Phase transitions and ferroelectricity in very thin films: single- versus multidomain state

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We discuss ferroelectric phase transitions into single- and multidomain states in very thin films using continuous theory. It is shown that in nearly cubic ferroelectrics the domain state may survive down to atomic film thicknesses, unlike the single domain state, which is almost always unstable or metastable. This conclusion is valid almost irrespective of the nature of electrodes (metallic or semiconducting) and whether or not the screening carriers may be present in the ferroelectric itself.

With a thrust towards developing nanoelectronics components, like ferroelectric (FE) memories [1] the question of phase transformation and the very existence of ferroelectricity (problem of “critical thickness”, first raised decades ago [2–5]) becomes ever more important. It is a focus of experimental and theoretical research, see e.g. [6,7]. Here we will present the thermodynamic results for phase behavior of ferroelectric thin films with various electrodes and consider both homogeneous and inhomogeneous states of the film as a function of temperature and thickness. Many of prior works have given some results almost exclusively for homogeneous (monodomain) ferroelectric film states [2–5,8] with estimates for a “critical thickness” ranging from ∼1 μm [2] to a few nm [8]. We shall call critical the thickness where either homogeneous or inhomogeneous spontaneous polarization becomes unfavorable. Obviously, it is non-universal, and depends on many details like the ferroelectric material, lattice mismatch, type of electrodes, etc. For instance, we show below that the homogeneous state studied in Ref. [7] may exist only when very special conditions are met, in most real situations the FE films are likely metastable or even unstable with regards to breaking into domains. Importantly, ferroelectric domains in nearly unstrained cubic FE films may exist down to practically one unit cell.

Consider a slab of uniaxial ferroelectric occupying the region −l/2 < z < l/2 between two metallic (or degenerate semiconductor) electrodes. The polar axis is perpendicular to the film plane (parallel to the z-axis), and the bias voltage is set as (−+)U/2 at the right (left) electrode. The electric field would penetrate into electrode over very short Thomas-Fermi screening length [9], comparable to the atomic distance d_{at}, n the net carrier density, ε_s the dielectric constant, q the elementary charge. According to this equation, the band bending is antisymmetric, φ(−z) = −φ(z), φ = φ_1 e^{−κ(z−l/2)} at z > l/2, with

$$\phi_1 = (2\pi Pl + U/2)/(1 + \varepsilon_s k l/2).$$

(1)

This is the local electrodynamic boundary condition. In fact, the surface has properties different from the bulk and generally produces an effective “field” w coupled to the normal component of polarization, as was pointed out recently [11]. This, in principle, requires to add to (1) the additional boundary conditions for polarization [12,13,10,11]. The solution (1) applies when |qφ_1| ≪ μ, that translates for metal, where κl ≈ l/d_{at} ≫ 1, into 4πq|P|/κ ≈ 4πq|P|d_{at} ≪ μ, which is always satisfied. The condition would be violated in moderately/lightly doped semiconductors.

The equation of state of a ferroelectric

$$AP + B P^3 = E,$$

(2)

where the homogeneous field in the monodomain ferroelectric would be $W = (ε_s κ U − 8π P)/[(ε_s κ l^2 + 1)]$, A = (T−T_c)/T_0, T_c is the critical temperature, T_0 the characteristic temperature, T_0 ∼ T_{at} in displacive ferroelectrics, where T_{at} ∼ 10^4 − 10^6 K is the characteristic “atomic” temperature. The field $E = E_0 + E_d$, where $E_0 = U/l$ is the external and

$$E_d = −P L_0/l$$

(3)

is the depolarizing field, $L_0 = 8π/ε_s κ$ the characteristic length scale in electrodes, and we have used the fact that in a metal the screening length is small, κl ≫ 1. The homogeneous ferroelectric state in short-circuited electrodes, $U = 0$, requires an intersection of the P(E) curves given by Eqs. (2) and (3) at $P = 0$ (Fig. 1). This necessary, but not sufficient, condition is realized at

$$A < A_h ≡ −L_0/l,$$

(4)

illustrated in Fig. 1a, where curves 1-3 are plotted for T_1 > T_2 > T_3. The nontrivial solutions exist only for
T2,3. If these solutions were stable with respect to formation of inhomogeneous states, the corresponding critical temperature would be suppressed by $\Delta T_c = -T_0 L_0/l \sim 8\pi T_0 d_{at}/\epsilon l$, compared to the bulk $T_c$ [4,10]. Hence, the homogeneous ferroelectric would become impossible in films with a thickness below

