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Phase transitions in ferroelectric-paraelectric superlattices: Stability of single domain state

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We studied stability of the single-domain state with respect to domain formation within Landau-Ginzburg-Devonshire theory for ferroelectric-paraelectric superlattices having equal layer thickness. Single-domain state is possible if dielectric constant of the paraelectric is larger than that of the ferroelectric for non-polar directions as in the $BaTiO_3/SrTiO_3$ system, which was taken as an example. Stability limit of the single-domain state is found as a function of temperature and layer thickness where we show a strong dependence of this limit on character of near-electrode regions, a point often overlooked. We also show that transition between single- and multi-domain states is discontinuous. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4829149]

Ferroelectric-paraelectric superlattices and multilayers have become a field of considerable activity since early 1990s.[1–19] Despite this interest, phenomena associated with domain structures in these systems have attracted considerable attention relatively recently.[5,8,9,13,14,18] Whether these systems are in single-domain or multi-domain state has immediate consequences for their functional properties such as the dielectric and pyroelectric response or data retention in memories. With this in mind, we try to explore here conditions of existence of single-domain (SD) or multi-domain (MD) ferroelectric state in a superlattice. In our previous paper[14] we had considered a finite thickness superlattice with top and bottom electrodes and applied a stability analysis within the Landau-Ginzburg-Devonshire theory to study phase transitions from high temperature paraelectric phase to the ferroelectric one. If the dielectric constant of the paraelectric material (ε_p) is much larger than the dielectric constant of the ferroelectric for non-polar directions $(\varepsilon_\perp)$, as in $BaTiO_3/SrTiO_3$ system coherently grown on electroded $SrTiO_3$ substrate, and thicknesses of the paraelectric and ferroelectric layers are not very different, this transition could be either into a SD or MD state depending on the layer thicknesses. For this case it is convenient to single out three MD regimes realized close to the transition: (i) Wide domain regime where period of the domain structure is larger than thickness of the ferroelectric layer; it has been considered that for the first time in Ref. 20 for films and in Ref. 5 for ferroelectric-paraelectric superlattices, we propose to call it non-Kittel regime. (ii) The narrow domain regime demonstrated first in Ref. 14, where the period of the domain structure is proportional to $l_f^{1/3}$ (l_f is the thickness of ferroelectric layer). We propose to call it quasi-Kittel regime. (iii) Narrow domain regime where the period and the domain structure is proportional to $l_f^{1/2}$, which is the classical Landau-Lifshitz-Kittel regime although close to the phase transition one observes rather frozen-in sinusoidal "polarization waves" than domains with well defined, sharp boundaries. For systems analogous to the $BaTiO_3/SrTiO_3$ with equal thicknesses of ferroelectric and paraelectric layers one deals practically only with non-Kittel and quasi-Kittel regimes (see Figure 3 of Ref. 14) which will be taken into account in the present work. The main point of Ref. 14 was the strong effect of structure of near-electrode regions for, however, long superlattices in MD state, which has been overlooked or not considered in many prior theoretical works while observed experimentally in Ref. 13. In this paper we apply the same method to analyze stability of the SD state which forms at small layer thicknesses of both layers if $\varepsilon_p \gg \varepsilon_\perp$. We report here results for superlattices with equal volumes of the two materials although more general results are available from the authors upon request. Similar to Ref. 14, we consider only superlattices consisting of an entire (and arbitrary) number of elementary two or three layer units and neglect the non-electrostatic effects at the layer interfaces because in this case analytical calculations are possible. The repeating units considered are given in Figure 1.

Since, unlike Ref. 14, we study stability of the single domain ferroelectric state instead of the linear governing equation (Eq. (1) of Ref. 14) relating ferroelectric polarization, P_z, to the electric field that suffices to check the stability of the paraelectric phase, we should now use the nonlinear governing equation due to the fact that we are already below the paraelectric-ferroelectric transition temperature

$$AP_z + BP_z^3 - g\frac{\partial^2 P_z}{\partial x^2} - g\frac{\partial^2 P_z}{\partial y^2} - \eta\frac{\partial^2 P_z}{\partial z^2} = E_z, \qquad (1)$$

where the gradient terms are in accordance with the tetragonal symmetry of the paraelectric phase. Here A is $(T - T_C)/\varepsilon_0 C$, where T is temperature, T_C is the transition temperature of bulk ferroelectric strained at the same extent as it is in the superlattice, ε_0 is the vacuum permittivity, C is Curie constant, and B is a positive coefficient. In Ref. 14 we assumed isotropy in the x–y plane but as to the gradient terms in Eq. (1) with gradient coefficient g, this gives the

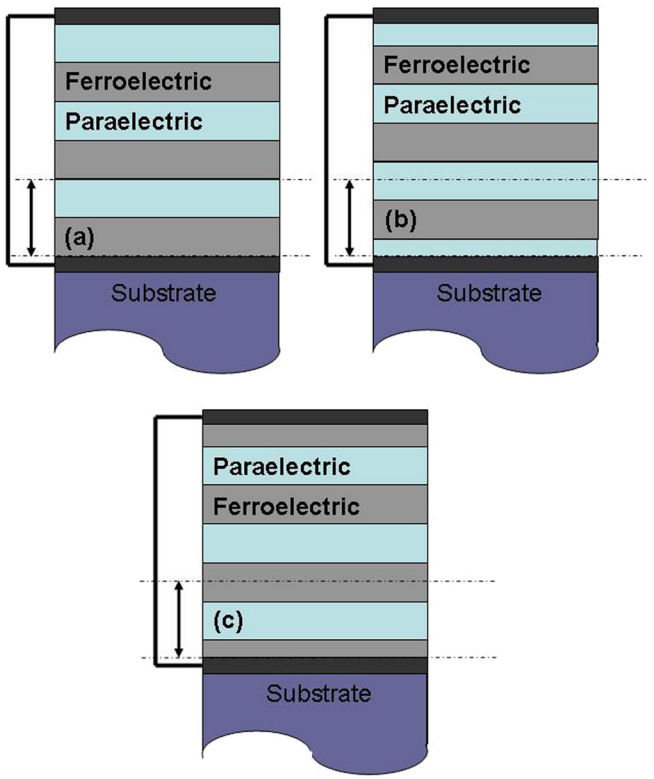

FIG. 1. Two types of superlattices analyzed in this work presented by systems consisting of three repeating units: (a) with bilayer as the repeating unit, (b), (c) with symmetrical (Chensky-Tarasenko type, see Refs. 14 and 20) repeating unit. