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Ferroelectricity in Pb$(\mathrm{Zr}_{0.5}\mathrm{Ti}_{0.5})\mathrm{O}_3$ thin films: Critical thickness and 180° stripe domains

Zhongqing Wu, Ningdong Huang, Zhirong Liu, Jian Wu, Wenhui Duan,* and Bing-Lin Gu
Center for Advanced Study and Department of Physics, Tsinghua University, Beijing 100084, People's Republic of China

Xiao-Wen Zhang
State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

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The ferroelectric properties of disorder Pb$(\mathrm{Zr}_{0.5}\mathrm{Ti}_{0.5})\mathrm{O}_3$ thin films are investigated with Monte Carlo simulations on the basis of a first-principles-derived Hamiltonian. It is found that there exists a critical thickness of about three unit cells (~ 12 Å) below which the ferroelectricity disappears under the condition that the in-plane polarizations are suppressed by sufficient clamping effect. Above the critical thickness, periodic 180° stripe domains with out-of-plane polarizations are formed in the systems in order to minimize the energy of the depolarizing field. The stripe period increases with increasing film thickness. The microscopic mechanism responsible for these phenomena is discussed.

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During the past decade, ferroelectric thin films have been investigated with a great deal of interest not only because their physical properties are different from those of bulk materials[1] but also because they are promising for microelectronic and micromechanical applications.[2] A fundamental problem attracting considerable attentions for ferroelectric thin film is the critical thickness for the ferroelectricity to occur. The observations that the ferroelectric ground states exist in 40-Å-thick perovskite oxide film[3] and in 10-Å-thick crystalline copolymer[4] seem to suggest the absence of the critical thickness. Some theoretical investigations supported that opinion by predicting ferroelectric ground states in various perovskite slabs.[5,6] Recently, Junquera and Ghosez investigated a realistic ferroelectric-electrode interface and, contrary to the current thought, revealed a critical thickness of about six unit cells in BaTiO_3 thin film.[7] It was proposed that the depolarizing electrostatic field[8] is responsible for the disappearance of the ferroelectricity. However, in their study, only the monodomain case, where the atomic off-center displacements in every cell are the same, was considered. In fact, polydomains or other atomic off-center displacements may come into being to remove the depolarizing electrostatic field. For example, Fu and Bellaiche found that a size reduction can lead to an unusual atomic off-center displacements vortex pattern in BaTiO_3 quantum dots.[9] Therefore, it is worth investigating whether the film will form special atomic off-center displacements pattern to remove the depolarization field and whether the nonzero critical thickness still exists in that case.

In this paper, by use of a first-principles-based approach, the ferroelectricity of disorder Pb$(\mathrm{Zr}_{0.5}\mathrm{Ti}_{0.5})\mathrm{O}_3$ thin films is investigated to clarify the role of the strain and the off-center displacement pattern in determining the critical thickness. It is shown that the ferroelectricity in thin films is closely related to the strain constraint imposed by the substrate. When the thin films are free from constraint, a nonzero polarization with an in-plane direction always exists in the system, which does not disappear even in the monolayer films. When there is a compressive strain, the in-plane polarization is suppressed while the out-of-plane polarization exhibits a strong dependence on the film thickness. Above a critical thickness of about three unit cells, the out-of-plane polarization forms periodic 180° stripe domains, and the period increases with the film thickness. Below the critical thickness, the stripe domain structure disappears, which suggests that the ferroelectricity can be suppressed even in the absence of the depolarizing electrostatic field. The orientation dependence of dipole-dipole interaction is revealed to be responsible for these phenomena, which is expected to generally work in perovskite ferroelectric films.

We adopt the effective Hamiltonian of PZT alloys proposed by Bellaiche, Garcia, and Vanderbilt[10,11] and Zhong *et al.*[12] to predict the properties of the disorder Pb$(\mathrm{Zr}_{0.5}\mathrm{Ti}_{0.5})\mathrm{O}_3$ thin film surrounded by the vacuum. All the parameters of the Hamiltonian are derived from the first-principles calculations and are listed in Refs. 10 and 11. Cohen[13] and Meyer *et al.*[14] demonstrated that the effect of surface relaxation is significant in perovskites. However, it should be noted that the effect of surface relaxation has been considered implicitly in our simulations,[15] and the influence of the surface upon the ferroelectric order parameter is modest, as pointed out by Meyer *et al.*[14] In our simulations, we do not include an external term of surface effect proposed by Fu and Bellaiche while simulating nanoscopic structures, since they demonstrated that the term has almost no effect on the polarization pattern.[9] From the above effective Hamiltonian, Monte Carlo simulations are conducted for large supercells typically containing between 5000 and 50 000 atoms mimicking the studied structures. The supercell average of the local soft modes $\mathbf{u}_i$ (i is the cell index) is directly proportional to the macroscopic electrical polarization. The influence of the substrate is imposed by confining the homogeneous in-plane strain.