$$l_{hc} = 8\pi/\epsilon_s \kappa |A|_{max} = L_0 T_0/T_c,$$

where $|A|_{max} = T_c/T_0$. In displacive systems $|A|_{max} \sim 10^{-2} - 10^{-3}$, so for $\epsilon_s \sim 1 - 10$ and $\kappa \sim d_{at}^{-1}$ we find $l_{hc} \sim (10^2 - 10^3) d_{at} \sim 50 - 500 \text{Å}$. One should bear in mind that the ferroelectricity was observed in thinner films [6] but it was not possible to check if the film was mono- or polydomain, the latter being much more likely scenario. Obviously, when the external field is larger than the depolarizing field (3), $E_0 \geq E_d$, the film will be in monodomain state. This indicates the boundary between poly- and monodomain states and correctly describes the tilt of the hysteresis loops with decreasing film thickness observed in Ref. [6].

The necessity to study the sufficient conditions is suggested by Fig. 1, since the homogeneous ferroelectric solution belongs in the regions which correspond to either unstable or metastable states in the bulk samples. The problem of stability loss with respect to small fluctuations is a nontrivial yet tractable (linear) problem [14,15]. The check on metastability requires the calculation of free energies, which are much more difficult to find, so only limiting cases will be discussed below. The question of stability with respect to small fluctuations splits into two parts: stability with respect to (i) homogeneous and (ii) inhomogeneous fluctuations. Any solution of Eqs. (2) and (3) is stable with regards to homogeneous fluctuations. One can prove this by solving a relaxation dynamics for polarization constructed by generalizing the equation of state (2):

$$\gamma \frac{\partial P}{\partial t} = -\tilde{A} P - BP^3,$$  

where the relaxation parameter $\gamma > 0$. Linearizing this equation about the point $P = P_0$, where

$$P_0 = \sqrt{-\tilde{A}/B}, \quad \tilde{A} = A + L_0/l,$$

one obtains for homogeneous fluctuations $\delta^h P = P - P_0$

$$\gamma \frac{\partial \delta^h P}{\partial t} = -\left(\tilde{A} + 3BP_0^2\right) \delta^h P,$$

so that the perturbation does indeed decay with time as $\delta^h P \propto e^{\alpha t}$ with the decrement $\alpha = 2\gamma < 0$.

Now let us discuss stability with respect to inhomogeneous fluctuations of polarization. The present situation with the field penetrating into electrode over the Thomas-Fermi length is analogous to a ferroelectric film separated from the electrodes by nonferroelectric “dead” layers [16,17,14] that promote breaking the film into domains. To obtain the conditions for domain instability in the present case, one looks for a nontrivial solution of the equation of state with the gradient term included [15]

$$AP + BP^3 - \varphi \nabla^2 P = E,$$  

where $\nabla^2 = \partial_x^2 + \partial_y^2$ is “in-plane” Laplacian, together with Maxwell equations. The solution is sought in a form of a “polarization wave” $P = P_0 + \delta P_k(z) e^{ikx}$, $\varphi = \varphi_k(z) e^{ikz}$, where $\delta P_k(z)$ is the small perturbation over the homogeneous polarization $P_0 [14,15]$. In the case of metallic screening we obtain the following condition for an existence of the nontrivial solution with certain $k$:

$$\chi \tan \frac{1}{2} \chi kl = \frac{\epsilon_s k}{\epsilon_s \sqrt{k^2 + \kappa^2}},$$

where $\chi^2 = -(A + gk^2)/4\pi > 0$, $A = A + 3BP_0^2$. The case of interest to us is $\kappa \gg k$, which is easy to meet in the present case of metallic electrodes. We assume (and check validity later) that $\epsilon_s k/\epsilon_s \sqrt{\chi} \ll 1$. Then, the equation simplifies to $\chi kl = \pi$, the same as in FE film without electrodes. Substituting there the above expression.
for $\chi(k, \hat{A})$, we find the maximal value of $\hat{A}_c = -2g k_c^2$ at $k = k_c$ where this equality is first met, defining the temperature where the instability sets in. The “polarization wave" forms at $\hat{A} < 0$ such that

$$-\hat{A}_c = 2g k_c^2 = -A_d = \lambda/l,$$

$$k_c = \left(\frac{4\pi^4}{\epsilon_\perp g^2}\right)^{1/4} \sim \frac{1}{\epsilon_\perp \sqrt{d_{at} l}},$$

where $g$ is the coefficient before the gradient term in the equation of state (9), $\lambda = 4\pi^{3/2} g^{1/2}/\epsilon_\perp^{1/2} \sim d_{at}/\epsilon_\perp^{1/2}$ is the characteristic thickness for the domains formation. Now, checking the assumption that we used to solve the Eq. (10), we see that it boils down to $\sqrt{4\pi\epsilon_\perp}/(\epsilon_s \sqrt{k^2 g}) \sim \sqrt{4\pi\epsilon_\perp}/\epsilon_s \gtrsim 1$, which is met in (e.g. perovskite) films with $\epsilon_\perp \sim 100 - 1000$, and the typical $\epsilon_s \sim 1 - 10$.

