Properties of Pb(Zr,Ti)O$_3$ ultrathin films
under stress-free and open-circuit electrical boundary conditions

Emad Almahmoud, Yulia Navtsenya, Igor Kornev, Huaxiang Fu and L. Bellaiche

*Physics Department, University of Arkansas, Fayetteville, Arkansas 72701, USA*

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Abstract

A first-principles-based scheme is developed to simulate properties of (001) PbO-terminated Pb(Zr$_{1-x}$Ti$_x$)O$_3$ thin films that are under stress-free and open-circuit boundary conditions. Their low-temperature spontaneous polarization never vanishes down to the minimal thickness, and continuously rotates between the *in-plane* $<010>$ and $<110>$ directions when varying the Ti composition around $x = 0.50$. Such rotation dramatically enhances piezoelectricity and dielectricity. Furthermore, the *order* of some phase transitions changes when going from bulk to thin films.
Ferroelectric thin films are currently of enormous technological interest, mostly because of the need in devices’ miniaturization [1]. Many fundamental questions are still unanswered/unsettled in these low-dimensional systems. For instance, whether or not there is a critical thickness below which no ferroelectricity can occur is still under debate [2–6]. Similarly, the precise effects of surface on properties of thin films are opened for discussion [5,7–10]. One may also wonder how striking features exhibited by some bulk materials may evolve in the corresponding thin films. Typical examples of such features are the unusual low-symmetry phases - that are associated with a composition-induced rotation of the spontaneous polarization and with an enhancement of dielectric and piezoelectric responses – recently discovered in the morphotropic phase boundary (MPB) of various alloys [11–15].

One reason behind this lack of knowledge is that thin (and, particularly, ultrathin) films are difficult to synthesize in a good quality form, and their characterization is by no means straightforward. Similarly, realistically simulating thin films is a theoretical challenge. For instance, while phenomenological and \emph{ab-initio}-based models have already provided a deep insight into thin films (see Refs. [2,16–18] and references therein), such models do not usually incorporate some subtle surface-related phenomena – e.g., charge transfer and modification of ferroelectric interactions near the surface. On the other hand, direct first-principles techniques can easily include such effects [3,7–10]. However, their large computational cost currently prevents them from being used to study complex phenomena and/or complex systems (e.g., thin films made of disordered solid solutions), especially at finite-temperature. The atomistic approach of Ref. [5] is a promising technique for investigating thin films at finite temperature, but its level of accuracy depends on the surface termination [5] – which emphasizes that mimicking well surface effects on physical properties is tricky.

The aims of this article are twofold. First, to present a first-principles-derived approach allowing accurate predictions of finite-temperature properties of complex ferroelectric thin films – under stress-free and open-circuit boundary conditions. Second, to use this approach to better understand thin films by, e.g., providing answers to the questions mentioned above.

Here, we extend the \emph{ab-initio} effective Hamiltonian scheme proposed in Ref. [12] to mimic
thin films that (1) are made of Pb(Zr,Ti)O$_3$ (PZT); (2) are grown on a substrate along the [001] direction; and (3) have vacuum above them. More precisely, the total energy $E_{tot}$ of such low-dimensional systems is written as:

$$E_{tot}(\{u(i)\}, \{v(i)\}, \eta, \{\sigma_i\}) = E_{mat}(\{u(i)\}, \{v(i)\}, \eta, \{\sigma_i\})$$

$$+ \ P \sum_j u_z(j) + T \sum_j v_z(j) + S \sum_{\alpha=x,y} \sum_j u_\alpha(j) (u_\alpha(j+\hat{\alpha}) + u_\alpha(j-\hat{\alpha})),$$

