains and stresses, the contribution of the intrinsic surface stress [41] (referred to as “surface tension”) associated with the particle curvature should also be considered. The intrinsic surface stress contribution is equal to $\frac{-2\mu}{R_c}$, where μ is the surface tension coefficient and its estimated value $|\mu| \cong 1-2 \text{ N/m}$ is typical for oxide ferroelectrics [42,43].

The relative dielectric permittivity tensor of the shell, ϵ_{ij}^s , is taken to be cubic, $\epsilon_{ij}^s = \delta_{ij}\epsilon_s$, and the dielectric permittivity ϵ_s can be relatively high due to the paraelectric state of the shell. The core-shell nanoparticle is embedded in a paraelectric (e.g., SrTiO_3 , KTaO_3) or dielectric (polymer, gas, liquid, air, or vacuum) environment with a relative dielectric permittivity ϵ_e . It has been shown [44]

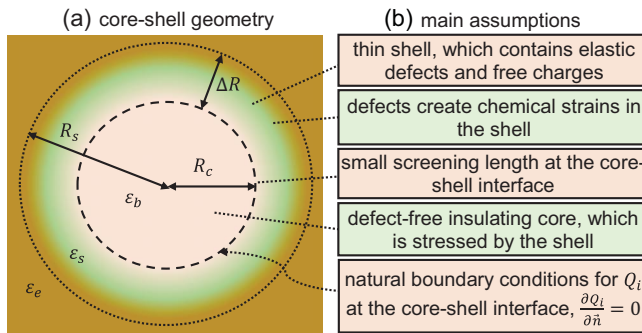


FIG. 1. (a) The cross section of a spherical HfO_2 core-shell nanoparticle: a defect-free core of radius R_c is covered with a shell of thickness ΔR , which is full of elastic defects (e.g., oxygen vacancies) and free charges. The nanoparticle is placed in an isotropic dielectric medium; ϵ_b , ϵ_s , and ϵ_e are the core background, shell, and ambient dielectric permittivities. (b) Block scheme of the main assumptions. Part (a) is adapted from Ref. [31].

that λ_{eff} is related to the Debye-Hückel length L_D as $\lambda_{\text{eff}} = \frac{L_D}{\epsilon_s}$, where $L_D = \sqrt{\frac{\epsilon_0 \epsilon_s k_B T}{2e^2 n}}$, ϵ_0 is the vacuum dielectric constant, k_B is the Boltzmann constant, T is the absolute temperature, and e is the elementary charge. The core-shell geometry is shown in Fig. 1(a) and a block scheme of the main assumptions is shown in Fig. 1(b).

III. FREE ENERGY FUNCTIONAL OF HAFNIA CORE-SHELL NANOPARTICLES

To study the influence of chemical stresses on the phase diagrams and polar properties (e.g., spontaneous polarization and related ferroelectric characteristics) of spherical HfO_2 nanoparticles with a core-shell structure, we use the LGD free energy functional that includes higher-order contributions together with trilinear and biquadratic couplings involving polar, antipolar, and nonpolar order parameters [17]. The form of the free energy functional is based on the results of Delodovici *et al.* [15,45] and Jung and Birol [46,47], who established the principal role of the trilinear coupling. The electrostriction coupling coefficients of HfO_2 were determined from the piezoelectric response reported by Datta *et al.* [48]. The dielectric permittivity was calculated by Zhao and Vanderbilt [49].

The LGD free energy of the HfO_2 nanoparticle core, corresponding to the FE o-phase, $F_{\text{o-phase}}$, is written as the volume integral of the free energy densities f_{bulk} , electric energy f_{el} , and surface energy F_s :

$$F_{\text{o-phase}} = \int (f_{\text{bulk}} + f_{\text{el}}) dV + F_s, \\ f_{\text{bulk}} = f_{\text{bq}} + f_{\text{tr}} + f_{\text{est}} + f_{\text{grad}}. \quad (1)$$

The bulk energy density f_{bulk} is the sum of biquadratic (denoted as f_{bq}) and trilinear (denoted as f_{tr}) coupling terms involving the polar, antipolar, and nonpolar order parameters; elastic, electrostriction, antipolar, and nonpolar-type striction energy contributions (collectively denoted as f_{est}); and the gradient energy of the order parameters (denoted as f_{grad}). The energy f_{bq} is an expansion over even 2-4-6-8 powers and f_{tr} is an expansion over odd 3-5-7 powers of the dimensionless amplitudes Q_{Γ_3} , Q_{Y_2} , and Q_{Y_4} of the polar phonon mode Γ_{3-} , nonpolar phonon mode Y_{2+} , and antipolar phonon mode Y_{4-} (see Refs. [15,17,45–47] for details). The energies f_{bq} , f_{tr} , f_{est} , f_{grad} , and f_{el} are listed in Appendixes S1 and S2 in Supplemental Material [50]. In a general case, the surface energy F_s is the quadratic form of Q_i , namely $F_s = \int \alpha_i Q_i^2 dS$, where $Q_i = Q_{\Gamma_3}$, Q_{Y_2} , and Q_{Y_4} represent the order parameters. Given the natural boundary conditions at the core-shell interface, $\frac{\partial Q_i}{\partial n} = 0$, the surface energy can be assumed to be zero.

The polarization P_3 is proportional to the amplitude Q_{Γ_3} of the Γ_{3-} mode [15,17,46]:

$$P_3 = \frac{Z_B d}{V_{\text{f.u.}}} Q_{\Gamma 3} \approx P_0 Q_{\Gamma 3}, \quad (2)$$

where Z_B is the effective Bader charge [47], d is the atomic displacement corresponding to the polar mode, $V_{\text{f.u.}}$ is the formula unit (f.u.) volume, and P_0 is the polarization amplitude. The values $V_{\text{f.u.}} \approx 134 \text{ \AA}^3$ and $P_0 \approx 54.8 \text{ \mu C/cm}^2$ at room temperature [15]; hereinafter $Q_{\Gamma 3}$ is dimensionless, while Q_{Y2} , and Q_{Y4} have the dimension of length and are measured in $\text{\AA}$.

Following Refs. [15,17], we consider the nonpolar t-phase as the reference “aristo-phase” of the HfO_2 core. The FE o-phase can be stable in the core when its free energy $F_{\text{o-phase}}$ is smaller than the energy of the m-phase, $F_m = \int f_m dV$, where $f_m \approx -92 \text{ meV/f.u.}$ is the energy density of a bulk HfO_2 m-phase [15]. The energy of the m-phase is significantly lower than the energy of the t-phase, which is set as zero energy. Note that the choice of zero energy is arbitrary, it is convenient to relate it with the physical mechanisms of the polarization switching in the HfO_2 core. Following Refs. [8–10], we assume that the polarization switching proceeds via the nonpolar t-phase; it seems reasonable to set its energy equal to zero. Thus, the critical sizes of the ferroelectricity

appearance/disappearance in the HfO_2 core-shell nanoparticles can be estimated from the phase stability boundary condition

$$F_{\text{o-phase}} = F_m. \quad (3)$$

Because the various energy contributions exhibit different size dependencies, the phase stability condition may yield several critical core radii, $R_{\text{cr}}^{(i)}$, where $i = 1, 2$, or more. At small R_c , the depolarization field energy destabilizes the ferroelectric state of the core; defect-induced chemical stress induces and stabilizes the FE o-phase at intermediate sizes; and the bulk m-phase becomes energetically favorable at large R_c . As a result, one can expect that the ferroelectricity may exist only within a finite size window $R_{\text{cr}}^{\text{min}} < R_c < R_{\text{cr}}^{\text{max}}$. This expectation is justified by the results of calculations presented in the next section.

Elastic and/or chemical stresses, surface tension, polarization gradient, and depolarization field energies “renormalize” the coefficients in the free energy (1). Elastic stresses σ_{ij}^c , induced by the chemical strain and intrinsic surface stress, have the following form in the nanoparticle core [50]:

$$\sigma_{11}^c = \sigma_{22}^c = \sigma_{33}^c \approx \frac{-2(R_s^3 - R_c^3)(q_c P_0^2 Q_{\Gamma 3}^2 + z_c Q_{\Gamma 3} Q_{Y2} Q_{Y4} - w_s) - 3R_s^3(s_{11}^s + s_{12}^s) \frac{2\mu}{R_c}}{2(R_s^3 - R_c^3)(s_{11}^c + 2s_{12}^c) + R_s^3(s_{11}^s - s_{12}^s) + 2R_c^3(s_{11}^s + 2s_{12}^s)}. \quad (4)$$

Here, s_{ij}^c and s_{ij}^s are the elastic compliances of the core and shell, respectively; $q_c = (Q_{13}^c + Q_{23}^c + Q_{33}^c)/3$ and $z_c = (Z_{13}^c + Z_{23}^c + Z_{33}^c)/3$ are the isotropic parts of the electrostriction and trilinear striction tensors of the core, respectively (see Appendixes S3 and S4 in Supplemental Material [50] and Ref. [51]). The non-diagonal stresses are absent, $\sigma_{12}^c = \sigma_{13}^c = \sigma_{23}^c = 0$. Note that the contribution of the intrinsic surface stress cannot add more than 0.3% to the stress of the nanoparticle core with radius $R_c \geq 5 \text{ nm}$, since the combination of elastic compliances $s_{11}^s + 2s_{12}^s$ does not exceed $3 \times 10^{-12} \text{ Pa}^{-1}$ in the HfO_2 material. For the considered case $\Delta R \ll R_c$, the stress

$$\sigma_{ii}^c \approx \frac{-2\Delta R(q_c P_0^2 Q_{\Gamma 3}^2 + z_c Q_{\Gamma 3} Q_{Y2} Q_{Y4} - w_s)}{R_c(s_{11}^s + s_{12}^s)} - \frac{2\mu}{R_c}.$$

Analytical calculations and FEM were performed to determine the applicability limits of the steplike core-shell model (4) relative to the diffuse step model and the continuous exponential decay of the defect concentration from the surface to the center of the nanoparticle (see Appendix S5 in Supplemental Material [50] for details). We used exponential and Fermi functions to describe the defect concentration because this choice is well-grounded by experimental studies and *ab initio* calculations of the defect formation energy (see Ref. [30] and references

therein). The obtained results confirm that the average elastic fields in the core calculated using the steplike core-shell model differ by no more than 5% from those calculated using the diffuse step and exponential decay models, provided that the total number of defects is the same. This result has a relatively simple explanation based on the Saint-Venant principle and the direct variational method. Indeed, we consider spatially averaged quantities in a free energy formulation with renormalized coefficients instead of local distributions of elastic and electric fields (see, e.g., Ref. [52]). The integration of the elastic fields over the core volume smooths out local differences between the defect distribution functions, making the result depend primarily on their average value. Therefore Eq. (4) is “robust” with respect to the details of the defect distribution function and is primarily sensitive to the average defect concentration n_d , shell thickness ΔR , and core radius R_c , because their product is proportional to the total number of defects N_d . For thin shells ($R_c \gg \Delta R$), the total number of defects, $N_d \approx \frac{4\pi}{3}(R_s^3 - R_c^3)n_d \approx 4\pi R_c^2 \Delta R n_d$, should be conserved for the validity of the core-shell model.

Note that the LGD phenomenology incorporating trilinear coupling was introduced in Ref. [17] for *epitaxial* thin HfO_2 films and cylindrical nanoclusters clamped to a

rigid substrate. However, the results of Ref. [17] are not applicable for nanoparticles. The ferroelectricity and related phenomena considered in this work depend critically on the magnitude and sign of chemical stresses created by the defect-enriched shell. The analytical form of the chemical stress in Eq. (4) differs fundamentally from the elastic strains in epitaxial thin films and/or nanoclusters with out-of-plane polarization. The physical difference is that the isotropic parts of the electrostriction and trilinear striction tensors of the core couple the emerging polarization and chemical stresses, and the stresses are radius-dependent (similarly to surface tension but in a more complex way). Anisotropic combinations of electrostriction and trilinear striction tensors, as well as the appearance of misfit dislocations, play a decisive role in the behavior of thin epitaxial films and nanoclusters clamped to a substrate.

The depolarization field E_3^d and external field E_3^e inside the single-domain spherical core with the ferroelectric polarization $P_3(\vec{r})$ directed along the polar axis “3” have the following form [24]:

$$E_3^d \approx -\frac{1}{\epsilon_b + 2\epsilon_s + (R_c/\lambda_{\text{eff}})} \frac{P_3}{\epsilon_0}, \quad (5a)$$

$$E_3^e \approx \frac{3\epsilon_e}{\epsilon_b + 2\epsilon_s + (R_c/\lambda_{\text{eff}})} E_3^0. \quad (5b)$$

Comparison of the electric fields, calculated by FEM in a self-consistent manner, with the approximate expressions

in Eqs. (5a) and (5b) showed that they are accurate to within a few percent for single-domain nanoparticles covered by a layer of screening charge with an effective screening length λ_{eff} less than λ_{cr} . The critical value of λ_{cr} is approximately 0.1–0.5 nm at room temperature [24]. For $\lambda_{\text{eff}} < \lambda_{\text{cr}}$, the free charges in the shell provide effective screening of the spontaneous polarization in the core, thereby preventing domain formation and ensuring that the single-domain approximation is self-consistent. We verified that the inequality $\lambda_{\text{eff}} < \lambda_{\text{cr}}$ was satisfied during the simulations.

In what follows, we assume that the dielectric permittivity of the shell ϵ_s and the ambient permittivity ϵ_e are approximately the same values, $\epsilon_s \approx \epsilon_e$. This assumption is justified in the case when elastic defects (e.g., oxygen vacancies) accumulate in a thin shell ($\Delta R \sim 1$ nm) at the surface of nanoparticles, as well as in the case of densely packed nanoparticles (e.g., dense ceramics), when the role of the environment is played by the particles themselves (e.g., in the effective medium approximation).

To derive a relatively simple equation for the critical radii of the nanoparticle core, we assume that the average spontaneous polarization $\bar{P}_s$ depends only weakly on stresses and core radius in the stability region of the FE o-phase (sufficiently far from the phase boundary). Using these assumptions and the strong inequality $\Delta R \ll R_c$, an approximate algebraic equation for the critical core radius, R_{cr} , acquires the form:

$$\frac{\lambda_{\text{eff}}}{2\epsilon_0[(\epsilon_b + 2\epsilon_s)R_{\text{cr}} + \lambda_{\text{eff}}]} + \left[\frac{6\Delta R}{s_{11}^s + s_{12}^s} \left(q_c \bar{P}_s^2 + z_c \bar{Q}_{Y2} \bar{Q}_{Y4} \frac{\bar{P}_s}{P_0} - w_s \right) + \mu \right] \frac{2q_c}{R_{\text{cr}}} = -\Delta_\beta, \quad (6)$$

where the positive parameter Δ_β is estimated at the end of Appendix S3 in Supplemental Material [50]. If we assume that the parameter Δ_β is size and stress independent, Eq. (6) becomes a quadratic equation. Under certain conditions, it may have two positive roots, denoted earlier as $R_{\text{cr}}^{\text{min}}$ and $R_{\text{cr}}^{\text{max}}$. The analytical expressions for the critical sizes of HfO_2 nanoparticles can be generalized for $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles, provided that the corresponding free energy parameters are known from first-principles calculations.

Results presented in the next section are calculated numerically using the Monte Carlo method to minimize the free energy functional (1). Equation (2) is used to recalculate the ferroelectric polarization P_3 from the amplitude Q_{Γ_3} of the Γ_{3-} mode. Condition (3) is used to calculate the phase boundary between the FE o-phase and the nonpolar m-phase. For the defect distribution, we use a diffuse step function described by a Fermi-like function $\frac{1}{1+\exp(\frac{R_c-r}{\delta R})}$ with a finite width $\delta R \ll R_c$ (see

Appendix S5 in Supplemental Material [50] for details). It should be emphasized that Eq. (6) was not used to calculate the results presented below, because Eq. (6) loses accuracy near the phase boundaries. Equation (6) should be considered as a “scaling law” that describes the critical sizes of the HfO_2 core-shell nanoparticles only qualitatively. The numerical results presented in Sec. IV were obtained and visualized using Mathematica 14.0 [53], whose built-in Monte Carlo algorithms and related optimization routines accelerate the calculations.

IV. RESULTS AND DISCUSSION

As argued in the introduction, the mechanisms of the FE o-phase stabilization in nanoscale HfO_2 remain under debate. Moreover, an interesting question arises: why is a stable FE o-phase observed in strained HfO_2 thin films but not in HfO_2 nanoparticles? An answer that follows from the calculated results and figures presented below is that

relatively large compressive chemical stresses are necessary to induce the FE o-phase in the nanoparticles. Such stresses are very unlikely to arise spontaneously; instead, their creation requires special treatment of the nanoparticles.

A. Stress-induced effects of the phase diagrams, spontaneous polar, antipolar, and nonpolar order parameters of hafnia core-shell nanoparticles

The spontaneous polarization $\bar{P}_s$ and the antipolar order parameter $\bar{Q}_{Y4s}$ of the HfO_2 core-shell nanoparticles as a

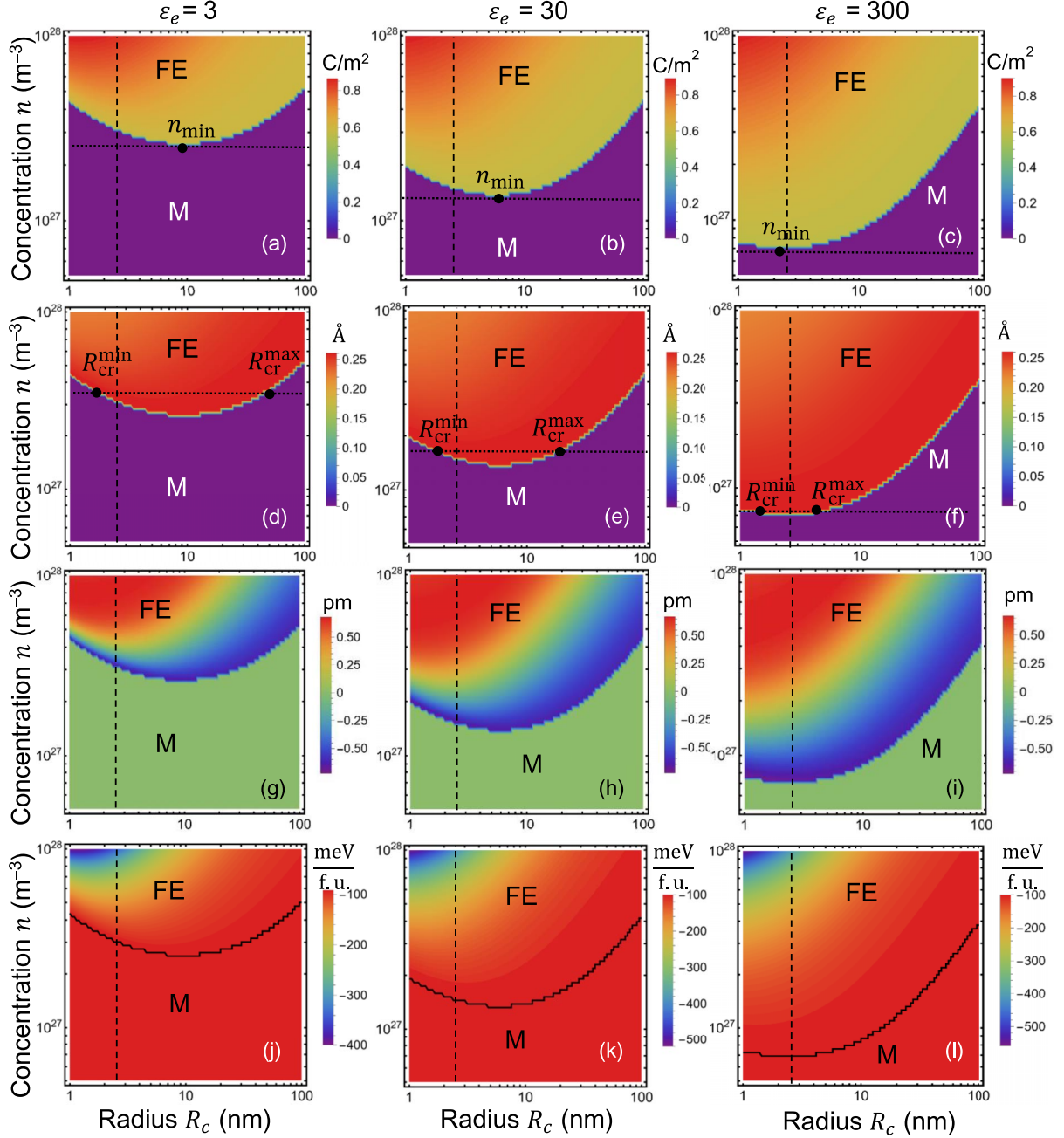


FIG. 2. The absolute value of the spontaneous polarization $\bar{P}_s$ (a)–(c), the amplitude of the antipolar order parameter $|\bar{Q}_{Y4s}|$ (d)–(f), the difference $|\bar{Q}_{Y4s}| - |\bar{Q}_{Y2s}|$ (g)–(i), and the deepest minimum of the free energy density $f_{\text{o-phase}}^{\text{min}}$ (j)–(l) as a function of core radius R_c and defect concentration n calculated for several values of the ambient permittivity $\epsilon_e = 3$ (a),(d),(g),(j), 30 (b),(e),(h),(k), and 300 (c),(f),(i),(l). Abbreviation “FE” denotes the FE o-phase, “M” denotes the nonpolar m-phase of the HfO_2 nanoparticle. Dashed vertical lines indicate the size limit for the applicability of the LGD approach. $\Delta R = 1 \text{ nm}$, $W_s = -1 \times 10^{-29} \text{ m}^3$, $\mu = 0$, $V_{\text{f.u.}} \approx 134 \text{ \AA}^3$, $T = 300 \text{ K}$, and $\epsilon_s \cong \epsilon_e$. Material parameters of HfO_2 used in calculations are listed in Tables S1 and S2 in Appendix S1 of Ref. [17].

function of defect concentration n and core radius R_c are shown in Figs. 2(a)–2(f) for several values of the ambient medium dielectric permittivity $\epsilon_e = 3$ (corresponding to a low- k medium such as oxides, polymers polyvinyl butyral, and ethyl cellulose), $\epsilon_e = 30$ [corresponding to a high- k polymer such as PV(DF-TrFE)], and $\epsilon_e = 300$ (corresponding to a paraelectric SrTiO₃). Thus, the choice of ϵ_e is linked to real materials, which are used as matrices for the preparation of ferroelectric nanocomposites (see, e.g., Refs. [54–56] and references therein).

In Fig. 2, the shell thickness is fixed at $\Delta R = 1.0$ nm, the Vegard tensor magnitude is set to $W_s = -1 \times 10^{-29}$ m³, and the temperature is $T = 300$ K. In the calculations, the effective screening length is assumed to depend on the defect concentration n as $\lambda_{\text{eff}} = \sqrt{\frac{\epsilon_0 k_B T}{2e^2 n \epsilon_s}}$, and the condition $\epsilon_s \cong \epsilon_e$ is imposed. The expression for λ_{eff} is derived in Ref. [44] using the Debye-Hückel approximation. The dependence of the chemical strain w_s on the defect concentration n obeys the linear Vegard law, $w_s \cong W_s n$.

The FE o-phase is stable only under compressive chemical strain $w_s \leq -(0.7\text{--}2.5)\%$, corresponding to $W_s < 0$ and $n > n_{\text{min}}$. The requirement of applying compressive strain to stabilize the FE o-phase in the HfO₂ core-shell nanoparticles is consistent with DFT results reported for thin films [14,15,17]. The region of the nonpolar m-phase stability decreases significantly as ϵ_e increases, which is replaced by the FE o-phase (compare the first, second, and third columns in Fig. 2). The FE o-phase is reentrant for $\epsilon_e \leq \epsilon_{\text{max}}$ and defect concentrations $n > n_{\text{min}}$. The maximal value $\epsilon_{\text{max}} \geq 300$ for material parameters of HfO₂, $W_s = -1 \times 10^{-29}$ m³, and room temperature. The minimal concentration of defects, n_{min} , decreases with an increase in ϵ_e from 2.5×10^{27} m⁻³ at $\epsilon_e = 3$ to 7×10^{26} m⁻³ at $\epsilon_e = 300$ [see the black circles in Figs. 2(a)–2(c)]. Since the depolarization field E_3^d scales as $\frac{\lambda_{\text{eff}}}{(\epsilon_b + 2\epsilon_e)R_c + \lambda_{\text{eff}}}$ according to Eq. (4), and the effective screening length λ_{eff} scales as $\sqrt{\frac{1}{\epsilon_e}}$, both E_3^d and λ_{eff} decrease simultaneously with an increase in ϵ_e . Thus, the simultaneous reduction of the m-phase stability region, the minimal concentration n_{min} , and the depolarization field E_3^d can be attributed to enhanced dielectric and space-charge screening with increasing ϵ_e .

Note that the values of λ_{eff} corresponding to the region of FE o-phase stability in Fig. 2 are significantly smaller than the critical value λ_{cr} required for domain formation. The FEM, which accounts for possible domain formation, shows that the FE o-phase disappears completely for $\lambda_{\text{eff}} > \lambda_{\text{max}}$, where $\lambda_{\text{max}} > \lambda_{\text{cr}}$ and increases with increasing magnitude of W_s . The calculations further indicate that domain formation slightly reduces the critical radius for ferroelectricity disappearance. A detailed analysis of domain formation in the HfO₂ core-shell nanoparticles will be presented elsewhere.

The color scale in Figs. 2(a)–2(c) represents the absolute value of the spontaneous polarization $\bar{P}_s$ in the deepest potential well (i.e., deepest minimum) of the free energy given by Eq. (1). The spontaneous polarization can reach relatively large values 60–70 $\mu\text{C}/\text{cm}^2$ for small core radii ($R_c < 10$ nm) and high elastic defect concentrations ($n > 10^{27}$ m⁻³). Although the required values of n are high, they are quite realistic and decrease strongly (from 5×10^{27} m⁻³ to 0.6×10^{27} m⁻³) with an increase in ϵ_e from 3 to 300. The spontaneous polarization of the HfO₂ core exceeds the experimentally observed values in Hf_xZr_{1-x}O₂ thin films by a factor of 3 [7]. The increase arises due to compressive chemical stress in the shell.

The color scale in Figs. 2(d)–2(f) represents the absolute value of the antipolar mode $\bar{Q}_{Y_{4s}}$ in the deepest potential well of the free energy (1). The sharp boundary between the FE o-phase (with $\bar{P}_s > 0$ and $\bar{Q}_{Y_{4s}} > 0$) and nonpolar m-phase (with $\bar{P}_s = 0$ and $\bar{Q}_{Y_{4s}} = 0$) corresponds to the first-order phase transition curve defining the critical radius R_{cr} as a function of defect concentration n .

It is seen from Figs. 2(g) to 2(i) that the difference between the antipolar and nonpolar order parameters amplitudes, $|\bar{Q}_{Y_{4s}}| - |\bar{Q}_{Y_{2s}}|$, is very small in the free energy minimum, reflecting the negligible anisotropy of the deepest potential well with respect to the Y_{4-} and Y_{2+} modes [17]. Specifically, the difference $|\bar{Q}_{Y_{4s}}| - |\bar{Q}_{Y_{2s}}|$ changes its sign along the curved stripe in the middle of the FE o-phase region and does not exceed ± 0.75 pm, which is more than 30 times smaller than the maximal value of $\bar{Q}_{Y_{4s}} \approx 0.25$ Å. The small splitting between the amplitudes of antipolar and nonpolar modes means that the distortion of the o-phase is strongly mixed between these two modes (assuming angular isotropy within the framework of the model used). This result explicitly indicates that the anisotropy in the $\{Y_{4-}, Y_{2+}\}$ subspace is weak and thus the pure antipolar ($\bar{Q}_{Y_{4s}} \neq 0$ and $\bar{Q}_{Y_{2s}} = 0$) and nonpolar ($\bar{Q}_{Y_{4s}} = 0$ and $\bar{Q}_{Y_{2s}} \neq 0$) states are unstable in the o-phase.

As follows from Eq. (5), the stress-dependent upper critical core radius $R_{\text{cr}}^{\text{max}}$, corresponding to the appearance of ferroelectricity, is primarily governed by the size dependence of the chemical stress σ_{ij}^c , which scales as $\frac{1}{R_{\text{cr}}}$ according to Eq. (3). In contrast, the lower critical radius $R_{\text{cr}}^{\text{min}}$, corresponding to the disappearance of ferroelectricity, is primarily governed by the size dependence of the depolarization field E_3^d , which is proportional to the function $\frac{\lambda_{\text{eff}}}{(\epsilon_b + 2\epsilon_e)R_{\text{cr}} + \lambda_{\text{eff}}}$ according to Eq. (4). The distinct radius scaling of chemical stress and depolarization field energy therefore produces a finite interval of core radii in which the ferroelectric phase is thermodynamically stable. For small radii, the depolarization field energy contribution dominates and suppresses the ferroelectric order, whereas at large radii the chemical stress-induced stabilization weakens and restores the nonpolar m-phase.

The critical radii $R_{\text{cr}}^{\text{max}}$ and $R_{\text{cr}}^{\text{min}}$ depend on the defect concentration n and the dielectric permittivity of the surrounding medium ϵ_e [see the black circles in Figs. 2(d)–2(f)]. Both radii, $R_{\text{cr}}^{\text{min}}$ and $R_{\text{cr}}^{\text{max}}$, exist only for $n > n_{\text{min}}$; they merge at $n \rightarrow n_{\text{min}}$ and disappear for $n < n_{\text{min}}$. For a broad range of ϵ_e , namely, $1 \leq \epsilon_e \leq \epsilon_{\text{max}}$, the FE o-phase is thermodynamically stable within the finite window $R_{\text{cr}}^{\text{min}} < R_c < R_{\text{cr}}^{\text{max}}$. For large permittivities, $\epsilon_e > \epsilon_{\text{max}}$, the lower critical radius decreases below the limiting size of the continuous LGD theory applicability. The limit is determined by several correlation lengths, which are about 5–10 lattice constants. Thus, in this regime, $R_{\text{cr}}^{\text{min}}$ is limited by several correlation lengths, because the depolarization field energy becomes negligibly small due to the effective dielectric screening at $\epsilon_e > \epsilon_{\text{max}}$.

The deepest minimum of the free energy density, $f_{\text{o-phase}}^{\text{min}}$, as a function of defect concentration n and core radius R_c , calculated for $\epsilon_e = 3, 30$, and 300 , is shown in Figs. 2(g)–2(i), respectively. The red background in the figure corresponds to the bulk m-phase with the energy density $f_m = -92$ meV/f.u. [15]. The first-order phase transition between the o-phase and m-phase is determined by the condition $f_{\text{o-phase}}^{\text{min}} = f_m$. The phase boundary is shown by the black curves in Figs. 2(g)–2(i). As expected, the deepest minimum in the o-phase, $f_{\text{o-phase}}^{\text{min}}$, occurs at large defect concentrations and small core radii [see the upper left region of the diagrams in Fig. 2(g)–2(i)], where defect-induced compressive chemical stress energetically favors the o-phase over the m-phase, driving the ferroelectric phase stabilization.

It should be emphasized that the continuum LGD description is quantitatively valid for system sizes larger than 10 lattice constants, which corresponds to 5-nm-diameter HfO₂ nanoparticles (see the dashed vertical lines in Fig. 2). The 5-nm nanoparticle contains about 490 f.u., which significantly exceeds the correlation volume (approximately 20 f.u.) required for the formation of long-range order. Results shown in Fig. 2 (as well as in Fig. 3) for smaller sizes (e.g., for $R_c < 2.5$ nm) may be only qualitatively valid. For larger radii, the applicability of the LGD theory is corroborated by the fact that the critical sizes for the onset of the long-range order calculated from atomistic and phenomenological theories are in good agreement with each other, as well as with experimental results for other ferroelectric systems [57–60]. It is significant that the role of thermal fluctuations is negligible in ferroelectric nanoparticles over a wide range of sizes, including the immediate vicinity of the size-induced transition to the ferroelectric phase, because the height of the potential barrier associated with the onset of spontaneous polarization greatly exceeds the thermal energy [see, e.g., Fig. 2(b) in Ref. [61]]. In the considered case of a 5-nm HfO₂ nanoparticle, the barrier is more than $10^2 k_B T$ at room temperature, since the transition from the m-phase

to the FE o-phase is of the first order. This contrasts with nanosized ferromagnets, where the potential barriers are typically shallow.

B. Polarization switching, dielectric and piezoelectric properties of hafnia core-shell nanoparticles: From modeling to applications

Note that the same LGD free energy functional that determines the chemical stress-induced stabilization of the FE o-phase also defines the switching pathway of the spontaneous polarization and the dielectric and piezoelectric properties of the HfO₂ core-shell nanoparticles. Below, we study the influence of chemical stress and size effects on polarization switching and polar properties of the nanoparticles.

Similarly to the case of strained HfO₂ thin films considered in Ref. [17], the switching path between the $-\bar{P}_s$ and $+\bar{P}_s$ states is mediated by the virtual $Ccce$ phase [15,45] in the HfO₂ core-shell nanoparticles. As a result, the lowest polarization switching barrier b_{af} is approximately +48 meV/f.u., corresponding to the energy difference between the $Ccce$ phase and the t-phase. The activation field for polarization switching can be estimated as $E_{\text{af}} \cong b_{\text{af}}/\bar{P}_s$, where $\bar{P}_s$ depends on the chemical strains w_s , defect concentration n , core radius R_c , and shell thickness ΔR . Color maps of E_{af} as a function of R_c and n are shown in Figs. 3(a)–3(c). The activation fields are calculated for several values of the ambient permittivity, $\epsilon_e = 3, 30$, and 300 . The values of E_{af} range from 0.65 MV/cm (far from the o-m phase boundary) to 0.95 MV/cm (near the o-m phase boundary) and are very close to the activation fields calculated for strained HfO₂ thin films [17]. The lowest values of E_{af} occur at large defect concentrations and small core radii, where the compressive chemical stress σ_{ii}^c is largest. The region expands with increasing ϵ_e due to a reduction in the depolarization field. The calculated activation fields are somewhat lower than the coercive fields $E_c \cong 1.05$ – 1.35 MV/cm observed experimentally in 10-nm-thick Hf_xZr_{1-x}O₂ films [7,62]. This result is expected from the activation rate theory, because the local nucleation of nanodomains (arising at $E_3^e \approx E_{\text{af}}$) precedes the global polarization switching (occurring at $E_3^e \approx E_c$). The calculated activation fields are of the same order of magnitude as experimentally reported coercive fields, indicating that the predicted switching barriers are physically consistent with experimental values.

Color maps of the linear relative dielectric permittivity ϵ_{33} as a function of R_c and n , calculated for $\epsilon_e = 3, 30$, and 300 at room temperature, are shown in Figs. 3(d)–3(f). As can be seen from the figure, the magnitude of ϵ_{33} can be tuned by varying the core radius and chemical strains from 10 to 35 at room temperature. The permittivity reaches maximal values (slightly above 30) relatively far from the boundary between the o- and m-phases. The permittivity

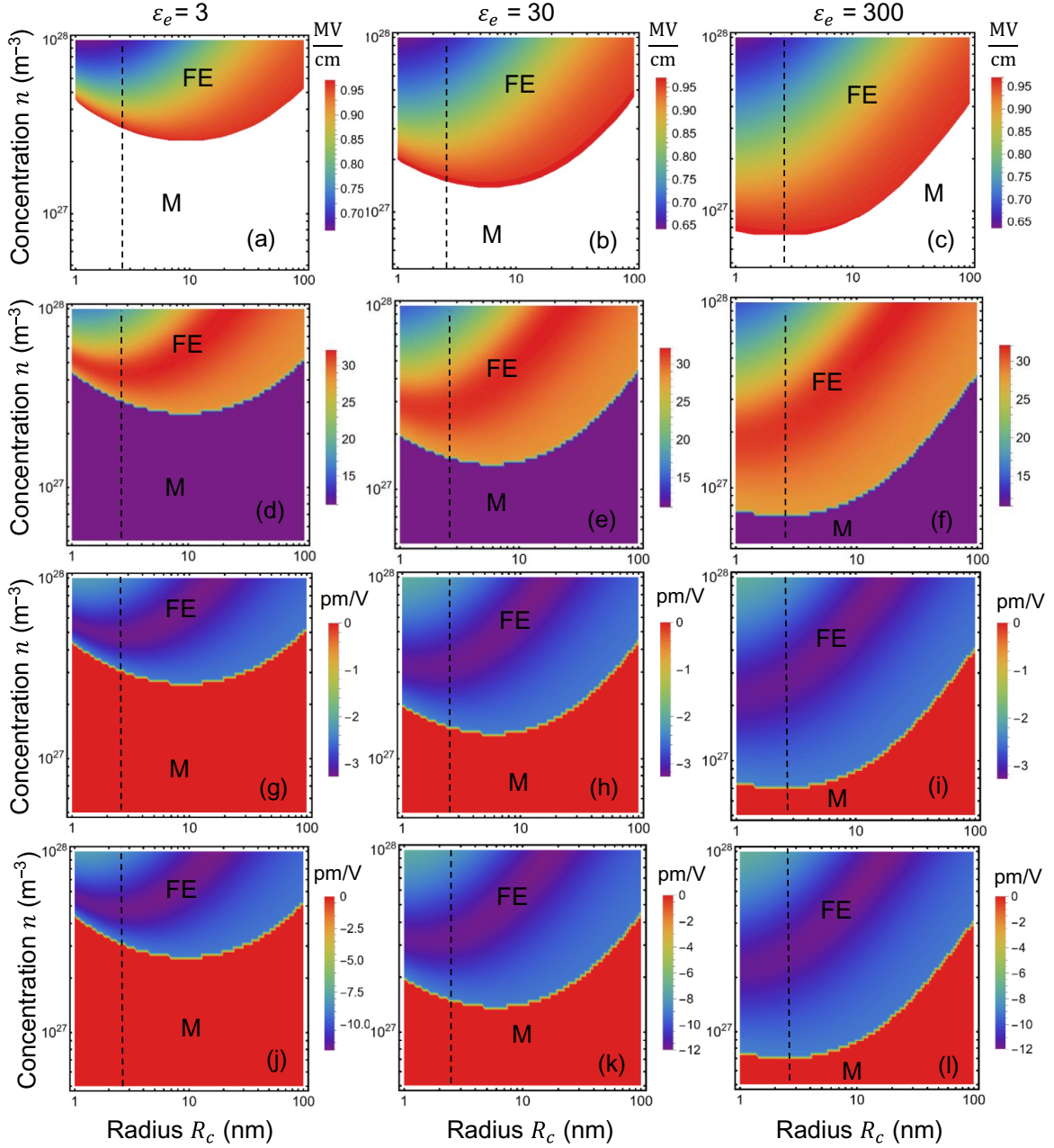


FIG. 3. The activation field E_{af} (a)–(c), relative dielectric permittivity ϵ_{33} (d)–(f), piezoelectric coefficient d_{333} (g)–(i) and volumetric piezo-response d_{vp} (j)–(l) as a function of core radius R_c and defect concentration n calculated for several values of the ambient permittivity $\epsilon_e = 3$ (a),(d),(g),(j), 30 (b),(e),(h), and 300 (c),(f),(i). The abbreviation “FE” denotes the FE o-phase, and “M” denotes the nonpolar m-phase of the HfO_2 nanoparticle. Dashed vertical lines indicate the size limit for the applicability of the LGD approach. $\Delta R = 1$ nm, $W_s = -1 \times 10^{-29}$ m³, $\mu = 0$, $V_{f.u.} \approx 134$ Å³, $T = 300$ K, and $\epsilon_s \cong \epsilon_e$. Material parameters of HfO_2 used in calculations are listed in Tables S1 and S2 in Appendix S1 of Ref. [17].

does not diverge at the o-m boundary because the transition is of the first order. The calculated values of $\epsilon_{33} \approx 10$ –30 agree well with the values of effective permittivity measured at 100–500 kHz in the densely pressed oxygen-deficient $\text{Hf}_x\text{Zr}_{1-x}\text{O}_{2-y}$ nanopowders ($x = 1, 0.6, 0.5$, and 0.4) with particle sizes of 7–10 nm [27]. Note that the nanoparticles studied in Ref. [27] were

annealed in a $\text{CO} + \text{CO}_2$ atmosphere to induce the maximal amount of oxygen vacancies near the surface. Thus, calculated values of ϵ_{33} are of the same order of magnitude as experimentally measured permittivity, being physically consistent with experimental results [27].

The region of maximal ϵ_{33} , which has the shape of a wide curved stripe located relatively far from the boundary

between the o- and m-phases, can be explained by the significant contribution of the nonpolar and antipolar orders to the permittivity due to the trilinear coupling in the free energy (1). Otherwise, the permittivity should be maximal at the o-m boundary, which is not the case shown in Figs. 3(d)–3(f). As seen in the color maps of the difference between antipolar and nonpolar order parameters shown in Figs. 2(g)–2(i), the difference $|\bar{Q}_{Y4s}| - |\bar{Q}_{Y2s}|$ is minimal in the same region where ϵ_{33} is maximal. Additional calculations show that the maximum of ϵ_{33} occurs at $|\bar{Q}_{Y4s}| = |\bar{Q}_{Y2s}|$, as anticipated from the specific form of the free energy (1) in the 3D order-parameter space $\{\bar{P}_s, \bar{Q}_{Y4s}, \bar{Q}_{Y2s}\}$.

It should be expected that the piezoelectric response reaches maximal values far from the o-m boundary because of the piezoelectric coefficients $d_{333} \sim \epsilon_{33}\bar{P}_s$. Color maps of the piezoelectric coefficient d_{333} as a function of R_c and n are shown in Figs. 3(g)–3(i). The figures are calculated for $\epsilon_e = 3, 30$, and 300 and room temperature. For all ϵ_e , the region of maximal d_{333} has the shape of a wide curved stripe located relatively far from the boundary between the o- and m-phases. As should be expected, $d_{333} = 0$ in the m-phase. Calculated values of d_{333} are negative in the FE o-phase and reach $-(2-3)$ pm/V, which is in good agreement with the experimental results and *ab initio* calculations for thin HfO₂ layers [48]. As can be seen from Figs. 3(g)–3(i), the magnitude of d_{333} can be tuned by size variation and chemical strains from nearly zero to -3.2 pm/V.

Note that all d_{3ij} appeared negative in the FE o-phase of HfO₂ [48], meaning that the HfO₂ core-shell nanoparticles belong to so-called “auxetic piezoelectrics” [63,64]. Auxetic piezoelectrics were introduced in Ref. [63] by analogy with auxetic materials with a negative Poisson’s ratio, which expand in all directions when stretched in one direction. In “conventional” piezoelectrics, the piezoelectric coefficients d_{322} and d_{311} are opposite in sign to d_{333} ,

and, as a rule, $d_{322} + d_{311} \approx -d_{333}$. Therefore, their volumetric piezoelectric effect, defined by the sum of piezoelectric coefficients, $d_{VP} = d_{333} + d_{322} + d_{311}$, is an order of magnitude smaller than the separate values of piezoelectric coefficients (as a rule, d_{VP} is less than 5–10 pm/V) [63]. Unlike conventional piezoelectrics, auxetic piezoelectrics with all positive (or all negative) d_{3ij} could have increased volumetric piezo-response, which is especially significant for highly sensitive piezoelectric applications. As can be seen from Figs. 3(j)–3(l), the magnitude of d_{VP} reaches 10–12 pm/V in the region of maximal ϵ_{33} . The increase in d_{VP} occurs due to the joint action of trilinear coupling between the polar, antipolar, and nonpolar modes, size effects, and chemical strains.

Thus, we predict that defect engineering can induce and control the polar, dielectric, and piezoelectric properties of HfO₂ core-shell nanoparticles. However, improving the dielectric and/or volumetric piezoelectric response of the HfO₂ nanomaterials remains a significant challenge for advanced electronic applications.

This result seems rather significant for applications, because densely packed core-shell HfO₂ nanoparticles, with preferentially oriented polar axes (or perfectly aligned in the ideal case), may overcome one of the principal limitations of ferroelectric HfO₂ films (i.e., their thickness, typically limited to less than 20–30 nm [17–19]). The high degree of orientation of the crystallographic axes can be achieved in dense composites (or ceramics) prepared by tape casting (or cold pressing) in a large orienting electric field, as well as by reactive templated grain growth [32]. The composite layer consisting of densely packed core-shell HfO₂ nanoparticles with minimal misorientation of the polar axes, or dense ceramics consisting of polarized nanosized HfO₂ grains, would maintain piezoelectric properties for much larger layer thicknesses (up to hundreds of microns) compared with thin epitaxial HfO₂ films (less than 30 nm). Increasing the piezoelectric layer

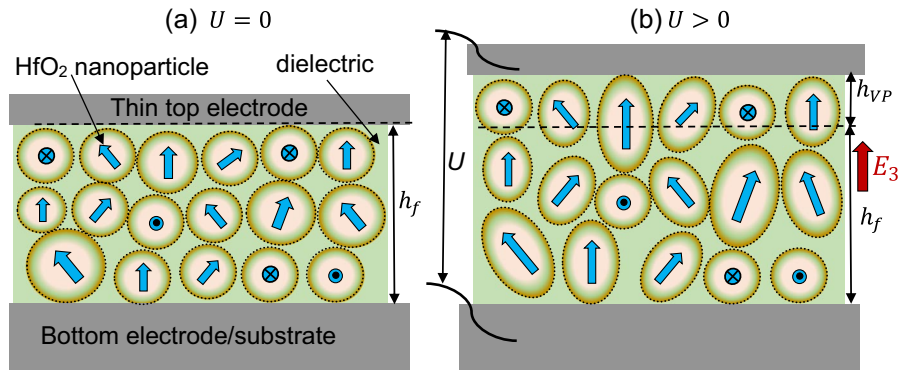


FIG. 4. Schematic illustration of a piezoelectric capacitor of thickness h_f consisting of densely packed polarized HfO₂ nanoparticles, without an applied voltage (a) and with an applied voltage, U (b). The blue arrows show the direction of the spontaneous polarization (aligned with the crystallographic direction of the polar axis) in the nanoparticle cores; the red arrow shows the direction of the electric field, $E_3 \cong \frac{U}{h_f}$.

thickness is required to minimize the risk of electric breakdown in high-performance piezoelectric actuators, pyroelectric sensors, and electrocaloric devices. The schematic illustration of a piezoelectric capacitor of thickness h_f , consisting of densely packed polarized HfO_2 nanoparticles placed in a high- k dielectric or paraelectric matrix (e.g., $\text{PV}(\text{DF-TrFE})$, rutile TiO_2 , or SrTiO_3), is shown in Fig. 4(a). The piezoelectric displacement of the capacitor surface is $h_{\text{VP}} \cong d_{\text{VP}}U$, where U is the applied voltage [see Fig. 4(b)]. Because the composite layer can be much thicker, substantially higher voltages can be applied while maintaining a similar electric field, allowing much larger h_{VP} to be achieved than in thin HfO_2 films.

V. CONCLUSIONS

We have investigated the influence of chemical stresses on phase diagrams and polar properties of spherical HfO_2 core-shell nanoparticles using the Landau-Ginzburg-Devonshire free energy functional with higher powers, and trilinear and biquadratic couplings of polar, antipolar, and nonpolar order parameters. We have shown that the reentrant stabilization of the FE o-phase arises from the competition between the size-dependent depolarization field energy, which suppresses ferroelectric order at small radii, and the stress-induced lowering of the orthorhombic free energy caused by defect-induced chemical strains in the shell.

We predict that the FE o-phase can be stable at compressive chemical strains exceeding 1%–5% in the shell. The minimal concentration of elastic defects, which create chemical strains, is determined by the ambient dielectric permittivity ϵ_e and Vegard stress tensor. For ambient dielectric permittivities $\epsilon_e \leq \epsilon_{\text{max}}$, the FE o-phase exhibits reentrant behavior with respect to the size of nanoparticles, such that the spontaneous polarization exists only in a finite interval of core radii $R_{\text{cr}}^{\text{min}} < R_c < R_{\text{cr}}^{\text{max}}$. The lower critical radius $R_{\text{cr}}^{\text{min}}$ is governed by depolarization and correlation effects, whereas the upper critical radius $R_{\text{cr}}^{\text{max}}$ is governed by size-dependent chemical stresses in the shell. For $\epsilon_e \geq \epsilon_{\text{max}}$, the FE o-phase is thermodynamically stable at $R_c < R_{\text{cr}}^{\text{max}}$ and $R_{\text{cr}}^{\text{min}}$ is limited by the correlation thickness being equal to several lattice constants. Increasing the ambient dielectric permittivity decreases the energy of depolarization field and expands the ferroelectric stability window. Embedding HfO_2 nanoparticles in high-permittivity environments therefore provides an additional thermodynamic pathway for stabilizing ferroelectricity. The maximal value $\epsilon_{\text{max}} \cong 300$ was calculated at room temperature, which corresponds to the SrTiO_3 environment of HfO_2 cores.

We predicted that the spontaneous polarization could reach relatively large values ($70 \mu\text{C}/\text{cm}^2$) for small core radii ($R_c < 10 \text{ nm}$) and realistic concentrations of elastic defects ($n > 10^{27} \text{ m}^{-3}$), which induce compressive

chemical stress in the shell. The increase in spontaneous polarization of the HfO_2 core is more than 3 times compared with the values observed experimentally in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films. The predicted switching barriers within the ferroelectric stability window of the HfO_2 core-shell nanoparticles are of the same order of magnitude as experimentally reported coercive fields in HfO_2 thin films, indicating that the stabilized FE o-phase remains switchable under accessible electric fields. Thus, defect engineering opens a remarkable possibility of significant enhancement of polar properties of HfO_2 core-shell nanoparticles for their applications in advanced memory cells and logic devices.

We also predict that defect engineering can induce and/or control the polar, dielectric, and piezoelectric properties of HfO_2 core-shell nanoparticles. This prediction can be useful for elaboration of dense ceramics and composites consisting of ferroelectric HfO_2 core-shell nanoparticles. The potential advantage of such nanomaterials lies in their silicon compatibility and their ability to exhibit a relatively large auxetic-type volumetric piezoelectric response (above $10 \text{ pm}/\text{V}$) over a wide range of external parameters, including particle size and defect concentration, without requiring operation close to the ferroelectric-paraelectric phase boundary. This is especially significant for highly sensitive piezoelectric sensors, actuators, and surface acoustic wave filters.

While nominally strain-free $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films can exhibit ferroelectricity [18,19], the experimentally reported polarization values are significantly smaller than those predicted in the present work for HfO_2 core-shell nanoparticles (more than $50\text{--}70 \mu\text{C}/\text{cm}^2$), where chemical stress stabilizes the FE o-phase. This contrast suggests that, although ferroelectricity in core-shell HfO_2 nanoparticles is not an intrinsic bulk property, it can emerge over a finite range of particle sizes through the control of stress and screening, resulting in a comparatively large polarization. This result seems significant for applications, because densely packed core-shell HfO_2 nanoparticles with preferentially aligned crystallographic axes, for example, in dense composites (or ceramics) prepared by tape casting (or cold pressing) in a large orienting electric field or by using the reactive templated grain growth [32], may overcome one of the principal limitations of ferroelectric HfO_2 films, namely their limited thickness (typically less than $20\text{--}30 \text{ nm}$ [17–19]). Dense composite films containing polarized core-shell HfO_2 nanoparticles or dense ceramics with polarized nanosized grains would maintain ferroelectric properties at much larger thicknesses (up to hundreds of microns), which is required for high-performance piezoelectric actuators, pyroelectric sensors, and electrocaloric devices while minimizing the risk of electric breakdown.

Analytical expressions derived for the critical radii can be generalized for $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles, providing that corresponding parameters of the free energy are

known from the first-principles calculations. Thus, this work identifies a stress-driven mechanism for reentrant ferroelectric phase stabilization in nanoscale HfO_2 , arising from the competition between the depolarization field suppression and shell-induced chemical stress.

Also, the obtained results may help answer the question of why the stable FE o-phase has been observed in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films but has not yet been observed in HfO_2 nanoparticles. We predicted that relatively large compressive chemical strains are necessary to induce the FE o-phase in the HfO_2 nanoparticles. However, the creation of such stress requires controllable treatment of the nanoparticles in a special environment and/or other special conditions of their synthesis. Assuming that the technological issues can be overcome, for example, by annealing HfO_2 nanoparticles in a $\text{CO} + \text{CO}_2$ atmosphere [26,27,56], the appearance of ferroelectric hysteresis and/or a domain structure in the small (≤ 10 nm) core-shell HfO_2 nanoparticles can be verified directly by switching spectroscopy piezoelectric force microscopy (SS-PFM) with dual-frequency resonance tracking (DART) [65]. For this purpose, HfO_2 nanoparticles should be deposited as a layer onto a conducting substrate (e.g., pyrolytic graphite). The presence of local piezoelectric response hysteresis loops and/or the direct visualization of domain structures has been demonstrated by SS-PFM and DART-PFM in nanoislands and nanoparticles of other ferroelectric materials [65]. Other experimental signatures of ferroelectricity in HfO_2 nanoparticles include pronounced pyroelectric and/or electrocaloric properties of prepoled nanopowders or nanograined ceramics prepared by cold pressing the nanoparticles.

ACKNOWLEDGMENTS

The work of A.N.M. is funded by the National Research Foundation of Ukraine (project “Manyfold-degenerated metastable states of spontaneous polarization in nanoferroelectrics: theory, experiment, and perspectives for digital nanoelectronics,” Grant No. 2023.03/0132). The work of E.A.E. is funded by the National Research Foundation of Ukraine (project “Silicon-compatible ferroelectric nanocomposites for electronics and sensors,” Grant No. 2023.03/0127). The work of S.V.K. is supported by S.V.K. start-up funds. A.N.M. also acknowledges (discussion of the results presented in the work) the Horizon Europe Framework Programme (HORIZON-TMA-MSCA-SE), Project No. 101131229, Piezoelectricity in 2D-materials: materials, modeling, and applications (PIEZO-2D) and the EOARD project 9IOE063 (related STCU partner project is P751c).

A.N.M. generated the idea of research, formulated the physical problem, performed analytical calculations of the critical size, analyzed results and wrote the manuscript draft. E.A.E. performed symmetry analysis, numerical

calculations and prepared corresponding figures. S.V.K. and D.R.E. worked on improvement of the manuscript. All coauthors discussed the results.

DATA AVAILABILITY

The data that support the findings of this article are openly available [53].

-
- [1] J. P. B. Silva, R. Alcala, U. E. Avci, N. Barrett, L. Bégon-Lours, M. Borg, S. Byun, S.-C. Chang, S.-W. Cheong, D.-H. Choe *et al.*, Roadmap on ferroelectric hafnia and zirconia-based materials and devices, *APL Mater.* **11**, 089201 (2023).
 - [2] K.-H. Kim, I. Karpov, R. H. Olsson III, and D. Jariwala, Wurtzite and fluorite ferroelectric materials for electronic memory, *Nat. Nanotechnol.* **18**, 422 (2023).
 - [3] X. Tao, L. Liu, L. Yang, and J.-P. Xu, Impacts of HfZrO_2 thickness and anneal temperature on performance of MoS_2 negative-capacitance field-effect transistors, *Nanotechnology* **32**, 445201 (2021).
 - [4] A. Paul, G. Kumar, A. Das, G. Larrieu, and S. De, Hafnium oxide-based ferroelectric field effect transistors: From materials and reliability to applications in storage-class memory and in-memory computing, *J. Appl. Phys.* **138**, 010701 (2025).
 - [5] N. Afroze, H. Fahravandi, G. Ren, P. Kumar, C. Nelson, S. Lombardo, M. Tian, P.-C. Lee, J. Chen, M. Noor *et al.*, Atomic-scale confinement of strongly charged 180° domain wall pairs in ZrO_2 , *arXiv:2507.18920*.
 - [6] B. Mukherjee, X. Diaz de Cerio, I. Robredo-Magro, N. S. Fedorova, and J. Íñiguez-González, The polarization of hafnia ferroelectrics is not a bulk property, *Phys. Rev. B* **114**, L080101 (2026).
 - [7] M. H. Park, Y. H. Lee, H. J. Kim, T. Schenk, W. Lee, K. D. Kim, F. P. G. Fengler, T. Mikolajick, U. Schroeder, and C. S. Hwang, Surface and grain boundary energy as the key enabler of ferroelectricity in nanoscale hafnia–zirconia: A comparison of model and experiment, *Nanoscale* **9**, 9973 (2017).
 - [8] K. Ooe, Y. Shen, K. Shitara, R. Maki, S. Kobayashi, Y. Shimakawa, D. Kan, and J. Etheridge, Direct observation of cation-dependent polarisation switching dynamics in fluorite ferroelectrics, *Nat. Commun.* **17**, 2660 (2026).
 - [9] Y. Qi and K. M. Rabe, Competing phases of HfO_2 from multiple unstable flat phonon bands of an unconventional high-symmetry structure, *Phys. Rev. Lett.* **135**, 046101 (2025).
 - [10] Y. Qi, S. Singh, and K. M. Rabe, Polarization switching in ferroelectric HfO_2 from first-principles lattice mode analysis, *Phys. Rev. B* **111**, 134106 (2025).
 - [11] K. Fujimoto, Y. Sato, Y. Fuchikami, R. Teranishi, and K. Kaneko, Orthorhombic-like atomic arrangement in hafnium-oxide-based nanoparticles, *J. Am. Ceram. Soc.* **105**, 2823 (2022).
 - [12] S. Estandia, N. Dix, J. Gazquez, I. Fina, J. Lyu, M. F. Chisholm, J. Fontcuberta, and F. Sánchez, Engineering

- ferroelectric $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ thin films by epitaxial stress, *ACS Appl. Electron. Mater.* **1**, 1449 (2019).
- [13] S. Estandia, N. Dix, M. F. Chisholm, I. Fina, and F. Sánchez, Domain-matching epitaxy of ferroelectric $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2(111)$ on $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3(001)$, *Cryst. Growth Des.* **20**, 3801 (2020).
- [14] Y. Tamura, K. Masuda, and Y. Kumagai, On-demand phase-field modeling: Three-dimensional Landau energy for HfO_2 through machine learning, *arXiv:2512.16207*.
- [15] F. Delodovici, P. Barone, and S. Picozzi, Trilinear-coupling-driven ferroelectricity in HfO_2 , *Phys. Rev. Mater.* **5**, 064405 (2021).
- [16] S. Zhou, J. Zhang, and A. M. Rappe, Strain-induced antipolar phase in hafnia stabilizes robust thin-film ferroelectricity, *Sci. Adv.* **8**, 47 (2022).
- [17] A. N. Morozovska, E. A. Eliseev, S. V. Kalinin, and M. V. Strikha, Critical sample sizes for appearance and disappearance of ferroelectricity in nanosized hafnia-zirconia: Landau-type theory, *Phys. Rev. B* **113**, 174102 (2026).
- [18] S. Kang, W.-S. Jang, A. N. Morozovska, O. Kwon, Y. Jin, Y.-H. Kim, H. Bae, C. Wang, S.-H. Yang, A. Belianinov, S. Randolph, E. A. Eliseev, L. Collins, Y. Park, S. Jo, M.-H. Jung, K.-J. Go, H. W. Cho, S.-Y. Choi, J. H. Jang, S. Kim, H. Y. Jeong, J. Lee, O. S. Ovchinnikova, J. Heo, S. V. Kalinin, Y.-M. Kim, and Y. Kim, Highly enhanced ferroelectricity in HfO_2 -based ferroelectric thin film by light ion bombardment, *Science* **376**, 731 (2022).
- [19] K. P. Kelley, A. N. Morozovska, E. A. Eliseev, Y. Liu, S. S. Fields, S. T. Jaszewski, T. Mimura, S. Calderon, E. C. Dickey, J. F. Ihlefeld, and S. V. Kalinin, Ferroelectricity in hafnia controlled via surface electrochemical state, *Nat. Mater.* **22**, 1144 (2023).
- [20] M. D. Glinchuk, A. N. Morozovska, A. Lukowiak, W. Stręk, M. V. Silibin, D. V. Karpinsky, Y. Kim, and S. V. Kalinin, Possible electrochemical origin of ferroelectricity in HfO_2 thin films, *J. Alloys Compd.* **830**, 153628 (2020).
- [21] L.-Y. Ma and S. Liu, Structural polymorphism kinetics promoted by charged oxygen vacancies in HfO_2 , *Phys. Rev. Lett.* **130**, 096801 (2023).
- [22] T. K. Paul, A. K. Saha, and S. K. Gupta, Oxygen vacancy-induced monoclinic dead layers in ferroelectric HfO_2 with metal electrodes, *J. Appl. Phys.* **137**, 144102 (2025).
- [23] G. Zhang, H. Wu, X. Xu, S. Lin, Z. Zhang, Z. Yan, X. Lu, G. Yuan, and J.-M. Liu, Enhanced reliability of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ ferroelectric memory through WO_x buffer layer to minimize oxygen vacancies, *Appl. Phys. Lett.* **127**, 112102 (2025).
- [24] E. A. Eliseev, S. V. Kalinin, and A. N. Morozovska, Ferro-ionic states and domains morphology in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles, *J. Appl. Phys.* **137**, 034103 (2025).
- [25] E. A. Eliseev, Y. O. Zagorodniy, V. N. Pavlikov, O. V. Leshchenko, H. V. Shevliakova, M. V. Karpec, A. D. Yaremkevych, O. M. Fesenko, S. V. Kalinin, and A. N. Morozovska, Phase diagrams and polarization reversal in nanosized $\text{Hf}_x\text{Zr}_{1-x}\text{O}_{2-y}$, *AIP Adv.* **14**, 055224 (2024).
- [26] E. A. Eliseev, I. V. Kondakova, Y. O. Zagorodniy, H. V. Shevliakova, O. V. Leshchenko, V. N. Pavlikov, M. V. Karpets, L. P. Yurchenko, and A. N. Morozovska, The origin of the ferroelectric-like orthorhombic phase in oxygen-deficient HfO_{2-y} nanoparticles, *Semicond. Phys. Optoelectron. Quantum Electron.* **28**, 134 (2025).
- [27] O. S. Pylypchuk, V. V. Vainberg, V. N. Poroshin, O. V. Leshchenko, V. N. Pavlikov, I. V. Kondakova, S. E. Ivanchenko, L. P. Yurchenko, L. Demchenko, A. O. Diachenko, M. V. Karpets, E. A. Eliseev, and A. N. Morozovska, A colossal dielectric response of $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles, *Phys. Rev. Mater.* **9**, 114412 (2025).
- [28] O. S. Pylypchuk, I. V. Fesych, V. V. Vainberg, Y. O. Zagorodniy, V. I. Styopkin, J. M. Gudenko, I. V. Kondakova, L. P. Yurchenko, V. N. Pavlikov, A. O. Diachenko, M. M. Koptiev, M. D. Volnyanskii, V. V. Laguta, E. A. Eliseev, M. P. Trubitsyn, and A. N. Morozovska, Resistive switching and charge accumulation in $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ nanoparticles, *J. Phys. Chem.* **129**, 14299 (2025).
- [29] A. N. Morozovska, O. S. Pylypchuk, N. V. Morozovsky, E. A. Eliseev, and D. R. Evans, Pyroelectric, electrocaloric and thermoelectric properties of core-shell $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ nanoparticles: Theory and experiment, *arXiv:2606.22654*.
- [30] S. Bourgeois, B. Domenichini, and J. Jupille, Excess electrons at oxide surfaces, in *Defects at Oxide Surfaces*, Springer Series in Surface Sciences, edited by J. Jupille and G. Thornton (Springer, Cham, 2015), Vol. 58.
- [31] E. A. Eliseev, A. N. Morozovska, S. V. Kalinin, and D. R. Evans, Strain-induced polarization enhancement in BaTiO_3 core-shell nanoparticles, *Phys. Rev. B* **109**, 014104 (2024).
- [32] S. Zhukov, Y. A. Genenko, J. Koruza, J. Schultheiß, H. von Seggern, W. Sakamoto, H. Ichikawa, T. Murata, K. Hayashi, and T. Yogo, Effect of texturing on polarization switching dynamics in ferroelectric ceramics, *Appl. Phys. Lett.* **108**, 012907 (2016).
- [33] Y. A. Genenko, O. Hirsch, and P. Erhart, Surface potential at a ferroelectric grain due to asymmetric screening of depolarization fields, *J. Appl. Phys.* **115**, 104102 (2014).
- [34] I. S. Vorotiahin, E. A. Eliseev, Q. Li, S. V. Kalinin, Y. A. Genenko, and A. N. Morozovska, Tuning the polar states of ferroelectric films via surface charges and flexoelectricity, *Acta Mater.* **137**, 85 (2017).
- [35] J.-J. Wang, B. Wang, and L.-Q. Chen, Understanding, predicting, and designing ferroelectric domain structures and switching guided by the phase-field method, *Ann. Rev. Mater. Res.* **49**, 127 (2019).
- [36] D. A. Freedman, D. Roundy, and T. A. Arias, Elastic effects of vacancies in strontium titanate: Short- and long-range strain fields, elastic dipole tensors, and chemical strain, *Phys. Rev. B* **80**, 064108 (2009).
- [37] Y. Kim, A. S. Disa, T. E. Babakol, and J. D. Brock, Strain screening by mobile oxygen vacancies in SrTiO_3 , *Appl. Phys. Lett.* **96**, 251901 (2010).
- [38] M. J. Highland, T. T. Fister, D. D. Fong, P. H. Fuoss, C. Thompson, J. A. Eastman, S. K. Streiffer, and G. B. Stephenson, Equilibrium polarization of ultrathin PbTiO_3 with surface compensation controlled by oxygen partial pressure, *Phys. Rev. Lett.* **107**, 187602 (2011).
- [39] G. B. Stephenson and M. J. Highland, Equilibrium and stability of polarization in ultrathin ferroelectric films with ionic surface compensation, *Phys. Rev. B* **84**, 064107 (2011).

- [40] S. M. Yang, A. N. Morozovska, R. Kumar, E. A. Eliseev, Y. Cao, L. Mazet, N. Balke, S. Jesse, R. K. Vasudevan, C. Dubourdieu, and S. V. Kalinin, Mixed electrochemical-ferroelectric states in nanoscale ferroelectrics, *Nat. Phys.* **13**, 812 (2017).
- [41] V. A. Shchukin and D. Bimberg, Spontaneous ordering of nanostructures on crystal surfaces, *Rev. Mod. Phys.* **71**, 1125 (1999).
- [42] W. Ma, Surface tension and Curie temperature in ferroelectric nanowires and nanodots, *Appl. Phys. A* **96**, 915 (2009).
- [43] W. Ma, Surface tension and Curie temperature in ferroelectric nanowires and nanodots (Erratum), *Appl. Phys. A* **96**, 1035 (2009).
- [44] A. N. Morozovska, E. A. Eliseev, Y. M. Fomichov, Y. M. Vysochanskii, V. Y. Reshetnyak, and D. R. Evans, Controlling the domain structure of ferroelectric nanoparticles using tunable shells, *Acta Mater.* **183**, 36 (2020).
- [45] F. Delodovici, P. Barone, and S. Picozzi, Finite-size effects on ferroelectricity in rhombohedral HfO_2 , *Phys. Rev. B* **106**, 115438 (2022).
- [46] S. Jung and T. Birol, Triggered ferroelectricity in HfO_2 from hybrid phonons and higher-order dynamical charges, *Adv. Mater.* **38**, e21602 (2026).
- [47] S. Jung and T. Birol, Electric polarization from nonpolar phonons, [arXiv:2512.00628](https://arxiv.org/abs/2512.00628).
- [48] S. Dutta, P. Buragohain, S. Glinsek, C. Richter, H. Aramberri, H. Lu, U. Schroeder, E. Defay, A. Gruverman, and J. Íñiguez, Piezoelectricity in hafnia, *Nat. Commun.* **12**, 7301 (2021).
- [49] X. Zhao and D. Vanderbilt, First-principles study of electronic and dielectric properties of ZrO_2 and HfO_2 , *MRS Proc.* **747** (2002).
- [50] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/yktz-flhv> for material parameters and calculation details.
- [51] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon Press, London, 1970).
- [52] E. A. Eliseev, I. S. Vorotiahin, Y. M. Fomichov, M. D. Glinchuk, S. V. Kalinin, Y. A. Genenko, and A. N. Morozovska, Defect driven flexo-chemical coupling in thin ferroelectric films, *Phys. Rev. B* **97**, 024102 (2018).
- [53] Mathematica Wolfram Research official website is <https://www.wolfram.com/mathematica>; the codes are freely available at <https://notebookarchive.org/2026-01-60qfsh4>.
- [54] O. S. Pylypchuk, S. E. Ivanchenko, Y. O. Zagorodniy, M. E. Yeliseiev, O. V. Shyrokov, O. V. Leschenko, O. Bereznykov, D. Stetsenko, S. D. Skapin, E. A. Eliseev, V. N. Poroshin, V. V. Vainberg, and A. N. Morozovska, Relaxor-like behavior of the dielectric response of dense ferroelectric composites, *Ceram. Int.* **50**, 45465 (2024).
- [55] O. V. Bereznykov, O. S. Pylypchuk, V. I. Styopkin, S. E. Ivanchenko, D. O. Stetsenko, E. A. Eliseev, Z. Kutnjak, V. N. Poroshin, A. N. Morozovska, and N. V. Morozovsky, Interfacial effects and negative capacitance state in P(VDF-TrFE) films with BaTiO_3 nanoparticles, *Compos. Interfaces* **33**, 621 (2026).
- [56] Y. O. Zagorodniy, E. A. Eliseev, V. V. Laguta, P. Jiricek, J. Houdkova, L. D. Demchenko, O. V. Leshchenko, V. N. Pavlikov, L. P. Yurchenko, A. O. Diachenko, M. D. Volnyanskii, O. S. Pylypchuk, M. V. Karpets, M. P. Trubitsyn, D. R. Evans, and A. N. Morozovska, Stabilization of the orthorhombic phases in $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ nanoparticles by oxygen vacancies, [arXiv:2603.14642](https://arxiv.org/abs/2603.14642).
- [57] C.-G. Duan, S. S. Jaswal, and E. Y. Tsymlal, Predicted magnetoelectric effect in Fe/BaTiO_3 multilayers: Ferroelectric control of magnetism, *Phys. Rev. Lett.* **97**, 047201 (2006).
- [58] D. D. Fong, G. B. Stephenson, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, and C. Thompson, Ferroelectricity in ultrathin perovskite films, *Science* **304**, 1650 (2004).
- [59] D. Yadlovker and S. Berger, Uniform orientation and size of ferroelectric domains, *Phys. Rev. B* **71**, 184112 (2005).
- [60] E. Erdem, H.-Ch Semmelhack, R. Bottcher, H. Rumpf, J. Banys, A. Matthes, H.-J. Glasel, D. Hirsch, and E. Hartmann, Study of the tetragonal-to-cubic phase transition in PbTiO_3 nanopowders, *J. Phys.* **18**, 3861 (2006).
- [61] A. N. Morozovska and E. A. Eliseev, Surface and finite size effect on fluctuations dynamics in nanoparticles with long-range order, *J. Appl. Phys.* **107**, 044101 (2010).
- [62] H. S. Park, J. C. Shin, K. D. Kim, S. J. Shin, J. H. Song, S. K. Ryoo, I. S. Lee, S. H. Lee, H. Nam, and C. S. Hwang, Enhancing ferroelectric properties of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ thin films using the HfN/TiN and W/TiN bi-layer bottom electrodes, *J. Mater.* **11**, 101109 (2025).
- [63] M.-M. Yang, T.-Y. Zhu, A. B. Renz, H.-M. Sun, S. Liu, P. M. Gammon, and M. Alexe, Auxetic piezoelectric effect in heterostructures, *Nat. Mater.* **23**, 95 (2024).
- [64] E. A. Eliseev and A. N. Morozovska, Breaking symmetry creates polar auxeticity, *Nat. Mater.* **23**, 37 (2024).
- [65] A. Gruverman, M. Alexe, and D. Meier, Piezoresponse force microscopy and nanoferroic phenomena, *Nat. Commun.* **10**, 1661 (2019).