To efficiently calculate the long-range dipole-dipole interaction energy in thin films which lack the periodicity in the out-of-plane direction, we adopt the corrected three-dimensional Eward method, whose validity has been verified analytically by Bródka and Grzybowski.[16] In that scheme, a small empty space (about three times the film thickness) in-

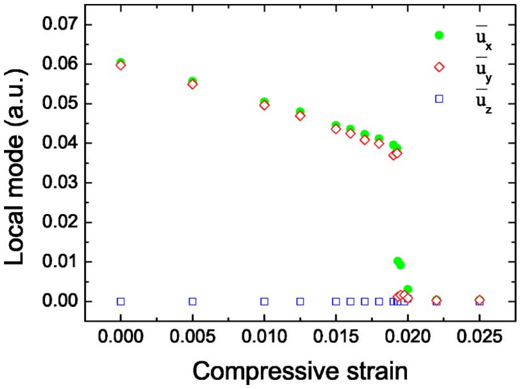

FIG. 1. The dependence of the supercell average ($\overline{u_x}$, $\overline{u_y}$, $\overline{u_z}$) of the local soft mode on the strain for the film with the thickness of four unit cells (i.e., $d=4$).

troduced in the simulation box to surround the film can lead to very well converged results. It is noted that the Eward sum we adopted for the macroscopic sphere is immersed in vacuum. Therefore the effect of depolarization field is considered in our model.

In our simulation, the z axis ([001] direction) lies along the growth direction of the film, and the x and y axes are chosen to be along the pseudocubic [100] and [010] directions. The film thickness d is measured by the number of unit cells along the z axis. As the first step, we simulate the ferroelectric properties of thin films without any constrain from the substrate, i.e., the free thin films are considered. It is found that for all the film thicknesses considered, there always exists a nonzero polarization along the x or y axis, and correspondingly, a tensile strain of about 2% along the same direction. (Data are not shown here.) It is consistent with the simulation results in quantum dots[9] where the normal component of polarization near the surface is suppressed by the vacuum. It also verifies the absence of any critical thickness for ferroelectricity in thin films under the condition of vanishing internal stress.[6]

In actual systems, the film strain will be imposed by the substrate (clamping effect) which has important effects on the ferroelectricity.[17–20] So we consider the strain effects in our simulations. We calculate the supercell average ($\overline{u_x}$, $\overline{u_y}$, $\overline{u_z}$) of the local soft mode as functions of the in-plane strain. The result with $d=4$ is shown in Fig. 1. It is clearly seen that $\overline{u_x}$ and $\overline{u_y}$ decrease with increasing (compressive) strain and disappear after the strain reaches a critical value, while $\overline{u_z}$ keeps zero at any strain. The disappearance of the in-plane polarization is of the first order. It should be noted that when the in-plane strain is fixed, $\overline{u_x}$ is equal to $\overline{u_y}$ due to the symmetry requirement. Small difference between $\overline{u_x}$ and $\overline{u_y}$ results from our treatment of avoiding effects of symmetry-equivalent rotations of the order parameter.[12] From the above results, it can be concluded that the ferroelectricity does not disappear in thin films (even for the monolayer case) if the strain imposed by the substrate is not strong enough to suppress the in-plane polarization.

Although the average value of the out-of-plane polarization ($\overline{u_z}$) always keeps zero, the local mode u_z exhibits completely different behavior below and above the critical strain. u_z is substantially small in any unit cell below the critical strain, while it quickly increases nearby the critical strain. Above the critical strain, periodic 180° stripe domains are formed in the system. An example with stripe domains aligned along y axis is shown in Fig. 2 for a thin film with $d=4$ under 2% compressive strain. The domain walls are rather diffuse and the spatial variation of u_z is close to a cosine function. The similar stripe domain stabilized by strain has also been found by Tinte and Stachiotti.[21] In the general cases, we find that the direction along which the stripe domains align is not certain. It may be the x or y axis and may also have an angle with the x or y axis. In each stripe domain, the z component (u_z) of local soft modes have the same sign. In other words, the stripe structure extends through the film in the z direction, which is important for ferroelectric field effect and has been observed in PZT[22] and $PbTiO_3$ (PT) film.[23] It is noted that the stripe domain only appears above a certain film thickness. We calculate many kinds of supercells with $d<4$. No domain structure or ferroelectricity is found in these supercells at 50 K even when the compressive strain is as large as 4%. Therefore, there is a critical thickness of about three unit cells (~1.2 nm) in disorder $Pb(Zr_{0.5}Ti_{0.5})O_3$ thin films below which the ferroelectricity disappears at large strains ($>2\%$).