where $u(i)$ are the (B-centered) local soft modes in unit cells $i$ of the film, and are directly proportional to the electrical polarization. $v(i)$ are inhomogeneous strains around the $i$ site, while $\eta$ is the homogeneous strain tensor. $\{\sigma_i\}$ characterizes the alloy configuration [12]. $E_{mat}$ represents the intrinsic ferroelectric and elastic interactions inside the film, with its analytical expression and first-principles-derived parameters being those of PZT bulks [12]. Only four (out of 26) parameters are composition-dependent in $E_{mat}$: they are those associated with the so-called local-mode self energy [12]. The last three terms of Eq (1) mimic explicit interactions between this film and the vacuum, with the $j$ index running over all the B-sites that are the closest to the free surface. $u_x(j)$, $u_y(j)$ and $u_z(j)$ denote the (x-, y- and z-) Cartesian component of $u(j)$ along the pseudo-cubic [100], [010] and [001] directions, respectively. $\alpha$ runs over the x- and y-axes (i.e., it does not include the growth direction). $u_\alpha(j+\hat{\alpha})$ (respectively, $u_\alpha(j-\hat{\alpha})$) is the $\alpha$-component of the local mode centered on the B-site that is the closest from the $j$ site that is parallel (respectively, antiparallel) to the $\alpha$-axis. The $P$ and $T$ parameters quantify how vacuum affects the out-of-plane components ($u_z$ and $v_z$) of the local modes and inhomogeneous strains near the surface, respectively. $S$ characterizes the change, with respect to the bulk, of the short-range interaction between the in-plane components of the local modes near the surface. The $P$, $T$ and $S$ parameters are determined from first-principles calculations on a PbO-terminated (001) 17-atom slab (corresponding to 3 B-O and 4 A-O atomic layers) of a PZT alloy, as mimicked by the virtual crystal alloy approximation [19], surrounded by a vacuum region being 2 lattice-constants thick [20]. Using Eq (1) with these parameters results in an excellent agreement with first-principles predictions for the layer-by-layer profile of the polarization in various
PbO-terminated slabs (e.g., in slabs that are not used in the fitting procedure) [21].

Furthermore, the substrate is assumed to be inert, i.e. no term analogous to the last three expressions of Eq. (1) is considered at the substrate/film interface. The local modes and inhomogeneous strain-related variables are also forced to vanish in the substrate (as well as, of course, in the vacuum), being consistent with the fact that some commonly-used substrates (e.g., MgO) are ferroelectric inactive. As a result, dipole-dipole interactions only occur in the film, which automatically guarantees the generation of a depolarizing field inside the film if this latter has a component of its electrical polarization along the growth direction. Our films are thus under open-circuit electrical boundary conditions. Technically, we use the total energy of Eq. (1) in Monte-Carlo simulations to compute the finite-temperature properties of PbO-terminated PZT ultrathin films having a number of layers – to be denoted by \( d \) – ranging between 1 and 6. These simulations use the Metropolis algorithm [22], and provide the thermodynamically equilibrated local soft modes and strains as outputs for each temperature. The strains (like the local modes, but unlike the alloy configuration that is kept frozen) are allowed to fully relax. Our studied films are thus stress-free in terms of mechanical boundary conditions. Typically, we use a huge number of Monte-Carlo sweeps (up to 20 millions) and large \( 10 \times 10 \times 40 \) periodic supercells — the regions made of substrate and vacuum are thus altogether \( 40 - d \) lattice constant thick along the growth direction — to get well-converged results. The B-atoms are randomly distributed in the film.

Figure 1 displays the predicted Cartesian coordinates \(< u_x >, < u_y >, < u_z >\) of the average of the local mode vectors in the \( \simeq 20\text{Å} \)-thick \( (d=5) \) PZT film having a 50% Ti composition, as a function of the rescaled temperature [23]. Two sets of calculations are reported: one incorporating all the surface-related terms of Eq. (1) vs. another for which the \( P, T \) and \( S \) coefficients are all turned off. In both cases, each coordinate is close to zero at high temperature, indicating a paraelectric phase. As the temperature is cooled down and passes through a \( T_c \) critical temperature, \(< u_y >\) jumps – and then increases when the temperature further decreases –, while \(< u_x >\) and \(< u_z >\) remain nearly null [25]. This characterizes a transition to a ferroelectric phase having a polarization pointing along a
< 100 > direction, as in the PZT bulk having the same Ti composition of 50% [12]. However, the polarization direction in the film can be along either the y-axis (as in Fig. 1) or the x-axis, but (unlike in the bulk) never along the [001] growth direction (z-axis) – in order to avoid the generation of a huge depolarizing field [5]. Interestingly, we also found (not shown here) that thinner PbO-terminated films, down to $d=1$, also exhibit a non-zero in-plane polarization in their ground-state. Our calculations thus predict that stress-free PZT films, under open-circuit electrical boundary conditions and with Ti compositions around 50%, do not have any critical thickness below which ferroelectricity disappears! Such conclusion seems to contradict recent studies (see, e.g. Ref [3]). However, one has to realize that, e.g., Ref. 3 defines the critical thickness with respect to the vanishing of the component of the polarization along the z-axis – while we define it here with respect to the vanishing of all the components of the polarization – and studies thin films that are under a compressive strain and close (but not equal to) short-circuit electrical boundary conditions. The specificity of our present study does not allow us to generalize our findings for the mechanical and electrical boundary conditions associated with some of these previous studies.