These results remain basically unchanged if one were to account for realistic boundary conditions and the fact that the interface creates the effective “field" $w$ coupled to the normal polarization component [11]. The surface field results in a “frozen" polarization $P_0(z)$, but since it extends over a short length on the order of a lattice spacing, it makes the film response “hard" just near the boundary. The film remains “soft" in the bulk and there the stability loss proceeds by the above scenario via appearance of the polarization wave. The effect of the surface field is basically that the surface layer of atomic thickness would be excluded from the process of domain formation.

Importantly, in nearly unstrained cubic ferroelectric films the multidomain states are much more likely than in standard uniaxial ferroelectrics. Indeed, upon cooling from the paraelectric phase of a uniaxial ferroelectric film a domain instability sets in a form of a “polarization wave" when $A = A_d$ (11) with the critical wave vector $k = k_c$ (12) found from

$$|A_d|_{\text{uniaxial}} = 4\pi^{3/2} g^{1/2}/\epsilon_\perp^{1/2} l,$$ (13)

Eq. (11), where $\epsilon_\perp = 1 + 4\pi/A_\perp$ is the dielectric constant in the direction perpendicular to ferroelectric axis in the plane of the film. This is the case of interest to us, since $\epsilon_\perp \sim 10^3$ in BaTiO$_3$ at 2% lattice misfit [18,7]. In standard situations Eq.(13) applies, but if cubic perovskite films are grown on a substrate with small to negligible lattice mismatch, the period of a domain structure in a cubic ferroelectrics would increase. At the limit of applicability of this formula one can estimate $A_1 \sim A_\parallel \sim g k_c^2$ and we will call them “near-cubic". Substituting this into (13), we obtain $k_c \sim \pi/(2^{1/2} l) \sim 1/l$, so that the domain width $\lambda \sim \pi k_c^{-1}$ tends to become comparable to the thickness of the film. In this case, according to (13), the transition occurs very near the bulk critical temperature at

$$|A_d|_{\text{near cubic}} \sim g/l^2 \sim (d_{at}/l)^2.$$ (14)

The minimal thickness, where the near cubic thin films can still transform into a polydomain ferroelectric state, is then estimated for e.g. BaTiO$_3$ as $l_{cd} \sim d_{at} (\max |A_d|_{\text{near cubic}})^{-1/2} \sim 6d_{at} \sim 10\text{Å}$ at low temperature. Therefore, the ferroelectricity in near cubic ferroelectric films can exist in a polydomain form down to “atomic" thicknesses (just about one unit cell thick), where the present continuous theory is at the border of validity but still able to produce semiquantitative results. One can estimate from (13) that this regime corresponds to $\epsilon_\perp \approx 4\pi^2/g \sim (l/d_{at})^2$. A more careful consideration suggests that the transition in a cubic ferroelectric film with a smaller lattice misfit with the substrate than the above borderline value proceeds into a monodomain state with homogeneous in-plane polarization, e.g. $P_x$. This threshold misfit is very small indeed, so in most cases the film remains uniaxial and splits into domains according to the above scenario.