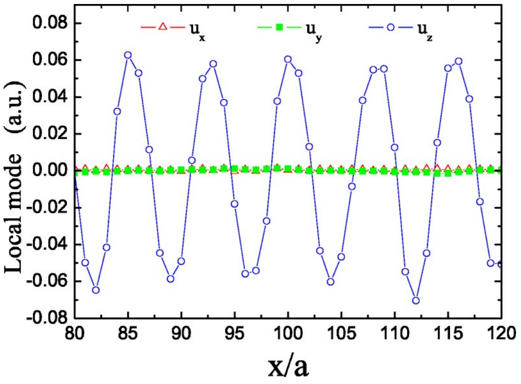

FIG. 2. The y-z plane average (u_x, u_y, and u_z) of the local soft mode as a function of x/a (a is the lattice constant) for $120\times5\times4$ supercell under 2% compressive strain. Only the data of $80<x<120$ are shown.

The dependence of ferroelectric-paraelectric phase transition temperature T_c on the film thickness also supports the existence of the critical thickness, as shown in Fig. 3. The temperature is rescaled as in Ref. 24 due to the fact that the effective-Hamiltonian approach overestimates T_c. We find that T_c, determined by the temperature dependence of the polarization amplitude (Fig. 3 inset), is far below T_c of the bulk material (dash line in Fig. 3). This is consistent with the experimental observation of a significant decrease of T_c in thinner films (below 20 nm).[23] As the film thickness decreases, T_c decreases quickly. Extrapolation of T_c in Fig. 3 shows that the ferroelectricity disappears at the thickness of about $d=3$. It is interesting to note that Ghosez and Rabe also observed a critical thickness of three layers in $PbTiO_3$ with completely different electrical boundary condition (perfectly screened condition).[5] Then, it seems that the electrical boundary conditions have little effect on the critical thickness, which is contrary to the common view.

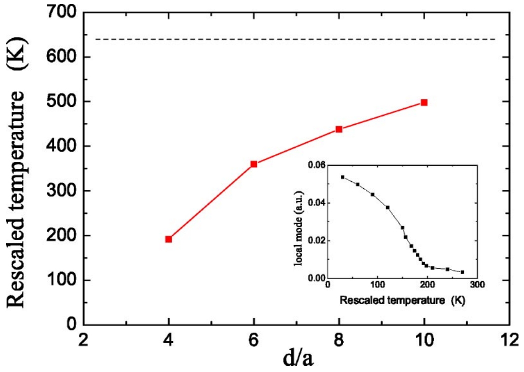

FIG. 3. Ferroelectric-paraelectric phase transition temperature as the function of the film thickness d under 2% compressive strain. Dash line corresponds to T_c of the bulk material. Inset: the polarization amplitude as a function of the temperature for $d=4$.

The stripe period for the film with $d=4$ (Fig. 2) is determined to be 7.1 ± 0.5 cell units ($\simeq 2.8\pm0.2$ nm) according to the fact that 17 periodic stripe domains are observed in an $120\times5\times4$ supercell. We find that the period λ of the strip domain has the same order of the film thickness d and increases with film thickness as shown in Fig. 4.

Our predictions are helpful for understanding many experimental results. The stripe domains revealed here, with out-of-plane polarizations and 180° domain walls extending through the film, are essentially identical to what have been observed in PT films by Streiffer *et al.* through the x-ray scattering measurements.[23] Their observed stripe period and the dependence on the film thickness are consistent with our calculated results. Based on our results, it is easy to understand why no detectable polarization was probed by the electrostatic force microscopy along the perpendicular directions of PZT film,[22] since it is demonstrated that the net polarization vanishes by forming the stripe domain with very short period.

From a fundamental point of view, ferroelectricity in materials is determined by the competition between the long-range electrostatic and the short-range covalent interactions. Our previous work revealed that the orientation dependence of dipole-dipole interaction is responsible for the appearance of unexpected phases in compositional modulation PZT alloys near the morphotropic phase boundary.[25] Here we indicate that the existence of the critical thickness and periodic stripe domains can be also understood by considering the orientation dependence of dipole-dipole interaction. The long-range polarization interactions are described in dipole-dipole interaction energy[11,12]

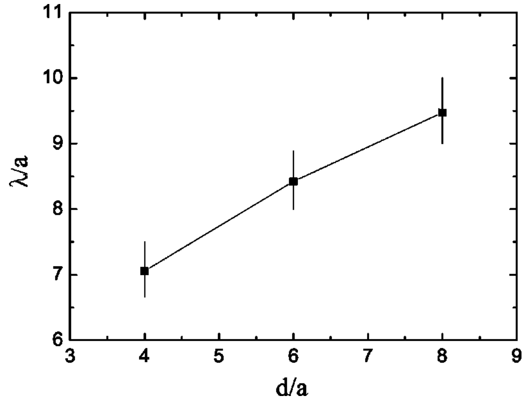

FIG. 4. The effect of the film thickness on the stripe period under 2% compressive strain. The simulations for the period of stripe domain are conducted respectively for $120\times5\times4$, $160\times5\times6$, and $180\times5\times8$ supercells. The errors are also indicated in the figure.