Figure 1 further tells us that the $T_c$ Curie temperature of the $d = 5$ PZT film is around 525 K, that is lower by $\simeq 120$ K from the one of the corresponding PZT bulk [24], when turning on $P$, $T$ and $S$ in Eq (1). Neglecting such parameters leads to a much smaller $T_c(\simeq 370$ K). Such large difference in $T_c$ is found to be mostly due to the $S$ parameter (which characterizes the vacuum-induced change of short-range interaction near the surface). Interestingly, this $S$ parameter is rather sensitive to the surface termination [7]. This implies that properties of ultrathin films having two differently-terminated surfaces can dramatically differ, even if those films are made from the same material and have similar thickness.

Figure 2 sheds more light on surface effects by displaying the layer-by-layer profiles of the local modes for the $d = 5$ ultrathin film having a Ti composition of 50%, when turning on and off the $P$, $T$ and $S$ parameters at 10K. One can clearly see that, in both cases, the $y$-component of the local dipoles centered in the B-layers, that are neither located near the interface nor the surface, has a more-or-less layer-independent value that is slightly smaller
than the one in the bulk ($\approx 0.107$ a.u.). On the other hand, the B-layer that is the closest to the substrate/film interface has much smaller in-plane dipoles. The $P$, $S$ and $T$ parameters also have a significant effect on the $y$-component of the dipole in the B-layer located near the vacuum: neglecting these parameters generates a small value that is comparable to the one near the interface, while turning them on yields a large enhancement of this $y$-component in this PbO-terminated ultrathin film. Such enhancement is due to the $S$ coefficient, and explains why the Curie temperature of the film increases when turning on the surface-related parameters – since it is commonly accepted that the larger the spontaneous polarization is at small temperature (see Fig 2) the higher $T_c$ (see Fig 1) [26]. Another difference worthy to be noticed between the two kinds of calculations is about the $z$-component of the dipole in the B-layer located near the vacuum: the fitted value of the $P$ parameter leads to a $u_z$ that does not vanish anymore and that is negative – mostly characterizing Pb-displacements oriented inwards the film near the PbO-terminated surface, as consistent with Ref. [8].

We now use our scheme to investigate properties of Pb($Zr_{1-x}Ti_x$)O$_3$ films, with a fixed thickness ($d=5$) at 10K, as a function of Ti composition; all the surface relaxations of Eq (1) being included. Figure 3a shows that the spontaneous polarization is nearly parallel to a $<010>$ direction, that is perpendicular to the growth direction, for Ti compositions larger than 49.6% [25]. The associated phase, to be denoted by $T$, can be considered to be tetragonal when solely focusing on the film (otherwise, it is orthorhombic when including the substrate and vacuum in addition to the film). This polarization becomes nearly parallel to a $<110>$ pseudo-cubic direction [25] – i.e., it changes of in-plane direction – for $x$ smaller than 47.0%. This yields a phase that can be classified as orthorhombic and will be denoted as $O$. One striking feature of Fig. 3a is the behavior of the local mode for compositions decreasing between 49.6% and 47.0%: $<u_y>$ decreases, while $<u_x>$ smoothly increases and $<u_z>$ remains nearly null [25]. This characterizes a continuous (in-plane) rotation of the polarization within a (001) plane from a $<010>$ to a $<110>$ direction, with a resulting phase adopting a monoclinic $M_C$ symmetry [27]! Interestingly, the phase diagram depicted in Fig. 3a can be rather well qualitatively and quantitatively deduced from the one
occurring in the MPB of PZT bulks, when imposing the additional constraint that $\langle u_z \rangle = 0$ to these latters. As a matter of fact, at small-temperature, the polarization of PZT bulks rotates from a $\langle 010 \rangle$ (tetragonal-associated) to the $\langle 111 \rangle$ (rhombohedral-associated) direction, via a newly-discovered monoclinic $M_A$ phase (characterized by a polarization lying along $\langle uvu \rangle$ with $u < v$ [11]), for Ti compositions decreasing between 49.5% and 47.0% [12]. One noticeable difference exists, however, for the nature of the composition-induced phase transition around 47.0% between the bulks and the films: the rhombohedral $R$–to–monoclinic $M_A$ phase transition occurring in the bulk is of first-order [12,27], while the orthorhombic $O$–to–monoclinic $M_C$ transition appears to be of second-order in the film (see the continuous rotation of the mode in Fig. 3a). Interestingly, such difference is consistent with the sixth-order Devonshire theory for the $R$–to–$M_A$ and $O$–to–$M_C$ transitions [27].