One can identify two possible cases from Eqs. (4) and (11), while considering possible phase transitions upon lowering temperature. (i) $A_h > A_d$, when $\lambda > L_0$, the phase transition is into a homogeneous state, and (ii) $A_h < A_d$ when $\lambda < L_0$, the phase transition proceeds into a multidomain state. The case (i) does not mean that the state remains homogeneous. It is stable with respect to inhomogeneous fluctuations, but when the temperature approaches $A \approx A_d$, domains would start to form. Indeed, at this point the domain wall thickness $W \sim \sqrt{-g/A_d}$ becomes smaller to the domain width $a$, $W \lesssim a$, and the existence of usual domains becomes possible. The situation with metallic electrode is analogous to a system with dead layers, which is metastable far from the critical point at $|A| \ll |A_d|$ with respect to domain structure at any thickness of the dead layer [16], and the domains are likely to form already at $A \approx A_d$. Consider now the case (ii) $\lambda < L_0$, where paraphase becomes unstable with respect to domains close to the phase transition point. Interestingly, it was found in Ref. [14] that the homogeneous state may be stable with respect to small inhomogeneous fluctuations not only in the paraphase but also in the ferrophase at some $T < T_s$. This result is formal, however, since the system is likely metastable in this region and domains will grow. The temperature $T_s$ is defined by the condition $A + 3BP_0^2 = A_d = -\lambda/l$. For $l = \lambda = 0$ this corresponds to a point where a depolarizing field equals thermodynamic coercive field, separating bulk homogeneous metastable from unstable states. At $T < T_s$ and negligible energy of the domain walls ($g = 0$) the depolarizing field would split the FE film into domains. Therefore, the homogeneous state below $T_s$ is actually metastable, and this is also easy to prove by comparing its free energy with the domain state. The case with $g \neq 0$ is more involved, but should be qualitatively similar, so that the low-temperature ho-
mogeneous state predicted in Ref. [14] is actually unob-
servable in the thermodynamic sense.

It has been found in first-principles modeling of
BaTiO$_3$ ferroelectric film with SrRuO$_3$ metallic elec-
trodes with in-plane lattice parameter corresponding to a
SrTiO$_3$ substrate (i.e. mimicking a capacitor structure
grown on top of SrTiO$_3$ with ~ 2% compressive
strain) that the state with a homogeneous polar-
ization in c–direction remains stable down to ~ 24Å
at zero temperature [7] (~10Å in unstrained PbTiO$_3$
[19]). Further, it was claimed that the depolarizing field
was solely responsible for vanishing of the ferroelectricity
in thinner films, the chemistry of the interface (within
the present nomenclature: the additional boundary con-
ditions, ABC) was deemed unimportant (however, see
[19]).

With regards to such phase transitions with thickness
of the film, there are again two possibilities for samples
with the thickness $l = l_h = \lambda_0/|A|$ where \(P_0 = 0\): (i)
paraelectric state with zero polarization is stable if \(A =
A_h > A_d\) (i.e. \(\lambda_0 < \lambda\)), and (ii) it is unstable and domains
form, \(\lambda_0 > \lambda\). The condition (i) is met when
\[
\frac{\sqrt{4\pi\epsilon_\perp}}{\left(\epsilon_\perp\sqrt{\kappa^2 q}\right)} < 1. \tag{15}
\]
For very moderate values for perovskites \(\epsilon_\perp \approx 100–1000\),
the electrode dielectric constant should then be \(\epsilon_\perp \gg
10 – 30\), which may or may not hold for particular elec-
trodes. This condition has not been checked in [7] and,
therefore, it remains unclear what regime corresponds to the
phase transitions studied in [7]. We see that the assump-
tion about the existence of homogeneous state made in [7]
is highly questionable and most likely the film in the ground
state would be split into domains. When the condition (15) is met [case (i)], the film is in a
paraelectric phase when \(l < l_h\), Fig. 1b. Indeed, at \(l > l_h\)
we have \(\Delta = A_d = 2l_0 \left(\frac{1}{2} - \frac{1}{2}\right)\) and \(\lambda_0 > \lambda\)
and the homogeneous state remains stable with regards to small inhomogeneous
fluctuations. However, it should become metastable at
\(l > l_d\), where domains become possible, i.e. \(W \lesssim a\),
which happens at \(l \lesssim l_d \approx \sqrt{\frac{2\lambda_0}{\lambda}} \approx \frac{\lambda_0}{2\lambda} > l_h\).

The paraelectric phase is stable at \(l < l_h\) with respect
to small fluctuations but may, at least in some cases, be
metastable [14].

In the second case one has \(\lambda_0 > \lambda\), so that \(l_d < l_h\), and
in films thinner than \(l_h\) the paraelectric is already unstable
with respect to domains. Certainly, domains would form
in thicker films too, so there is no chance that the film
can become homogeneously polarized. Summarizing, we
see, that the film can transform with increasing thickness
(i) from paraphase into homogeneous ferrophase at \(l_h <
\) \(l < l_d\) (which in some cases may be metastable), and
then into domain state at \(l > l_d\), or (ii) the paraphase
goes over directly into domain state at \(l > l_d\).

