

Critical sample sizes for appearance and disappearance of ferroelectricity in nanosized hafnia-zirconia: Landau-type theory

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Nanosized hafnia-zirconia $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ in the form of thin films, multilayers, and heterostructures are indispensable silicon-compatible ferroelectric materials for advanced electronic memories and logic devices. The distinctive feature of nanoscale hafnia-zirconia are the critical sizes of ferroelectricity appearance, whereas the critical sizes of ferroelectricity disappearance exist in other ferroelectrics. Using the Landau-Ginzburg-Devonshire free energy functional with higher powers, trilinear and biquadratic couplings of polar, nonpolar, and antipolar order parameters, we calculated analytically the strain-dependent critical sizes of the ferroelectricity appearance and disappearance, analyzed how the size effect and mismatch strains influence the phase diagrams and polarization switching barrier in epitaxial HfO_2 thin films and nano-islands with the out-of-plane spontaneous polarization. We have shown that the critical thickness/height of out-of-plane spontaneous polarization disappearance is determined by the size dependence of the depolarization field and correlation effects. The critical thickness/height of the ferroelectricity appearance is determined by the size dependence of the effective mismatch strain considering possible appearance of misfit dislocations and lateral relaxation of strains. Derived analytical expressions can be generalized for $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ solid solutions, providing that corresponding parameters of the free energy are known from the first-principles calculations.

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I. INTRODUCTION

Nanosized hafnia-zirconia $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ ($x \geq 0.5$), further abbreviated as HZO, in the form of thin films, multilayers, and heterostructures are indispensable silicon-compatible ferroelectric materials for advanced electronic memories [1,2] and logic devices [3–5]. It was demonstrated that 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 happen in the nanoscale HZO with decrease in sizes below 30 nm [2–5]. For instance, HZO thin films reveal ferroelectric properties only when their thickness is less than the critical one, that does not exceed 30 nm, because the FE *o* phase becomes metastable for larger thicknesses [6]. This experimental fact is opposite to the common trend for

vast majority of ferroelectric films and particles, which have ferroelectric properties only when the film thickness or particle sizes are above the critical value, changing from several nanometers to sub- μm in dependence on the elastic strains and electric screening conditions at their surface. Thus, the distinctive feature of nanoscale hafnia-zirconia are the critical sizes of ferroelectricity appearance, whereas the critical sizes of ferroelectricity disappearance exist in other ferroelectrics. The critical size of ferroelectricity disappearance also exists in nanosized HZO at lower scales, because ferroelectricity is a collective phenomenon, which cannot exist in the volume smaller than the correlation volume.

At the same time, the physical mechanisms responsible for the emergence of ferroelectric and/or antiferroelectric properties in nanosized HZO are still unclear [7,8]. According to the first-principles theories, they are probably related with the dominant role of surface and size effects [6,9], trilinear coupling between the soft polar and hard nonpolar modes enhanced by mismatch strains [10], hybridized [11], and/or nonpolar [12] phonon modes. Indeed, it was shown that the negative biquadratic coupling between polar and nonpolar modes [13] enhanced by large tensile strains the in-plane directions may induce the nonpolar mode instability in HfO_2 [14].

There are no comprehensive and widely accepted Landau-like models of either HfO_2 or ZrO_2 , even the symmetry of

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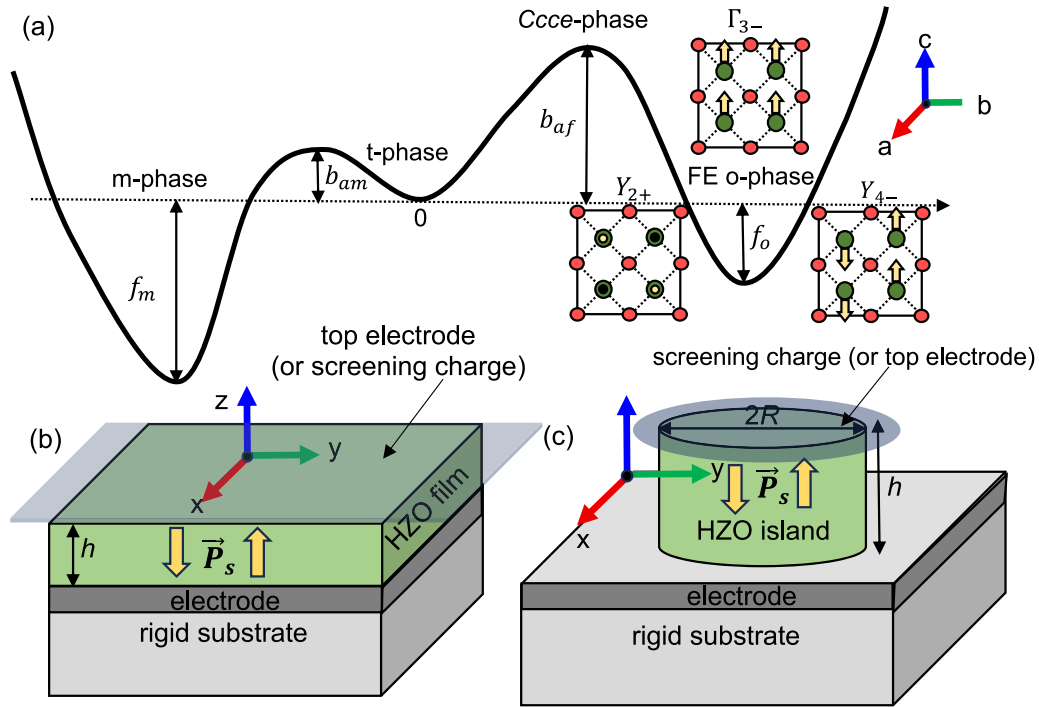


FIG. 1. (a) Free energy density relief with the minima corresponding to the m, t, and FE o phases. Small insets show atomic displacements in the polar Γ_{3-} , nonpolar Y_{2+} and antipolar Y_{4-} modes, which exist in the FE o phase of HfO_2 . The barrier heights b_{am} and b_{af} determine activation energies of possible t-m and t-o transitions. Geometry of (b) epitaxial thin films and (c) nanoislands of HZO subjected to epitaxial mismatch strain u_m . Two directions of the out-of-plane spontaneous polarization $\vec{P}_s$ in the FE o phase of HZO are shown by the thick arrow. Z axis coincides with the polar c axis. The direction of a axis is determined by the condensation of coupled Y_{2+} and Y_{4-} modes [10].

their paraelectric and/or intermediate phases is still under debate. Despite the presence of the high-temperature cubic (space group $Fm\bar{3}m$) phase of HZO, the symmetrical considerations do not allow one to suppose that the polarization vector could cause the transition between the $Fm\bar{3}m$ and $Pca2_1$ phases. Instead, the series of phase transitions should take place, and at least three order parameters (polar, antipolar, and nonpolar) should be considered to achieve the correct description of the ferroelectric order in HfO_2 , as it was shown by Jung and Birol [11] from the density functional theory (DFT) and Landau-type approach. Next, Jung and Birol [12] introduced the second-order dynamical charge along with phonon mode effective charge and applied these concepts to the HfO_2 and SrTiO_3 materials to show that the contribution of second-order dynamic charges to the HfO_2 polarization is rather large in contrast to perovskite ferroelectrics. They also obtained that the local polarization arising from the second-order effective charges is aligned opposite to the first-order polarization.

Using the DFT, Delodovici *et al.* [10] considered the transition from the high-symmetry nonpolar tetragonal phase $P4_2/nmc$ (t phase) to the polar o phase ($Pca2_1$) in HfO_2 . They noted that two Brillouin zone centered modes Γ_{1+} (volume expansion) and Γ_{4+} (shear strain) transform the $P4_2/nmc$ phase to the nonpolar orthorhombic structure (space group $Ccce$). Considering the $Ccce$ phase as the parent phase, they have shown that the combined action of three coupled modes (polar Γ_{3-} , nonpolar Y_{2+} , and antipolar Y_{4-}) are needed to achieve the energy minimum for the $Pca2_1$ structure experimentally observed in HfO_2 films [see the black curve in Fig. 1(a)].

Also, Delodovici *et al.* [9,10] studied the influence of biaxial elastic strains on ferroelectric properties of HfO_2 and its thin films. They obtained that compressive biaxial strains could induce ferroelectric polarization in rhombohedral r phase of HfO_2 , suggesting the absence of any critical thickness for the in-plane direction of the polarization [9]. At the same time, the stretching along the a axis with simultaneous compression along other two axes (under the condition of volume conservation) is required to stabilize the out-of-plane ferroelectric polarization along the polar c axis in HfO_2 films [10].

There exists experimental evidence about the decisive role of mismatch strains in appearance of the FE o phase in epitaxial HZO thin films. For instance, Estandia *et al.* [15] experimentally studied epitaxial HZO ($x = 0.5$) films grown on different (001)-oriented cubic substrates and revealed that the appearance of the FE o phase depends significantly on the mismatch strain. Later on, Estandia *et al.* [16] studied (111)-oriented HZO films with (100)-LSMO electrodes and revealed the pronounced ferroelectric properties of the films, as well as report about an unusual epitaxy mechanism based on the observation of dislocations arrays of with short periodicities. Using the DFT and piezoelectric response force microscopy (PFM), Dutta *et al.* [17] explored the leading role of piezoelectricity in HfO_2 films, which allows us to relate the mismatch-induced effects with the high piezoelectric coupling in HZO. Zhou *et al.* [18] proposed a model based on the three order parameters, namely the tetragonal distortion mode, antipolar, and polar modes, considering cubic fluorite structure as the parent phase. Tamura *et al.* [19] considered the influence

of mismatch strains on the stability of FE o phase in thin HfO₂ films.

It is important to note that competing phases determine an indirect switching path of their spontaneous polarization $\vec{P}_s$ [20,21]. According to direct experimental observations [22], the switching path of polarization in thin HZO films is indirect, because the transition from $+\vec{P}_s$ to $-\vec{P}_s$ goes through the nonpolar t phase. Actually, Ooe *et al.* [22] observed that the pathways of 180- and 90-degree polarization rotation involve different nonpolar intermediate states with distinct spatial scales. For instance, the 180-degree domain walls between polar domains could be separated by either the t-phase $P4_2/nmc$ or by the nonpolar o-phase $Pbcm$, depending on the wall orientation. The barrier height between different phases determines the activation energies of possible transitions, and so the most probable transition path [see, e.g., Fig. 1(a)].

The situation with ferroelectricity existence and polarization switching is much more complicated in small HZO nanoparticles. Due to the small sizes in all three directions, it is hardly possible to separate the t phase (space group $P4_2/nmc$) and o phases (space groups $Pbca$, $Pbcm$, and ferroelectric $Pca2_1$) using x-ray diffraction analysis, because corresponding peaks are very close, diffused, and merge together [23]. Several experimental [24,25] and theoretical [26,27] works revealed a leading role of oxygen vacancies [28,29] in the appearance and stabilization of the FE o phase in nanoscale HZO. Recently, it was shown that the oxygen-deficient Hf_xZr_{1-x}O_{2-y} nanoparticles could exhibit ferroelectriclike properties, such as a colossal dielectric response in a wide frequency range [30], as well as demonstrate resistive switching and pronounced charge accumulation [31].