Fig. 3b and 3c reveal that – when representing the dielectric and piezoelectric tensors in the basis formed by the $x$-, $y$- and $z$-axes – the $d_{16}$ piezoelectric and $\chi_{11}$ dielectric coefficients of PZT films not only peak at both transitions (as consistent with phase-transition theory) but also adopt remarkably large values anywhere between 47.0% and 49.5%. As in bulks [12,13,15], these large values result from the composition-induced rotation of the polarization. PZT ultrathin films may thus be promising to design miniaturized ferroelectric devices with large dielectric and piezoelectric responses.

In summary, we developed a first-principles-based scheme to investigate finite-temperature properties of (001) PZT stress-free ultrathin films under open-circuit electrical boundary conditions, that are PbO-terminated and have a Ti composition around 50%. We found that (1) such films do not have any critical thickness below which ferroelectricity disappears; (2) their polarization are perpendicular to the growth direction; (3) surface effects, and especially vacuum-induced changes of short-range interaction, significantly affect their local and macroscopic properties; (4) these ultrathin films exhibit a morphotropic phase boundary where their polarization continuously rotates, in a (001) plane between a $\langle 010 \rangle$ and $\langle 110 \rangle$ direction, as the Ti composition decreases; (5) such rotation leads to large piezoelectricity and dielectricity; and (6) the nature of phase transitions can change when
going from bulks to ultrathin films.

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FIGURES

FIG. 1. Film average of the cartesian coordinates ($<u_x>$, $<u_y>$ and $<u_z>$) of the local modes in the $\simeq 20\text{Å}$-thick ($d=5$) PZT film having a 50% Ti composition, as a function of the rescaled temperature. The filled symbols represent predictions when all the surface-related parameters of Eq. (1) are turned on, while the open symbols show the corresponding results when neglecting the $P$, $T$ and $S$ parameters. The y-component of the local modes is indicated via circles, while the triangles and squares display the x- and z-components, respectively, of these local modes. (The z-component of the local modes is always null for each temperature and is not shown for clarity, when neglecting the $P$, $T$ and $S$ parameters.)

FIG. 2. Local modes for the $d=5$ PZT ultrathin film as a function of the layer index along the growth direction, at 10K. An index of 1 characterizes the B-layer that is closest to the substrate, while the B-layer located near the vacuum has an index of 5. The solid line and filled symbols represent predictions when all the surface-related parameters of Eq. (1) are turned on, while the dashed line and open symbols show the corresponding results when neglecting the $P$, $T$ and $S$ parameters. The y-component of the local modes is indicated via circles, while the squares display the z-component of these local modes. (The x-component of the local modes is always null in each layer, and is not shown for clarity.) The simulated film has a composition of 50% of Ti.

FIG. 3. Properties of the the $d=5$ ultrathin PZT films as a function of Ti composition, at 10K. Panel (a) displays the film average of the cartesian coordinates ($<u_x>$, $<u_y>$ and $<u_z>$) of the local modes. Panel (b) shows the $d_{22}$ and $d_{16}$ piezoelectric coefficients. Panel (c) displays the $\chi_{11}$ and $\chi_{22}$ dielectric susceptibilities. All the parameters of Eq. (1) are turned on in these simulations. All the calculations are performed using $10 \times 10 \times 40$ supercells, except those corresponding to a Ti composition around 0.47 – for which $20 \times 20 \times 40$ supercells are used to confirm that some piezoelectric and dielectric coefficients peak around this composition, as expected by phase-transition theory.