Now, we would like to see the effect of a finite band gap
\(E_g\) and free carriers in the ferroelectric itself on stability
of homogeneous state. One sees from Eq. (3) that at

\[
P > E_g/qL_0, \tag{16}
\]
where \(E_g\) is the band gap of the FE, the depolarizing
field in the FE exceeds \(|E_d| \approx E_g/qL\), the band bend-
ing in the film becomes larger than \(E_g/2\), and pockets with degenerate screening carriers form in atomically
thin layers at the interface [3]. We can rewrite this into a
more useful form \(P > \epsilon_S \pi d_L / qL d_{at}\)
where \(P = q/d_{at}^2 \sim 200\mu C/cm^2\) is the “atomic”
polarization, \(E_{at} = q^2/d_{at} \sim 10eV\) the “atomic” energy. For metallic
contacts \(\epsilon_\perp \sim 1 – 3\), \(\kappa d_{at} \sim 1\), and a typical band gap in
\(E_g = 2 – 3eV\) the condition is \(P \gtrsim 10 – 20\mu C/cm^2\),
so it seems as if it can be met in many ferroelectrics of
interest not very close to the phase transition. However,
the system will split into domains close to \(T_{c}\) and is
unlikely to reach such a homogeneous state, for the same
reason as in FE film without electrodes or in a film with
lightly doped semiconductor electrodes below.

In the FE slab without electrodes, the screening by the
carriers is possible only when the depolarizing field
again exceeds \(|E_d| \approx E_g/qL\), and pockets of screening
carriers can form in atomically thin layers at the sur-
face of FE [2]. Before pockets form, the depolarizing
field is huge, \(E_d = -4\pi P\) and it totally suppresses the
homogeneous polarization. Therefore, the film cannot
get into monodomain state until the absolute value of
thermodynamic coercive field becomes \(\gtrsim E_g/qL\).
This is certainly not possible until such a low temperature
where \(|A| > |A_1| = \left(\frac{3^{3/2}E_g d_{at}}{2^{3/2}qL}\right)^{2/3}\). Using the estimate
\(B \sim P_{at}^2, P \sim q/d_{at}^2\), we obtain

\[
|A_1| \sim \left(\frac{3^{3/2}E_g d_{at}}{2^{3/2}qL}\right)^{2/3} \sim \left(\frac{d_{at}}{l}\right)^{2/3}, \tag{17}
\]

where \(k_B\) is the Boltzmann constant. If this state could
be reached, the system would experience a discontinu-
ous transition into a state with large polarization. But
it could not, since domains appear much closer to \(T_{c}\).
Indeed, according to Eqs. (11),(17)

\[
\frac{A_d}{A_1} \sim \frac{1}{\epsilon_\perp} \left(\frac{d_{at}}{l}\right)^{1/3} \ll 1. \tag{18}
\]

The result (17) suggests that in typical ferroelectrics thinner
than 1-10 \(\mu m\) the monodomain state is simply im-
possible: the equation of state has only a trivial solu-
tion \(P = 0\). Similar reasoning applies to the case of
intrinsic semiconductor electrodes [5,4], where \(E_g\) now
means the band gap of the semiconductor. These au-
thors have found that the transition into a homogeneous
state should become first order but did not realize that it
cannot compete with domains. The above results are in striking disagreement with claims [8] that carriers can stabilize the homogeneous polarization in the few-nm thick FE films with semiconductor electrodes. There is no comment on a disagreement with earlier calculations by Ivanchik and Guro et al. [2], who obtained the results by solving the equation of state, accounting for presence of the pockets with degenerate carriers that were disregarded in [8].

We have shown that carriers in either ferroelectric itself or semiconductor electrodes are usually insufficient to screen the depolarizing field not far from the phase transition. Far from the transition other mechanisms of screening may operate, e.g. generation of bulk/surface charged defects like oxygen vacancies [20], surface reconstruction [21], or local charge disproportionation between ion layers [22,20]. Yet, the formation of domains seems to be the dominant screening mechanism in ferroelectric films, at least near the phase transition. Our results suggest that nearly unstrained cubic ferroelectrics go over into a multidomain state upon cooling to below the critical temperature especially easily. In certain cases (perhaps, not observed yet) they could transform into a monodomain state. In a multidomain state, the electric response of the film would be determined by the properties of the domain structure, including pinning. In this regard, it may be relevant to the present discussion that the gonne group has detected domains [23]. In their case the top electrode was absent, but we know that the conditions for the domain formation in non-electroded films are similar to those in electroded samples (capacitors) if one takes into account possible dead layers or finite screening length in the electrodes, see above discussion of Eq. (11). Theoretically, at least, the ferroelectric domains may survive down to thicknesses comparable to one unit cell.

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