Analysis of the spatial-temporal evolution of polarization in HZO thin films was performed in the framework of effective Landau-Ginzburg-Devonshire (LGD) thermodynamic approach [32,33]. This approach incorporates the elements of the Kittel-type model [34] with polar and antipolar modes [35,36] to the Landau-type free energy with effective parameters extracted either from the experiment [37] or from the DFT calculations. The influence of elastic strain and electrostriction coupling can be considered approximately by the renormalization of LGD coefficients [38]. Effective LGD approach [39], accomplished by Stephenson and Highland (SH) [40,41] approach and corroborated by the DFT calculations [42], predicted that ferro-ionic states can be stable in spherical HZO nanoparticles of sizes 5–30 nm, being in agreement with recent experimental observations [30,31].

In this work we propose the Landau-type theory for the determination of the ferroelectricity appearance and disappearance critical sizes in epitaxial HZO thin films and nanoislands with the out-of-plane spontaneous polarization. Our approach is based on results of Delodovici *et al.* [10], Jung and Birol [11], who determine the role of trilinear coupling, and Datta *et al.* results [17], which allowed us to extract the piezoelectric and electrostriction coupling coefficients. In result we constructed the LGD free energy functional considering higher powers, biquadratic, and trilinear couplings of three order parameters (polar Γ_{3-} , nonpolar Y_{2+} , and antipolar Y_{4-} modes), size and strain effects. Using the functional, we calculated analytically the strain-dependent critical sizes

of the ferroelectricity appearance and disappearance, analyzed the mismatch strains influence and size effect of the phase diagrams and polarization switching barrier in epitaxial HfO₂ thin films and nanoislands, whose geometry is shown schematically in Figs. 1(b) and 1(c), respectively. Our approach for the determination of critical sizes can be generalized for HZO thin films and nanoparticles, provided that the relevant material parameters determining the LGD free energy coefficients can be found from first-principles calculations.

II. THEORETICAL RESULTS

A. Landau-Ginzburg-Devonshire free energy functional of nanosized hafnia-zirconia

Following Ref [10], we consider the nonpolar t phase as the reference “aristo-phase” of the HZO ($x \geq 0.5$). The free energy of a uniaxial HZO was expanded with respect to the powers of the order parameters, introduced as the dimensionless amplitudes $Q_{\Gamma 3}$, $Q_{Y 2}$, and $Q_{Y 4}$ of the corresponding phonon modes normalized to their equilibrium values.

The full form of the expression for the LGD free energy bulk density f_{bulk} , which is the expansion up to the eighth powers of $Q_{\Gamma 3}$, $Q_{Y 2}$, and $Q_{Y 4}$ considering the t symmetry of aristo-phase is derived in Sec. S1 in the Supplemental Material [43] (see also Refs. [44,45] therein). The compact form of f_{bulk} is the sum of the 2–4–6–8 powers and 1–5–7 powers of the three phonon modes (f_{bl} and f_{tr}), elastic and striction energy contributions (f_{est}), and the gradient energy of the order parameters (f_{grad}):

$$f_{\text{bulk}} = f_{\text{bl}} + f_{\text{tr}} + f_{\text{est}} + f_{\text{grad}}, \quad (1a)$$

$$f_{\text{bl}} = \beta_i Q_i^2 + \delta_{ij} Q_i^2 Q_j^2 + \eta_{ijk} Q_i^2 Q_j^2 Q_k^2 + \xi_{ijkl} Q_i^2 Q_j^2 Q_k^2 Q_l^2, \quad (1b)$$

$$f_{\text{tr}} = (\gamma + \epsilon_i Q_i^2 + \zeta_{ij} Q_i^2 Q_j^2) Q_{\Gamma 3} Q_{Y 2} Q_{Y 4}, \quad (1c)$$

$$f_{\text{est}} = \frac{1}{2} c_{ijkl} u_{ij} u_{kl} - \tilde{q}_{ijkl} u_{ij} Q_k Q_l - (1 + v_i Q_i^2 + k_{ij} Q_i^2 Q_j^2) \tilde{r}_{ijklmn} u_{ij} Q_k Q_l Q_m - \tilde{z}_{ijklmn} u_{ij} Q_k Q_l Q_m Q_n + \tilde{w}_{ijklmn} u_{ij} u_{kl} Q_m Q_n, \quad (1d)$$

$$f_{\text{grad}} = \frac{1}{2} g_{ijkl} \frac{\partial Q_k}{\partial x_i} \frac{\partial Q_l}{\partial x_j}. \quad (1e)$$

Here the subscripts $i, j, k, l, m, n, \dots$, either designate the modes Γ_{3-} , Y_{2+} , and Y_{4-} , or are the Cartesian indexes coupled to the strains u_{ij} , or to the Cartesian coordinates x_i . For instance, Q_i stands for $Q_{\Gamma 3}$, $Q_{Y 2}$, or $Q_{Y 4}$. The summation rule is performed over repeated subscripts. Following Ref. [10], we pay special attention to the strong trilinear coupling of the $Q_{\Gamma 3}$, $Q_{Y 2}$, and $Q_{Y 4}$ modes, which energy f_{tr} is proportional to the product $Q_{\Gamma 3} Q_{Y 2} Q_{Y 4}$, since the coupling can stabilize the FE o phase.

Nonzero components of β_i , γ , δ_{ij} , ϵ_i , η_{ijk} , ζ_{ij} , and ξ_{ijkl} used in calculations for HfO₂ are listed in Tables S1–S2 in Sec. S1 [43]. c_{ijkl} are elastic stiffnesses, u_{ij} are elastic strains, $\tilde{q}_{ijkl}$, $\tilde{z}_{ijklmn}$, and $\tilde{w}_{ijklmn}$ are the components of the second-order and higher-order striction stress tensors; $\tilde{r}_{ijklm}$ are the tensor of trilinear striction; g_{ijkl} are the components of the gradient energy tensor.

Note that Delodovici *et al.* [10] demonstrated that the free energy expansion with the terms up to sixth powers gives satisfactory accuracy with respect to their DFT results (see black open circles in Fig. S1 in Sec. S1 [43]). However, the six-order thermodynamic potential becomes unstable at $|Q_i| > 1$, because some of the six-order power expansion coefficients of the order parameters appeared negative (see blue curves in Fig. S1 [43]). This means that the local free energy minimum, located at $|Q_i| < 1$ in the hypothetical HfO_2 material, can become unstable under the application of external field and/or in result of the free energy coefficient renormalization by epitaxial strains and/or finite-size effects considered in this work. That is why we were subjected to adding next higher power expansion coefficients (up to eighth power) of the order parameters, which appeared positive and stabilize the thermodynamic potential, also providing high accuracy of fitting to the Delodovici *et al.* [10] data (see green curves in Fig. S1 [43]). At the same time, the fourth-order thermodynamic potential, which is stable, provides only a qualitative description of the potential relief calculated by the first principles (see red curves in Fig. S1 [43]).

The ferroelectric polarization components P_i , both spontaneous and induced by external electric field E_i , contribute to the electric energy f_{el} :

$$f_{\text{el}} = -P_i E_i - \frac{1}{2} P_i E_i^d. \quad (2a)$$

Here the subscript $i = 1, 2, 3$ and E_i^d is the depolarization field, which should be determined from electrostatic equations $\text{div} \vec{D} = 0$, where the electric displacement $\vec{D}$ is equal to $\epsilon_0 \epsilon_b \vec{E} + \vec{P}$, in a self-consistent way. The sources of the depolarization field $\vec{E}_d$ are the uncompensated bound charges related to the surface and/or polarization gradient. The long-range electrostatic interactions, proportional to the scalar product $-\frac{1}{2} P_i E_i^d$ in the free energy (2a), vanish with increase in film thickness (or nanoisland height). They are also absent in the case of ideal screening of single-domain ferroelectric films, because $\text{div} \vec{P} = 0$ in this case. The energy of depolarization field is responsible for the disappearance of the out-of-plane spontaneous polarization (and thus ferroelectricity) in thin films under imperfect screening conditions [46]. The disappearance of the in-plane ferroelectric polarization (e.g., $P_x(y, z)$, which obeys the condition $\text{div} \vec{P} = 0$) is determined by the correlation effects [47]. These speculations are valid for all spatially confined single-domain ferroelectrics, including hafnia-zirconia thin films and nanoislands, they are not material specific.

Following Refs. [10–12], the spontaneous polarization $\vec{P}_s$ is proportional to the amplitude Q_{Γ_3} of the Γ_{3-} mode. Let us assume that

$$P_3 = \frac{Z_B^* d}{V_{\text{f.u.}}} Q_{\Gamma_3} \approx P_s Q_{\Gamma_3}, \quad (2b)$$

where Z_B^* is the effective Bader charge [12], $V_{\text{f.u.}}$ is the formula unit (f.u.) volume and d is the elementary displacement corresponding to the polar Γ_{3-} mode. The spontaneous polarization value $P_s \approx 54.8 \mu\text{C}/\text{cm}^2$ was calculated in Ref. [10] for the hypothetical bulk HfO_2 . At the same time the amplitude of the maximal atomic displacement d was reported as 0.284, 0.278, and 0.268 Å for the polar, nonpolar, and antipolar modes, respectively.

Substitution of P_3 in Eqs. (1) instead of Q_{Γ_3} , leads to the rescaling of the coefficients β_i , γ , δ_{ij} , ϵ_i , η_{ijk} , ζ_{ij} , ξ_{ijkl} , q_{ijkl} , and g_{ijkl} proportional to the powers of the factor $\frac{V_{\text{f.u.}}}{Z_B^* d} \approx \frac{1}{P_s}$. In particular, the biquadratic 2–4–6–8 coupling coefficients $\tilde{\beta}_{\Gamma_3}$, $\tilde{\delta}_{\Gamma_3}$, $\tilde{\eta}_{\Gamma_3}$, $\tilde{\xi}_{\Gamma_3}$ and the trilinear coupling coefficient $\tilde{\gamma}$, responsible for the behavior of the polar mode Γ_{3-} , have the form:

$$\begin{aligned} \tilde{\beta}_{\Gamma_3} &= \frac{\beta_{\Gamma_3}}{P_s^2}, & \tilde{\delta}_{\Gamma_3} &= \frac{\delta_{\Gamma_3}}{P_s^4}, & \tilde{\eta}_{\Gamma_3} &= \frac{\eta_{\Gamma_3}}{P_s^6}, \\ \tilde{\xi}_{\Gamma_3} &= \frac{\xi_{\Gamma_3}}{P_s^8}, & \tilde{\gamma} &= \frac{\gamma}{P_s}. \end{aligned} \quad (3)$$

In what follows we consider nanosized HZO, such as thin films epitaxially grown on a rigid substrate and epitaxial nanoislands, whose geometry are shown schematically in Figs. 1(b) and 1(c). Following Refs. [6, 10, 11, 19], we consider the nanosized HZO as a uniaxial ferroelectric material with the out-of-plane spontaneous polarization, whose polar z axis is normal to the film surfaces. Hereinafter we regard that surfaces of nanosized HZO are covered with ideally conducting or semiconducting electrodes, or with ionic-electronic screening charges. The screening charges may originate from the oxygen vacancies accumulation by the surface.