$$E_{\mathrm{dipole}} = \frac{Z^{*2}}{\epsilon_\infty}\sum_{i<j}\frac{\mathbf{u}_i\cdot\mathbf{u}_j - 3(\hat{\mathbf{R}}_{ij}\cdot\mathbf{u}_i)(\hat{\mathbf{R}}_{ij}\cdot\mathbf{u}_j)}{R_{ij}^3}, \tag{1}$$

where Z^* is the Born effective charge and ϵ_∞ the optical dielectric constant of the material. To simplify the theoretical analyses, we assume that all $\mathbf{u}_i$ are along the z axis. For the monolayer film, the dipole-dipole interactions are constrained to be intralayered. Then the second term of Eq. (1) is zero and the dipole-dipole interaction coefficient is always positive for the ferroelectric phase. Therefore, in the monolayer film, the dipole-dipole interaction does not support the formation of ferroelectricity along the z axis. The ferroelectric phase will not appear in this case unless the in-plane polarization is considered, as what we have demonstrated above.

In contrast to the intralayer dipole interaction, the interlayer dipole interaction is in favor of the ferroelectric order, and its effect becomes more and more important with increasing film thickness. So after the film thickness reaches a certain critical value, the ferroelectricity appears. If the depolarization field has not been eliminated by such effects as the surface charge screening, domain structures will occur to decrease the intralayer dipole interaction energy.

The variation of the stripe period with the film thickness comes from the delicate balance between the long-range dipole interaction and the short-range interaction. The dipole-dipole interaction energy increases with increasing modulation period, while the short-range interaction energy decreases with increasing period. Compared with the short-range interaction, the dipole interaction is long-range and thus more closely related to the film thickness. This feature determines that the stripe period varies with the film thickness. To further clarify this point, we present a simple numerical analysis in the following. The local modes are assumed to vary along the x axis as

$$\mathbf{u_z} = u_{z0}\cos\left(\frac{2\pi x}{\lambda}\right), \tag{2}$$

where λ is the period of the strip domain and u_{z0} is the amplitude of local mode u_z. In Fig. 5, the average dipole-dipole interaction energy and short-long interaction energy of one unit cell are shown as functions of λ for thin films with different thickness. The larger the period is, the more quickly the dipole-dipole interaction energy decreases with increasing film thickness. On the contrary, the energy difference between different modulation periods is almost independent of the film thickness for the short-range interaction, i.e., increasing the film thickness only shifts the curve upward. Therefore, the minimum of the total energy (see the inset in

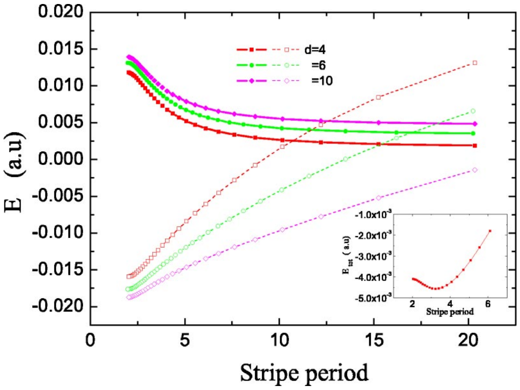

FIG. 5. The dipole-dipole interaction energy (dash line) and short-range interaction energy (solid line) as functions of the stripe period λ for the thin film with different thickness *d*. Inset: the sum of the dipole-dipole interaction energy and short-range interaction energy as functions of the stripe period for $d=4$.

Fig. 5) moves to higher λ values while increasing the film thickness.

The formation of domain structure helps to decrease the dipole interaction energy by screening the depolarizing electrostatic field. However, whether the polarization will appear is also affected by the short-range interaction. If the minimum of the total energy of domain structure is higher than that of the paraelectric phase, the ferroelectricity will be suppressed, which is just the cases occurring below the critical film thickness (note that the total energy shown in Fig. 5 will increase with decreasing thickness). It suggests that the critical thickness exists even if the 180° domains are formed to screen the depolarizing field.

In summary, we have demonstrated the existence of periodic 180° stripe domains with the out-of-plane polarization and a critical thickness for ferroelectricity in disorder PZT thin films, which may widely exist in perovskite thin films. It seems that the electrical boundary conditions have little effect on the critical thickness since the critical thickness is almost the same for completely different electrical boundary condition. It is pointed out that the critical thickness appears only when the strain imposed by the substrate is strong enough to suppress the in-plane polarization. Otherwise, ferroelectricity can be maintained even in monolayer film.

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*Author to whom correspondence should be addressed.

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