Next, we assume that the surface/interface energy excess F_s of the HZO is the biquadratic form of Q_i :

$$F_s = \int \alpha_i Q_i^2 dS = F_{SP} + F_{SY}, \quad (4a)$$

$$F_{SP} = \int (\alpha_{\Gamma_3} P_3^2 + \alpha_{\Gamma_3 Y_2} P_3 Q_{Y_2} + \alpha_{\Gamma_3 Y_4} P_3 Q_{Y_4}) dS, \quad (4b)$$

$$F_{SY} = \int (\alpha_{Y_2} Q_{Y_2}^2 + \alpha_{Y_4} Q_{Y_4}^2 + \alpha_{Y_2 Y_4} Q_{Y_2} Q_{Y_4}) dS. \quad (4c)$$

Since the m phase is stable in the bulk, the energy $F_{SY} \geq 0$ at arbitrary values of Q_{Y_2} and Q_{Y_4} , that is true for $\alpha_{Y_2} > 0$, $\alpha_{Y_4} > 0$, and $2\sqrt{\alpha_{Y_2} \alpha_{Y_4}} > -\alpha_{Y_2 Y_4}$. Since the FE o phase can be stable in the nanosized HZO only, the surface energy F_{SP} , related to the appearance of the polar order, may be negative. Following the surface stability conditions, the total surface energy F_s should be positive. In what follows we consider the simplest diagonalized form of the surface energy, with $\alpha_{\Gamma_3 Y_2} = \alpha_{\Gamma_3 Y_4} = \alpha_{Y_2 Y_4} = 0$ and $\alpha_{Y_2} > 0$, $\alpha_{Y_4} > 0$. The case $\alpha_{\Gamma_3} < 0$ supports the stability of the polar Γ_{3-} mode at the nanoscale and contributes to the surface-induced phase transition. However, since the microscopic mechanisms, which may be responsible for $\alpha_{\Gamma_3} < 0$, are not considered, we put $\alpha_{\Gamma_3} \geq 0$ in numerical calculations.

The free energy of the nanosized HZO corresponding to the FE o phase, $F_{\text{o-phase}}$, is the volume integral of the LGD free energy bulk f_{bulk} given by Eq. (1), electric energy f_{el} given by Eq. (2) and the surface/interface energy F_s given by Eqs. (4):

$$F_{\text{o-phase}} = \int (f_{\text{bl}} + f_{\text{tr}} + f_{\text{est}} + f_{\text{grad}} + f_{\text{el}}) dV + F_s. \quad (5a)$$

The FE o phase can be stable in the nanosized HZO when its free energy $F_{\text{o-phase}}$ is smaller than the energy of the m phase, $F_m = \int f_m dV$. The critical sizes of the ferroelectricity appearance in nanosized HZO can be estimated from the condition

$$F_{\text{o-phase}} = F_m. \quad (5b)$$

The density of a bulk HfO_2 m phase energy f_m , counted from the t phase, is about -92 meV/f.u. [10].

Due to elastic strains, surface tension, polarization gradient energy, and depolarization field, coefficients in the free energy (5) become renormalized. Their renormalization depends on the geometry, mismatch strains, size effects, and screening conditions (see, e.g., Refs. [32,33,39]). In next sections we consider the cases of epitaxial HZO thin films and nanoislands with a single-domain out-of-plane spontaneous polarization.

B. Epitaxial thin films of hafnia-zirconia

Next let us consider a single-domain HZO thin film epitaxially grown on a rigid substrate [corresponding geometry is shown in Fig. 1(b)]. The epitaxial biaxial strain u_m induced by the film-substrate lattice constants mismatch is $u_m = \frac{b-a}{a}$, where a and b are the film and substrate in-plane lattice constants, respectively. The depolarization field inside the single-domain film with an out-of-plane polarization can be estimated as [48]:

$$E_3(z) = \frac{\bar{P}_3 - P_3(z)}{\varepsilon_0 \varepsilon_b} - \frac{\bar{P}_3}{\varepsilon_0 \varepsilon_b} \frac{\lambda_{\text{eff}}}{\lambda_{\text{eff}} + h/\varepsilon_b}, \quad (6)$$

where $P_3(z)$ is the out-of-plane polarization directed along z axis, $\bar{P}_3$ is the z -averaged polarization, h is the film thickness, $\lambda_{\text{eff}} = \lambda_1/\varepsilon_{g1} + \lambda_2/\varepsilon_{g2}$ is the effective screening length corresponding to conducting or semiconducting top (subscript “1”) and bottom (subscript “2”) electrode(s) with the dielectric constants ε_{gi} , ε_b is a background dielectric permittivity [49] of the film, ε_0 is a universal dielectric constant. Domain formation can emerge in thin films under imperfect screening conditions [50], but in this work we would like to focus on the strain-induced effects emerging in single-domain epitaxial films and nanoislands. Below we use the depolarization field model, proposed by Tagantsev *et al.* [51], who introduced the effective surface screening length and showed that the effective depolarization factor depends on the ratio of the screening length to the system size along the polarization direction. According to Refs. [51,52], the single-domain state of the film with the out-of-plane polarization can be stable for very small effective screening lengths, $\lambda_{\text{eff}} \leq 1$ Å, when the depolarization field becomes negligibly small and the domain formation is not energetically favorable. Despite λ_{eff} is much smaller than the lattice constant, its value may be quite realistic, because λ_{eff} is related with the real charge-surface separation λ_i as $\lambda_{\text{eff}} \cong \lambda_i/\varepsilon_{gi}$. Since the dielectric constants ε_{gi} can be large enough, the separation λ_i can appear higher than the lattice constant. The limiting case $\lambda_{\text{eff}} \rightarrow 0$ corresponds to the ideally conducting electrodes. The case of large $\lambda_{\text{eff}} > 1$ nm may correspond to the sluggish ionic-electronic screening charges (instead of the top electrode). Suggesting that the Debye-Hückel model is valid, one could estimate the surface screening length as the bare Debye-Hückel length $L_D = \sqrt{\frac{\varepsilon_0 k_B T}{2e^2 n}}$, where ε_0 is the vacuum dielectric constant, k_B is the Boltzmann constant, T is the absolute temperature, and e is the elementary charge. For the carrier concentrations from 10^{20} to 10^{22} cm $^{-3}$, which corresponds to TiN and TaN, semimetal (La, Sr)MnO $_3$ or metal Au, Pt, W electrodes covering HfO_2 films in typical experiments (see Table 1 in Ref. [4] and [16]), this expression gives that L_D changes from 80 to 8 pm at room temperature.

Using the approach evolved in Refs. [53,54] for single-domain epitaxial ferroelectric films, the free energy of the FE o phase of a single-domain epitaxial HZO thin film is given by approximate expression:

$$F_{\text{o-phase}} \approx \tilde{\beta}_f \bar{P}_3^2 + \tilde{\beta}_{Y2} \bar{Q}_{Y2}^2 + \tilde{\beta}_{Y4} \bar{Q}_{Y4}^2 + \tilde{\delta}_f \bar{P}_3^4 + \tilde{\delta}_{Y2} \bar{Q}_{Y2}^4 + \tilde{\delta}_{Y4} \bar{Q}_{Y4}^4 + \tilde{\delta}_{Y24} \bar{Q}_{Y2}^2 \bar{Q}_{Y4}^2 + \delta_{Y2} \bar{P}_3^2 \bar{Q}_{Y2}^2 + \delta_{Y4} \bar{P}_3^2 \bar{Q}_{Y4}^2 + \eta_{Y2} \bar{Q}_{Y2}^6 + \eta_{Y4} \bar{Q}_{Y4}^6 + \xi_{Y2} \bar{Q}_{Y2}^8 + \xi_{Y4} \bar{Q}_{Y4}^8 + \dots + \tilde{\eta}_f \bar{P}_3^6 + \tilde{\xi}_f \bar{P}_3^8 + \tilde{\gamma}_f \bar{Q}_{Y2} \bar{Q}_{Y4} \bar{P}_3 - \bar{P}_3 E_3, \quad (7a)$$

where “...” means all higher-order cross terms, listed in Eqs. (S11)–(S13) [43], and renormalized coefficients $\tilde{\beta}_{\Gamma3}$, $\tilde{\delta}_{\Gamma3}$, $\tilde{\eta}_{\Gamma3}$, $\tilde{\xi}_{\Gamma3}$ and $\tilde{\gamma}_f$ have the form:

$$\tilde{\beta}_f = \tilde{\beta}_{\Gamma3} + \frac{\lambda_{\text{eff}}}{2\varepsilon_0 \varepsilon_b (h + \lambda_{\text{eff}})} + \frac{g}{h\Lambda_P + h^2/\pi} - u_m^* \left(\tilde{q}_{13} + \tilde{q}_{23} - \frac{c_{13} + c_{23}}{c_{33}} \tilde{q}_{33} \right), \quad (7b)$$

$$\tilde{\delta}_f = \tilde{\delta}_{\Gamma3} - \frac{\tilde{q}_{33}^2}{2c_{33}} - u_m^* \left(\tilde{z}_{133} + \tilde{z}_{233} - \frac{c_{13} + c_{23}}{c_{33}} \tilde{z}_{333} \right), \quad (7c)$$

$$\tilde{\eta}_f = \tilde{\eta}_{\Gamma3} - \frac{\tilde{q}_{33} \tilde{z}_{333}}{c_{33}}, \quad (7d)$$

$$\tilde{\xi}_f = \tilde{\xi}_{\Gamma3} - \frac{\tilde{z}_{333}^2}{2c_{33}}, \quad (7e)$$

$$\tilde{\gamma}_f = \tilde{\gamma} - u_m^* \left[\tilde{r}_{133} + \tilde{r}_{233} - \frac{c_{13} + c_{23}}{c_{33}} \tilde{r}_{333} \right]. \quad (7f)$$

Here $\bar{P}_3$, $\bar{Q}_{Y2}$, and $\bar{Q}_{Y4}$ are the averaged order parameters; c_{ijkl} are elastic compliances, $\tilde{q}_{ijkl}$, $\tilde{r}_{ijklm}$, and $\tilde{z}_{ijkmn}$ are the second-order and the higher-order electrostriction stress tensor components, written in Voigt or mixed notations. The renormalization of δ_{Yi} , η_{Yi} , ξ_{Yi} , and higher-order cross terms, omitted in Eq. (7a), is insignificant.

Exactly the presence of misfit dislocations leads to the relaxation of the seeding mismatch strain u_m , and it should be substituted with the effective misfit strain

$$u_m^* = u_m \left(1 - \exp \left[-\frac{h_d}{h} \right] \right), \quad (7g)$$

where $u_1 = u_2 = u_m$ are the components of the seeding biaxial mismatch strain, h_d is the critical thickness of dislocation appearance [55]. The relaxation of mismatch strains, that inevitably happens in thin films with thickness $h > h_d$, leads to decrease in the mismatch-driven electrostriction coupling between the emerging ferroelectric polarization and the elastic strains. The changes in strains lead to the change in the position of the boundary between the ferroelectric and paraelectric phases in the phase diagrams of the hafnia-zirconia film. As a result, the ferroelectricity can emerge at the thickness, which corresponds to high enough u_m^* , and is absent for larger sizes. This condition is distinct from other ferroelectrics, where the ferroelectricity exists in a strain-free state.

The second term in Eq. (7b) originates from the depolarization field. The third term originates from the polarization gradient energy [56]; $g = \frac{1}{2}(g_{3311} + g_{3322})$ is the combination of the gradient energy tensor components, and $\Lambda_P = \frac{\alpha_{\Gamma3}}{g}$ is the polarization extrapolation length at the film surfaces

[57]. Since $\lambda_{\text{eff}} \geq 0$ and $\Lambda_P \geq 0$, these two terms are always positive and thus can only increase the value of $\tilde{\beta}_f$, thereby worsening the ferroelectric properties of the HZO film. The last term in Eq. (5b) is the strain-induced renormalization of $\tilde{\beta}_f$ proportional to u_m . It has different trends for tensile ($u_m > 0$) and compressive ($u_m < 0$) mismatch strains and thus can enhance or worsen the ferroelectric properties of the HZO film.

The strain-induced renormalization of the coefficients $\tilde{\delta}_f$ and $\tilde{\gamma}_f$ is linearly u_m dependent according to Eqs. (7b) and (7f), and so $\tilde{\delta}_f$ and $\tilde{\gamma}_f$ can change their sign due to the mismatch strain. At the same time, clamping to substrate changes the nonlinear coefficients $\tilde{\eta}_r$ and $\tilde{\xi}_r$ in a global mismatch-independent way [see Eqs. (7d) and (7e)]. Thus, a film clamping to a rigid substrate can make the potential well corresponding to the FE o phase more shallow or deeper and shift its position due to the change of the spontaneous polarization magnitude. The change of the potential well depth is defined by the magnitudes and signs of the renormalized coefficients in Eqs. (7a). Note that $\tilde{\beta}_f = \tilde{\beta}_{f3} + \frac{\lambda_{\text{eff}}}{2\epsilon_0\epsilon_b(h+\lambda_{\text{eff}})} + \frac{2g}{h\Lambda_P+h^2/4}$, $\tilde{\delta}_f = \tilde{\delta}_{f3}$, $\tilde{\eta}_f = \tilde{\eta}_{f3}$, $\tilde{\xi}_f = \tilde{\xi}_{f3}$, and $\tilde{\gamma}_f = \tilde{\gamma}$ for a free-standing single-domain HZO film.

Next, the critical thickness h_{cr} of the ferroelectricity appearance in strained thin HZO films can be estimated from the condition $F_{\text{o-phase}} = F_m$. The energy $F_{\text{o-phase}}$ is given by approximate expression (5a), where the order parameters $\tilde{P}_3$, $\tilde{Q}_{Y2}$, and $\tilde{Q}_{Y4}$, averaged over the film thickness, satisfy the coupled equations. Neglecting the higher-order cross terms and using the simplest 2–4 power expansion for $\tilde{Q}_{Y2}$, $\tilde{Q}_{Y4}$, and $\tilde{P}_3$, these equations have the following form:

$$2(\tilde{\beta}_f + \delta_{Y2}\tilde{Q}_{Y2}^2 + \delta_{Y4}\tilde{Q}_{Y4}^2)\tilde{P}_3 + 4\tilde{\delta}_f\tilde{P}_3^3 = \tilde{E}_3 - \tilde{\gamma}_f\tilde{Q}_{Y2}\tilde{Q}_{Y4}, \quad (8a)$$

$$2(\tilde{\beta}_{Y2} + \delta_{Y2}\tilde{P}_3^2)\tilde{Q}_{Y2} + 4\tilde{\delta}_{Y2}\tilde{Q}_{Y2}^3 + 2\tilde{\delta}_{Y24}\tilde{Q}_{Y4}^2\tilde{Q}_{Y2} = -\tilde{\gamma}_f\tilde{P}_3\tilde{Q}_{Y4}, \quad (8b)$$

$$2(\tilde{\beta}_{Y4} + \delta_{Y4}\tilde{P}_3^2)\tilde{Q}_{Y4} + 4\tilde{\delta}_{Y4}\tilde{Q}_{Y4}^3 + 2\tilde{\delta}_{Y24}\tilde{Q}_{Y2}^2\tilde{Q}_{Y4} = -\tilde{\gamma}_f\tilde{P}_3\tilde{Q}_{Y2}. \quad (8c)$$

Using the materials parameters, listed in Tables S1–S2 [43], we obtained that only trivial solution $\tilde{Q}_{Y2s} = \tilde{Q}_{Y4s} = 0$ is stable at zero and small strength of the trilinear coupling [see Fig. S5(a) in Sec. S4 [43]]. Nonzero amplitudes of the antipolar and nonpolar modes, become stable at higher trilinear coupling strength, which values are listed in Tables S1–S2 [43]. They can be estimated as $\tilde{Q}_{Y2s} \cong \tilde{Q}_{Y4s} \cong \pm \sqrt{\frac{-\tilde{\gamma}_f\tilde{P}_3 + \tilde{\beta}_{Y4} + \delta_{Y2}\tilde{P}_3^2 + \delta_{Y4}\tilde{P}_3^2}{4(\tilde{\delta}_{Y4} + \delta_{Y2}) + 2\tilde{\delta}_{Y24}}}$. In this case the out-of-plane polarization obeys the equation

$$2(\tilde{\beta}_f + \delta_{Y2}\tilde{Q}_{Y2}^2 + \delta_{Y4}\tilde{Q}_{Y4}^2)\tilde{P}_3 + 4\tilde{\delta}_f\tilde{P}_3^3 = \tilde{E}_3 \pm \tilde{\gamma}_f\tilde{Q}_{Y2s}\tilde{Q}_{Y4s}. \quad (9)$$

It is seen from Eq. (9), that spontaneous polarization can be incipient, because the term $\tilde{\gamma}_f\tilde{Q}_{Y2s}\tilde{Q}_{Y4s}$ plays the role of external field at $\tilde{E}_3 = 0$. For negative $\tilde{\beta}_f + \delta_{Y2}\tilde{Q}_{Y2}^2 + \delta_{Y4}\tilde{Q}_{Y4}^2$, a reversible ferroelectric polarization could appear. The values of $\tilde{P}_s$ can be estimated from Eq. (9) at $\tilde{E}_3 = 0$. In the simplest case, when $\tilde{\delta}_f > 0$, $\tilde{\eta}_f$, and $\tilde{\xi}_f$ are negligibly small, the condition $\tilde{\beta}_f + \delta_{Y2}\tilde{Q}_{Y2}^2 + \delta_{Y4}\tilde{Q}_{Y4}^2 = 0$ determines the borderline between incipient and reversible ferroelectric states.

However, this condition is necessary but not sufficient for the polar phase stability. The sufficient condition is

$$(\tilde{\beta}_f + \delta_{Y2}\tilde{Q}_{Y2}^2 + \delta_{Y4}\tilde{Q}_{Y4}^2)\tilde{P}_s^2 + \tilde{\delta}_f\tilde{P}_s^4 + \tilde{\gamma}_f\tilde{Q}_{Y2s}\tilde{Q}_{Y4s}\tilde{P}_s \leq F_m - F_{QY}, \quad (10a)$$

where F_{QY} is the average energy density of antipolar and nonpolar modes energy:

$$F_{QY} = \tilde{\beta}_{Y2}\tilde{Q}_{Y2s}^2 + \tilde{\beta}_{Y4}\tilde{Q}_{Y4s}^2 + \tilde{\delta}_{Y2}\tilde{Q}_{Y2s}^4 + \tilde{\delta}_{Y4}\tilde{Q}_{Y4s}^4 + \tilde{\delta}_{Y24}\tilde{Q}_{Y2s}^2\tilde{Q}_{Y4s}^2. \quad (10b)$$

To derive relatively simple equation for the critical thickness from Eqs. (10), we should assume that the spontaneous polarization $\tilde{P}_s$ relatively weakly depends on the mismatch strain and film thickness in the deep FE o phase. Using these assumptions, an approximate transcendental equation for the critical thickness h_{cr} acquires the form:

$$\tilde{\beta}_{f3} + \frac{\lambda_{\text{eff}}}{2\epsilon_0\epsilon_b(h_{\text{cr}} + \lambda_{\text{eff}})} + \frac{g}{h_{\text{cr}}\Lambda_P + h_{\text{cr}}^2/\pi} - u_m \left(1 - \exp\left[-\frac{h_d}{h_{\text{cr}}}\right] \right) \times \left(\tilde{q}_{13} + \tilde{q}_{23} - \frac{c_{13} + c_{23}}{c_{33}}\tilde{q}_{33} \right) = -\Delta_s, \quad (11)$$

where we introduced the positive parameter Δ_s as:

$$\Delta_s = \tilde{\delta}_f\tilde{P}_s^2 + \tilde{\eta}_f\tilde{P}_s^4 + \tilde{\xi}_f\tilde{P}_s^6 + \tilde{\gamma}_f\frac{\tilde{Q}_{Y2s}\tilde{Q}_{Y4s}}{\tilde{P}_s} + \frac{F_{QY} - F_m}{\tilde{P}_s^2}. \quad (12)$$

Assuming that the contribution of higher-order electrostriction components $\tilde{z}_{ijk}$ and $\tilde{r}_{ijk}$ are small, we can neglect the mismatch-dependent terms proportional in the coefficients $\tilde{\delta}_f$ and $\tilde{\gamma}_f$, given by Eqs. (7c) and (7f), respectively. Considering this and other abovementioned assumptions, the parameter Δ_s can be regarded as mismatch independent.

Note that all figures, discussed below, are calculated using exact Eqs. (7), because the accuracy of approximate Eqs. (8)–(11) is not high enough near the boundaries between different phases. However, Eqs. (8)–(11) well describe qualitatively the polarization behavior and critical sizes in thin HZO films.

Phase state of the epitaxial HfO₂ film as a function of mismatch strain u_m and thickness h is shown in Fig. 2 for several typical values of the effective screening length: $\lambda_{\text{eff}} = 0$ (which corresponds to the ideally conducting electrodes), $\lambda_{\text{eff}} = 0.2 \text{ \AA}$ (which corresponds to the semiconducting electrodes with high conductivity) and $\lambda_{\text{eff}} = 1 \text{ \AA}$ (which corresponds to the semiconducting electrodes or to the ionic-electronic screening charge layer [39] at the film surface).

It is seen that the FE o phase can be stable at compressive mismatch strains $u_m < u_{\text{min}}$ only, where the minimal strain u_{min} changes from -0.25% at $\lambda_{\text{eff}} = 0$ to -2% at $\lambda_{\text{eff}} = 1 \text{ \AA}$ due to the size effect of depolarization field [see Eq. (6)]. The conclusion about an urgency to apply compressive mismatch strains to induce the FE o phase in HfO₂ films agrees with DFT results [10,19]. The area of the FE o-phase region stability decreases strongly with increase in λ_{eff} , being replaced by the nonpolar m phase (compare the first, the second, and

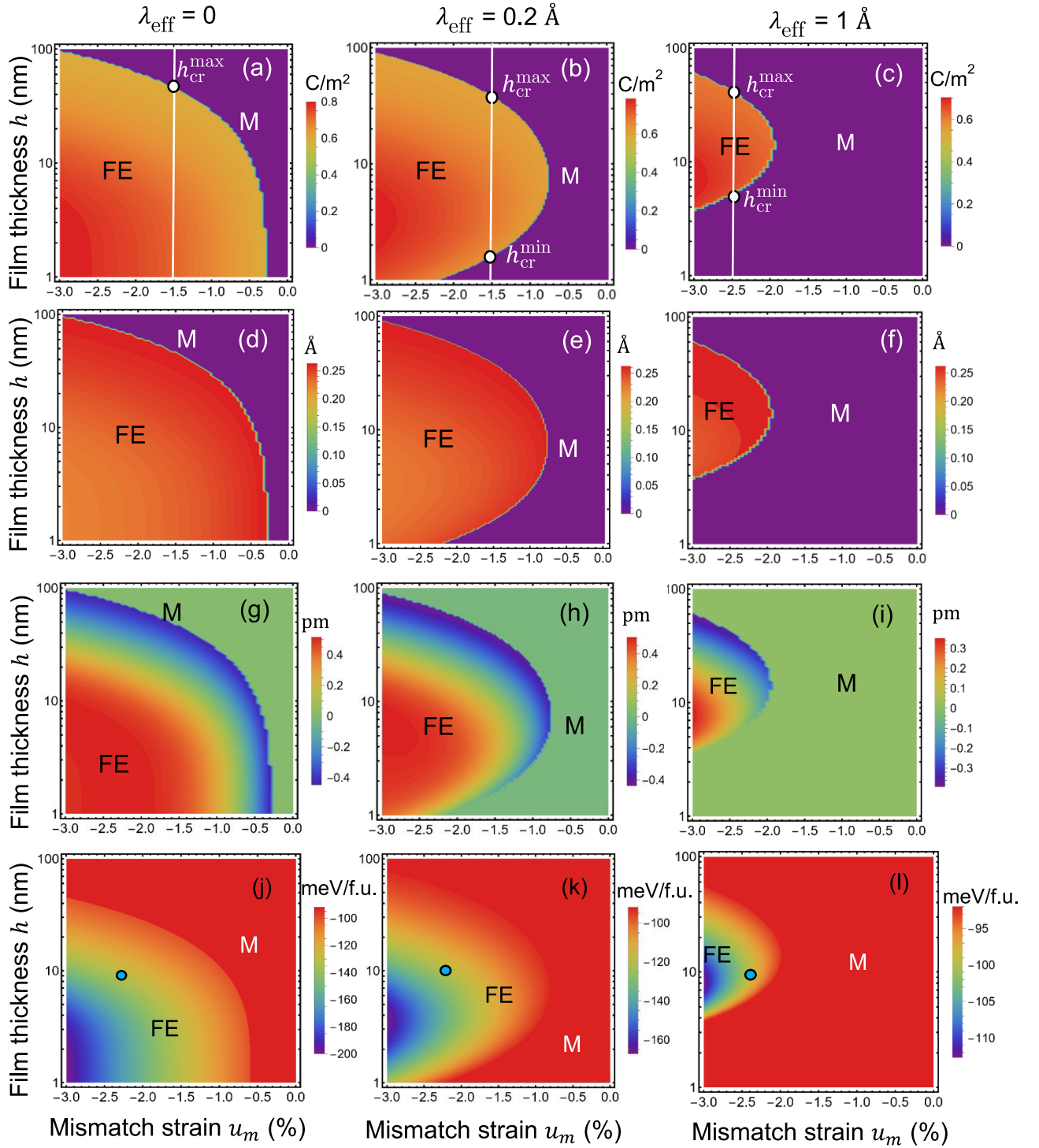


FIG. 2. (a)–(c) The absolute value of polarization $\bar{P}_s$, (d)–(f) the amplitude of nonpolar order parameter $|\bar{Q}_{Y2s}|$, (g)–(i) the difference $|\bar{Q}_{Y4s}| - |\bar{Q}_{Y2s}|$, and (j)–(l) the deepest minimum of the free energy density $f_{\text{o-phase}}^{\text{min}}$ as a function of mismatch strain u_m and HfO₂ film thickness h calculated for different screening lengths $\lambda_{\text{eff}} = 0$ (a), (d), (g), (j), $0.2 \text{ \AA}$ (b), (e), (h), (k), and $1 \text{ \AA}$ (c), (f), (i), (l). Abbreviation “FE” is the FE o-phase, “M” denotes the nonpolar m-phase. White circles in the plots (a)–(c) correspond to $h_{\text{cr}}^{\text{min}}$ and $h_{\text{cr}}^{\text{max}}$ at fixed u_m . Other parameters are $\Delta_P = 10 \mu\text{m}$ and $h_d = 10 \text{ nm}$.

the third columns in Fig. 2). The m-phase becomes reentrant for $\lambda_{\text{eff}} > 0$. The FE o phase disappears completely for $\lambda_{\text{eff}} > \lambda_{\text{max}}$, where λ_{max} increases with increase in the maximal compressive mismatch strain u_{max} . In particular, $\lambda_{\text{max}} \approx 2 \text{ \AA}$ at $u_{\text{max}} \approx -3\%$. Since the domain formation should be

considered in the case $\lambda_{\text{max}} > 1 \text{ \AA}$, which may decrease the critical thickness of ferroelectricity disappearance, the case of larger λ_{max} and u_{max} will be considered elsewhere.

Color scale in Figs. 2(a)–2(c) is the absolute value of spontaneous polarization $\bar{P}_s$ in the deepest potential well of

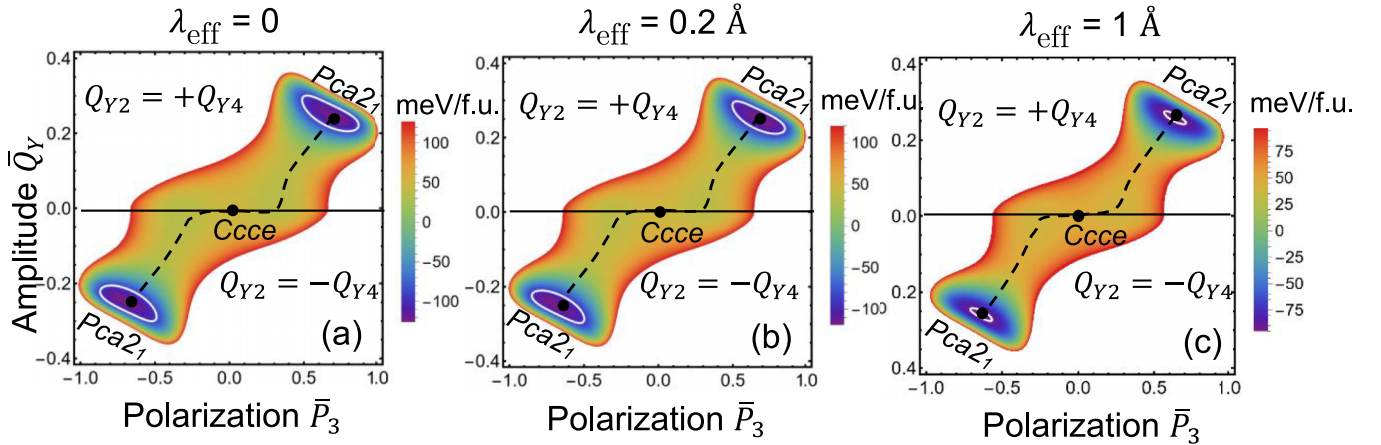


FIG. 3. Free energy density as a function of $\bar{P}_3$ and $\bar{Q}_Y$. The amplitude $\bar{Q}_Y = Q_{Y2} = Q_{Y4}$ in the top half-plane and $\bar{Q}_Y = Q_{Y2} = -Q_{Y4}$ in the bottom half-plane. The plots are calculated for different screening lengths (a) $\lambda_{\text{eff}} = 0$, (b) $0.2 \text{ \AA}$, (c) $1 \text{ \AA}$, $h = 10 \text{ nm}$, and $u_m = -2.2\%$. Chosen values of h , u_m , and λ_{eff} correspond to the blue circles in Figs. 2(j), 2(k), and 2(l), respectively. White elliptic contours in the plots correspond to the energy density of the bulk HfO₂ m-phase $f_m = -92 \text{ meV/f.u.}$ Dashed curves show the polarization switching path, which corresponds to the lowest energy barrier $f_{\text{Cce}} = +48 \text{ meV/f.u.}$ (counted from the t phase). Other parameters are the same as in Fig. 2.

the free energy (7). The sharp boundary between the FE o phase (with $\bar{P}_s > 0$) and nonpolar m phase (with $\bar{P}_s = 0$) is the first-order phase transition curve describing the dependence of the critical thickness h_{cr} on the mismatch strain u_m . As follows from Eq. (11), the strain-dependent critical thickness of the ferroelectricity appearance ($h_{\text{cr}}^{\text{max}}$) is determined by the size dependence of the effective mismatch strain u_m^* [proportional to the function $u_m(1 - \exp[-\frac{h_d}{h}])$] according to Eq. (7g)]. Due to dislocation appearance, the power decay of mismatch strains occurs in films of thickness $h > h_d$, namely $u_m^* \sim u_m \frac{h_d}{h}$. Thus, the estimation $h_{\text{cr}}^{\text{max}} \leq 10h_d$ may be valid. The critical thickness of the ferroelectricity disappearance ($h_{\text{cr}}^{\text{min}}$) is determined by the size dependence of the depolarization field [proportional to the function $\frac{\lambda_{\text{eff}}}{2\epsilon_0\epsilon_b(h+\lambda_{\text{eff}})}$] according to Eq. (6)] and correlation effects (proportional to the function $\frac{g}{h\Lambda_P + h^2/\pi}$). Hence, the estimations $h_{\text{cr}}^{\text{min}} \gg \lambda_{\text{eff}}$ and $h_{\text{cr}}^{\text{min}} \gg \sqrt{g\epsilon_0\epsilon_b}$ should be valid. Dependence of the film critical thicknesses, $h_{\text{cr}}^{\text{max}}$ and $h_{\text{cr}}^{\text{min}}$, on the mismatch strain u_m is given by the boundary between the FE o phase and the m phase [see white circles in Figs. 2(a)–2(c)]. For ideal screening conditions, when $\lambda_{\text{eff}} = 0$, the FE o phase is thermodynamically stable in HZO films with thickness $h < h_{\text{cr}}^{\text{max}}$ [see Fig. 2(a)]. In this case the minimal thickness is limited by the correlation thickness being equal to several lattice constants. For incomplete screening conditions, when $0 < \lambda_{\text{eff}} < \lambda_{\text{max}}$, the FE o phase is thermodynamically stable in HZO films with thickness $h_{\text{cr}}^{\text{min}} < h < h_{\text{cr}}^{\text{max}}$ [see white circles in Figs. 2(b) and 2(c)]; at that λ_{max} is determined by the maximal mismatch strain u_{max} . The thicknesses $h_{\text{cr}}^{\text{min}}$ and $h_{\text{cr}}^{\text{max}}$ become equal at $\lambda_{\text{eff}} \rightarrow \lambda_{\text{max}}$ and disappear at $\lambda_{\text{eff}} > \lambda_{\text{max}}$.

Color scale in Figs. 2(d)–2(f) is the absolute value of the nonpolar mode $\bar{Q}_{Y2s}$ in the deepest potential well of the free energy. The difference of the antipolar and nonpolar modes magnitudes, $|\bar{Q}_{Y4s}| - |\bar{Q}_{Y2s}|$, is shown in Figs. 2(g)–2(i). It is seen that the difference $|\bar{Q}_{Y4s}| - |\bar{Q}_{Y2s}|$ is very small: it does not exceed 0.5 pm , that is 50 times smaller than the maximal value of $\bar{Q}_{Y2s}$ ($\approx 25 \text{ \AA}$). The small value of the difference

means that the approximation $|\bar{Q}_{Y4s}| \approx |\bar{Q}_{Y2s}|$ is valid with high accuracy in the minimum of the free energy (7). From a physical standpoint, the approximate equality $|\bar{Q}_{Y4s}| \approx |\bar{Q}_{Y2s}|$ means a negligible anisotropy of the free energy potential well as a function of $|\bar{Q}_{Y4s}|$ and $|\bar{Q}_{Y2s}|$. Note that the approximate equality $|\bar{Q}_{Y4s}| \approx |\bar{Q}_{Y2s}|$ follows from the choice of parameters, listed in Tables S1–S2 [43], despite it is working well [see Fig. S5(b) in Sec. S4 [43]].

The deepest minimum of the free energy density, $f_{\text{o-phase}}^{\text{min}}$, as a function of u_m and h , calculated for $\lambda_{\text{eff}} = 0, 0.2 \text{ \AA}$ and $1 \text{ \AA}$, are shown in Figs. 3(g), 3(k), and 3(l), respectively. A red background in the figure corresponds to the bulk m phase with the energy density $f_m = -92 \text{ meV/f.u.}$ [10]. The first-order phase transition between the o phase and m phase corresponds to the condition $f_{\text{o-phase}}^{\text{min}} = f_m$.

Color maps of the free energy density of epitaxial HfO₂ films as a function of $\bar{P}_3$ and $\bar{Q}_Y$ are shown in Figs. 3(a)–3(c), where the amplitude $\bar{Q}_Y = Q_{Y2} = Q_{Y4}$ in the top half-plane and $\bar{Q}_Y = Q_{Y2} = -Q_{Y4}$ in the bottom half-plane. The plots are calculated for the same values of λ_{eff} as in Fig. 2 and fixed other parameters ($h = 10 \text{ nm}$ and $u_m = -2.2\%$). The signs of spontaneous polarization, antipolar, and nonpolar order parameters are interdependent in the minimum of the free energy due to the trilinear coupling term $\sim \bar{Q}_{Y2}\bar{Q}_{Y4}\bar{P}_3$. From Fig. 3, the triple product $\tilde{\gamma}_f \bar{Q}_{Y2}\bar{Q}_{Y4}\bar{P}_3$ should be negative in the absolute minimum of the free energy (7), being consistent with equations of state (8). It is seen from the dashed curves in Figs. 3(a)–3(c), that the switching path between the $-\bar{P}_s$ and $+\bar{P}_s$ states goes through the virtual Ccce phase, because the height b_{af} of the lowest barrier of polarization switching, which changes from $+48 \text{ meV/f.u.}$ (at $\lambda_{\text{eff}} = 0 \text{ \AA}$) to $+49 \text{ meV/f.u.}$ (at $\lambda_{\text{eff}} = 1 \text{ \AA}$), well corresponds to the energy density of the Ccce phase counted from the t phase (see Table S3 in Ref. [43]). An activation field E_{af} of polarization reversal, which corresponds to the domain nucleation onset, can be estimated as $E_{\text{af}} \cong b_{\text{af}}/\bar{P}_s$, which gives 0.72 MV/cm at $\lambda_{\text{eff}} = 0 \text{ \AA}$ and 0.84 MV/cm at $\lambda_{\text{eff}} = 1 \text{ \AA}$ at $V_{\text{f.u.}} \approx 134 \text{ \AA}^3$. The calculated domain nucleation fields are lower (but of the

same order) than the coercive field $E_c \cong 1.05\text{--}1.35$ MV/cm observed in 10-nm thick $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ films [6,58], as it should be expected from the nucleation rate theory, because the local nucleation of nanodomains (arising at $E_3^e \approx E_{af}$) precedes the global polarization switching (occurring at $E_3^e \approx E_c$). From our calculations, the barrier of polarization switching and the activation field very weakly increases with increase in λ_{eff} . At the same time the depth of the deepest potential well decreases with increase in λ_{eff} slightly more strongly, changing from 110 meV/f.u. (at $\lambda_{\text{eff}} = 0$ Å) to +95 meV/f.u. (at $\lambda_{\text{eff}} = 1$ Å). The width of the deepest potential well, estimated using the energy of the bulk m phase ($f_m = -92$ meV/f.u. counted from the t phase), decreases with increase in λ_{eff} more strongly [see white elliptic contours in Figs. 3(a)–3(c)].

C. Epitaxial nanoislands of hafnia-zirconia

Next let us consider a single-domain HZO nanoisland epitaxially grown on a rigid substrate [corresponding geometry is shown in Fig. 1(c)]. The lateral size $2R$ of the nanoisland can be larger or smaller than its height h . The assumption $2R \gg h$ allows us to neglect the edge effects in the first approximation, and the elastic strain of the nanoisland is almost the same as for the epitaxial film in the case. In the opposite case, $2R \leq h$, a pronounced size effect related with the relaxation of elastic stresses appears due to the edge effects. The relaxation of mismatch strains is proportional to the ratio $\frac{h}{2R}$ at $2R \gg h$ (see Refs. [59,60]). This allows us to introduce the effective mismatch strain u_m :

$$u_m^* = u_m \left(1 - \exp\left[-\frac{h_d}{h}\right] \right) \exp\left[-\frac{h}{2R}\right]. \quad (13)$$

Hereinafter we regard that the evolution of misfit dislocations inside the island obeys the same law as in epitaxial thin films.

The depolarization field inside the single-domain nanoisland of quasicylindrical shape can be estimated as [56]:

$$E_3(z) \approx \frac{\bar{P}_3 - P_3(z)}{\varepsilon_0 \varepsilon_b [1 + (h/2R)^2]} - \frac{\bar{P}_3}{\varepsilon_0 \varepsilon_b [1 + (h/2R)^2]} \frac{\lambda_{\text{eff}}}{\lambda_{\text{eff}} + h/\varepsilon_b}, \quad (14)$$

where $P_3(z)$ is the out-of-plane polarization directed along z axis, $\bar{P}_3$ is the z -averaged polarization; λ_{eff} is the effective screening length, which contributions come from to the top ionic-electronic screening charge layer and the bottom electrode [see in Fig. 1(c)]. Note that Eq. (14) for nanoislands transforms into Eq. (6) for thin films in the limiting case $R \rightarrow \infty$.

Expressions (7a)–(7f) for renormalized coefficients are approximately valid for nanoislands, at that u_m^* is given by Eq. (13) and depolarization field is given by Eq. (14). The latter leads to the depolarization field contribution $\frac{\lambda_{\text{eff}}}{2\varepsilon_0 \varepsilon_b (h + \lambda_{\text{eff}}) [1 + (h/2R)^2]}$ in Eq. (7b).

To derive relatively simple equation for the critical height of HZO nanoislands, we should assume that the reversible spontaneous polarization $\bar{P}_s$ relatively weakly depends on the mismatch strain and the island height in the deep FE o phase. Using these assumptions, an approximate transcendental equation for the critical thickness h_{cr} acquires

the form:

$$\begin{aligned} & \tilde{\beta}_{r3} + \frac{\lambda_{\text{eff}}}{2\varepsilon_0 \varepsilon_b (h_{\text{cr}} + \lambda_{\text{eff}}) [1 + (h_{\text{cr}}/2R)^2]} + \frac{g}{h_{\text{cr}} \Lambda_P + h_{\text{cr}}^2/\pi} \\ & - u_m \left(1 - \exp\left[-\frac{h_d}{h_{\text{cr}}}\right] \right) \exp\left[-\frac{h_{\text{cr}}}{2R}\right] \\ & \times \left(\tilde{q}_{13} + \tilde{q}_{23} - \frac{c_{13} + c_{23}}{c_{33}} \tilde{q}_{33} \right) = -\Delta_s, \end{aligned} \quad (15)$$

where the positive parameter Δ_s is introduced in Eq. (12). Considering the same assumptions as for thin HZO films, the parameter Δ_s can be regarded as mismatch independent. All figures below are calculated using exact Eqs. (7)–(8), because the accuracy of approximate Eq. (15) is not high enough near the boundaries between different phases. However, Eq. (15) well describes qualitatively the critical sizes of HZO nanoislands.

Phase state of the epitaxial HfO_2 nanoislands as a function of mismatch strain u_m and their height h is shown in Fig. 4 for several aspect ratios $h/R = 0.4$ (which corresponds to the strongly flattened island), $h/R = 1$ (which corresponds to the slightly flattened island) and $h/R = 2$ (which corresponds to the island with a square cross section in the plane, normal to the substrate surface) and fixed effective screening length $\lambda_{\text{eff}} = 0.2$ Å. Since the domain formation starts λ_{eff} larger than 1 Å, we postpone the case of large screening lengths for next studies.

It is seen that the FE o phase can be stable at compressive mismatch strains $u_m < u_{\text{min}}$ only, where the minimal strain u_{min} changes from -1.15% at $h/R = 0.4$ to -1.6% at $h/R = 2$ due to the size effect of the depolarization field [see Eq. (14)]. The area of the FE o-phase region decreases strongly with increase in the aspect ratio h/R , being replaced by the reentrant nonpolar m phase (compare the first, the second, and the third columns in Fig. 4). The FE o phase disappears completely for $h > h_{\text{max}}$, where h_{max} increases and saturates with increase in R , increases with increase in the maximal compressive strain u_{max} and decreases strongly with increase in λ_{eff} . In particular, the FE o phase disappears completely for $h > 4R$, $\lambda_{\text{eff}} = 0.2$ Å, and $u_{\text{max}} = -3\%$.

Color scale in Figs. 4(a)–4(c) is the absolute value of $\bar{P}_s$ in the deepest potential well of the free energy (7). As in the case of thin films, the boundary between the FE o phase (with $\bar{P}_s > 0$) and nonpolar m phase (with $\bar{P}_s = 0$) is sharp for nanoislands, being the first-order phase transition curve describing the dependence of the island critical height h_{cr} on the mismatch strain u_m . It is seen from Eq. (15) that the strain-dependent critical height of the ferroelectricity appearance ($h_{\text{cr}}^{\text{max}}$) is determined by the size dependence of the effective mismatch strain u_m^* [proportional to the function $u_m(1 - \exp[-\frac{h_d}{h}])\exp[-\frac{h}{2R}]$ according to Eq. (13)]. Due to a possible dislocation appearance, the power decay of mismatch strains occurs for $h > h_d$; the lateral relaxation of strains occurs at $h > 2R$. Thus, the estimations $h_{\text{cr}}^{\text{max}} \leq 10h_d$ and $h_{\text{cr}}^{\text{max}} \leq 3R$ may be valid. The critical height of the spontaneous polarization disappearance ($h_{\text{cr}}^{\text{min}}$) is determined by the size dependence of the depolarization field [proportional to the function $\frac{\lambda_{\text{eff}}}{2\varepsilon_0 \varepsilon_b (h + \lambda_{\text{eff}}) [1 + (h/2R)^2]}$ according to Eq. (14)] and correlation effects (proportional to the function $\frac{g}{h\Lambda_P + h^2/\pi}$). Hence,

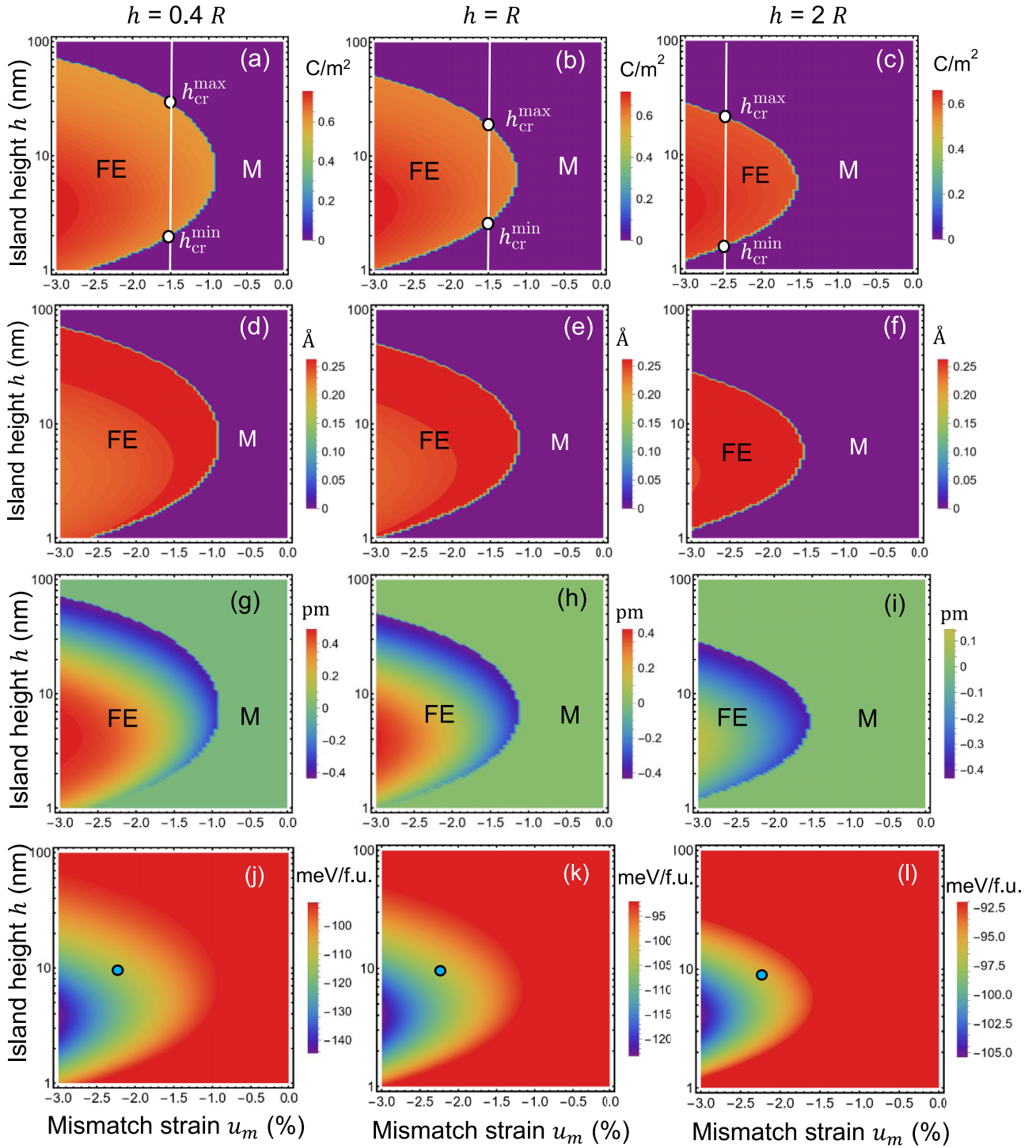


FIG. 4. (a)–(c) The absolute value of polarization $\bar{P}_s$, (d)–(f) the amplitude of nonpolar order parameter $|\bar{Q}_{Y2s}|$, (g)–(i) the difference $|\bar{Q}_{Y4s}| - |\bar{Q}_{Y2s}|$, and (j)–(l) the deepest minimum of the free energy density $f_{o\text{-phase}}^{\min}$ as a function of mismatch strain u_m and HfO₂ island height h calculated for different aspect ratios $h/R = 0.4$ (a), (d), (g), (j), 1 (b), (e), (h), (k), and 2 (c), (f), (i), (l). Abbreviation “FE” is the FE o phase, “M” denotes the nonpolar m phase. White circles in the plots (a)–(c) correspond to $h_{cr}^{\min}$ and $h_{cr}^{\max}$ at fixed u_m . Other parameters are $\lambda_{\text{eff}} = 0.2 \text{ \AA}$, $\Delta\rho = 10 \text{ \mu m}$, and $h_d = 10 \text{ nm}$.

the estimations $h_{cr}^{\min} \gg \lambda_{\text{eff}}$ and $h_{cr}^{\min} \gg \sqrt{g\varepsilon_0\varepsilon_b}$, made for thin films, are valid for nanoislands also. The critical heights $h_{cr}^{\min}$ and $h_{cr}^{\max}$ for the fixed mismatch strain u_m are shown by white circles in Figs. 4(a)–4(c). For incomplete screening conditions ($\lambda_{\text{eff}} > 0$), the FE o phase is thermodynamically

stable in the HZO nanoislands with thickness $h_{cr}^{\min} < h < h_{cr}^{\max}$ when $R > R_{\min}$. The minimal lateral size $R_{\min}$ is determined by the maximal mismatch strain $u_{\max}$. The thicknesses $h_{cr}^{\min}$ and $h_{cr}^{\max}$ become equal at $R \rightarrow R_{\min}$ and disappear at $R < R_{\min}$.

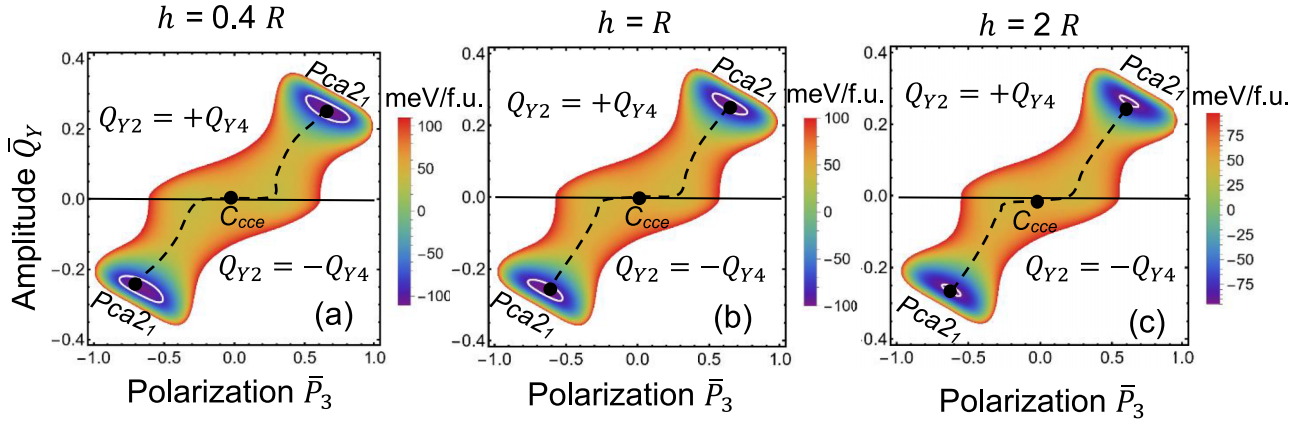


FIG. 5. Free energy density as a function of $\bar{P}_3$ and $\bar{Q}_Y$. The amplitude $\bar{Q}_Y = Q_{Y2} = Q_{Y4}$ in the top half-plane and $\bar{Q}_Y = Q_{Y2} = -Q_{Y4}$ in the bottom half-plane. The plots are calculated for different radii (a) $R = 25$ nm, (b) 10 nm, (c) 5 nm, $h = 10$ nm, $\lambda_{\text{eff}} = 0.2$ Å, and $u_m = -2.2\%$. Chosen values of h , u_m , and λ_{eff} correspond to the blue circles in (a), (b), and (c), respectively. White elliptic contours in the plots correspond to the energy of the bulk m-phase $f_m = -92$ meV/f.u. Dashed curves show the polarization switching path, which corresponds to the lowest energy barrier $f_{Cce} = +48$ meV/f.u. Other parameters are the same as in Fig. 4.

Color scale in Figs. 4(d)–4(f) is the absolute value of $|\bar{Q}_{Y2s}|$ in the deepest potential well. The difference $|\bar{Q}_{Y4s}| - |\bar{Q}_{Y2s}|$ is shown in Figs. 4(g)–4(i). It is seen that the difference $|\bar{Q}_{Y4s}| - |\bar{Q}_{Y2s}|$ is very small: it does not exceed 0.42 pm, that is 60 times smaller than the maximal value of $\bar{Q}_{Y2s}$ (~ 25 Å). The deepest minimum of the free energy density, $f_{\text{o-phase}}^{\text{min}}$, is shown in Figs. 4(j)–4(l) as a function of u_m and h . A red background in the figure corresponds to the bulk m phase with the energy density $f_m = -92$ meV/f.u. [10].

Color maps of the free energy density of epitaxial HfO_2 nanoislands as a function of $\bar{P}_3$ and $\bar{Q}_Y$ are shown in Figs. 5(a)–5(c), where the amplitude $\bar{Q}_Y = Q_{Y2} = Q_{Y4}$ in the top half-plane and $\bar{Q}_Y = Q_{Y2} = -Q_{Y4}$ in the bottom half-plane. The figures are calculated for the same ratios h/R as in Fig. 4 and fixed other parameters ($h = 10$ nm, $\lambda_{\text{eff}} = 0.2$ Å, and $u_m = -2.2\%$). Similarly to the situation in thin HfO_2 films, the switching path between the $-\bar{P}_s$ and $+\bar{P}_s$ states goes through the virtual C_{cce} phase in HfO_2 nanoislands, because the lowest barrier of polarization switching b_{af} is about +48 meV/f.u., which corresponds to the energy of C_{cce} phase counted from the t phase [see the color scale and dashed curves in Figs. 5(a)–5(c)]. An activation field E_{af} of polarization reversal, estimated as $E_{\text{af}} \cong b_{\text{af}}/\bar{P}_s$, is about 0.7–0.8 MV/cm at $V_{\text{f.u.}} \approx 134$ Å³. The values of E_{af} are very close to the ones calculated in thin films in Sec. II B.

Let us underline an evident similarity of the free energy maps of HfO_2 nanoislands, shown in Fig. 5, to the free energy maps of HfO_2 thin films, shown in Fig. 3. Both figures are almost the same, and the increase in λ_{eff} leads to the same changes of the energy surface as the increase in h . The result can be explained by the similar influence of these parameters on the depolarization field factor of thin films and nanoislands, namely $\frac{\lambda_{\text{eff}}}{2\epsilon_0\epsilon_b(h+\lambda_{\text{eff}})}$ and $\frac{\lambda_{\text{eff}}}{2\epsilon_0\epsilon_b(h+\lambda_{\text{eff}})[1+(h/2R)^2]}$, which increase proportional to $\frac{1}{1+(h/\lambda_{\text{eff}})}$ with increase in λ_{eff} . The factor of nanoislands increases proportional to $\frac{1}{1+(h/2R)^2}$ with increase in h . Thus, the key factor influencing the free energy surface, phase diagrams and polar properties are the screening

length-thickness ratio $\frac{\lambda_{\text{eff}}}{h}$ for thin films and the aspect ratio $h/2R$ for nanoislands (at fixed $\lambda_{\text{eff}} > 0$).

D. Applicability of theoretical results to real HZO films

The applicability of the results obtained in sections B and C to real structures, which contain thin or ultrathin HZO films, is determined by the film growth conditions and the growth mechanism realized in concrete cases. As a rule, three modes of epitaxial film growth are usually distinguished (see, e.g., Ref. [61] and references therein). In the Frank-van der Merwe regime, atomic monolayers are sequentially formed on the substrate. In the Volmer-Weber regime, nanoislands grow on the substrate, which surface remains partially uncovered by the film material. In the intermediate Stranski-Krastanov regime, a monolayer is formed on the substrate at first (as in the Frank-van der Merwe regime), but after that the Volmer-Weber regime of nanoisland growth is realized. The growth regime, that is realized in each specific case, depends on the ratio of surface energies of the film, substrate, and film-substrate interface.

In fact, Sec. II B considers the film grown in the Frank-van der Merwe regime, and Sec. II C considers the film grown in the Volmer-Weber regime within an idealized approximation of the nanoislands by a cylindrical shape, which allows obtaining semianalytical results. Real nanoislands can have a wide variety of shapes: domes, pyramids, etc., (see, e.g., Refs. [62–65]). In both cases, the mismatch-dependent critical thicknesses, $h_{\text{cr}}^{\text{min}}$ and $h_{\text{cr}}^{\text{max}}$, exist under incomplete screening conditions at $\lambda_{\text{eff}} > 0$. The FE o phase is thermodynamically stable in HZO films with thickness $h_{\text{cr}}^{\text{min}} < h < h_{\text{cr}}^{\text{max}}$.

However, there is a significant difference. The critical thicknesses of the film grown in the Frank-van der Merwe regime are determined by the film and substrate lattice constants mismatch u_m (via the epitaxial strains caused by the mismatch) and effective screening length λ_{eff} (via the conductivity of electrodes and/or screening conditions at the electrically open surfaces). The critical thickness of the film grown in the Volmer-Weber regime also depends strongly

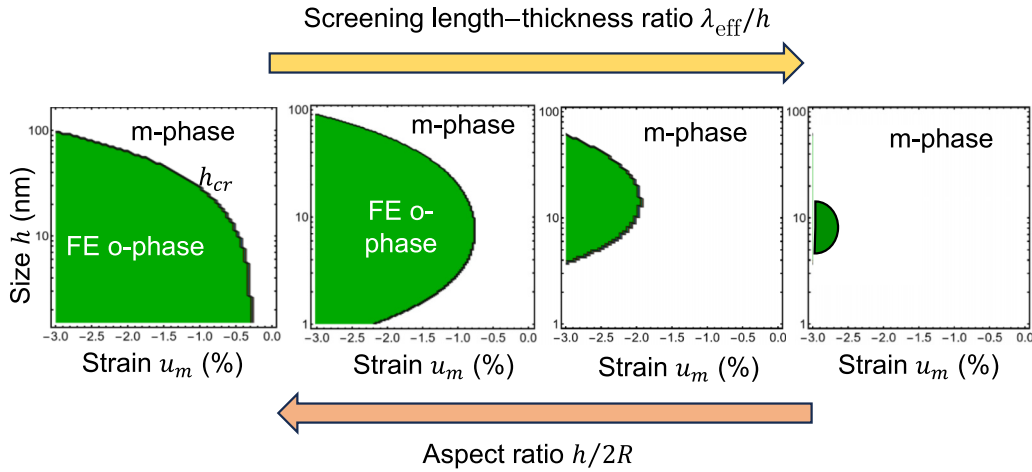


FIG. 6. Schematic evolution of the phase diagrams of nanosized HZO subjected to epitaxial mismatch strain u_m , which happens with increase in the screening length–thickness ratio λ_{eff}/h and/or with decrease in the aspect ratio $h/2R$. The black solid curve, which separates the FE o phase from the m phase, gives the dependence of the critical size h_{cr} on the strain u_m at fixed other parameters.

on the average lateral size $2R$ of the nanoisland because of the dependence of mismatch strain on the aspect ratio [see Eq. (13), where we neglected the spread of the size in the first approximation]. Due to the formation of sufficiently large islands in the HZO films, grown in the Stransky-Krastanov regime, the presence of an additional monolayer at the substrate changes slightly the overall physical picture. Thus, it can be expected that the conclusions obtained for the Volmer-Weber regime are also applicable (at least qualitatively) to the Stransky-Krastanov regime.

Since the modern technological processes for growing thin HZO films implement the Volmer-Weber regime (see, e.g., Refs. [58,66,67]), the critical film thicknesses of the ferroelectricity appearance and disappearance give us (at least by an order of magnitude) the diameter $2R$ of the nanoislands, from which the film is composed. At that, the key factors influencing the free energy surface, phase diagrams, and corresponding polar properties of nanosized HZO are screening length–thickness ratio λ_{eff}/h (for epitaxial thin films) and the aspect ratio $h/2R$ (for nanoislands). Schematic evolution of the phase diagrams of nanosized HZO subjected to epitaxial mismatch strain u_m , which happens with increase in the screening length–thickness ratio λ_{eff}/h and/or the aspect ratio $h/2R$, is shown in Fig. 6.

The ranges of critical thickness 10–100 nm, calculated in this work for small $\lambda_{\text{eff}} \cong 0.1\text{--}1 \text{ \AA}$ (which corresponds to TiN electrodes), are within the thickness range listed in Table 1 in Ref. [4]. At the same time, the critical thickness depends strongly on the mismatch strain (see Fig. 2). According to the experimental results [4,68], ferroelectricity is observed in the HZO films with 50% of Zr or significant percentage of other dopants. Therefore, direct comparison with available experimental results is difficult. Using the lattice parameters of HfO_2 , $a = 5.04 \text{ \AA}$, and $b = 5.23 \text{ \AA}$ according to Materlik *et al.* [69], we estimated mismatch strains in thin epitaxial HfO_2 films on the different substrates (see Table S6 in Sec. S3 [43]). Since most experimental observations of the robust ferroelectricity in epitaxial thin HfO_2 films correspond to the heterostructures $\text{TiN}/\text{HfO}_2/\text{TiN}$ and $\text{TiN}/\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{TiN}$ (see Table 1 in Ref. [4]), we can say that the ferroelectricity

is supported by high compressive mismatch strains in the case (the nominal unrelaxed misfit strain is as high as -20%). This experimental observation is in qualitative agreement with our theoretical predictions. Note that real mismatch strains are much smaller in the $\text{TiN}/\text{HfO}_2/\text{TiN}$ heterostructure due to the strain relaxation effects.

III. CONCLUSIONS

Using the LGD free energy functional considering higher powers, biquadratic, and trilinear couplings of the polar Γ_{3-} , nonpolar Y_{2+} , and antipolar Y_{4-} modes, we calculated the strain-dependent critical sizes of the ferroelectricity appearance and disappearance, analyzed the mismatch strains influence and size effect of the phase diagrams, polar, antipolar, and nonpolar order parameters, and polarization switching barrier in epitaxial HfO_2 thin films and nanoislands with the out-of-plane spontaneous polarization.

We have shown that the critical thickness/height of the out-of-plane spontaneous polarization disappearance $h_{\text{cr}}^{\text{min}}$ is determined by the size dependence of the depolarization field and correlation effects. The critical thickness/height of the ferroelectricity appearance $h_{\text{cr}}^{\text{max}}$ is determined by the size dependence of the effective mismatch strain u_m^* considering possible appearance of misfit dislocations and lateral relaxation of strains. The key factors influencing the free energy surface, phase diagrams, and order parameters of nanosized HZO are thickness–screening length ratio λ_{eff}/h (for epitaxial thin films covered by electrodes with effective screening length λ_{eff}) and the aspect ratio $h/2R$ (for nanoislands with the lateral size $2R$).

In this work we consider the single-domain state of the out-of-plane spontaneous polarization in epitaxial HfO_2 thin films and nanoislands, which is stable at small effective screening lengths, $\lambda_{\text{eff}} \leq 1 \text{ \AA}$. The domain formation should occur at larger λ_{eff} ; it may decrease the critical thickness of ferroelectricity disappearance, and the case of larger λ_{eff} deserves further studies. Our approach can be generalized for HZO thin films and nanoparticles, providing that corresponding parameters of the free energy are known from the first-principles calculations.

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work are obtained and visualized using a specialized software, Mathematica 14.0 [70].

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 M.V.S. proposed the concept and 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 [70].

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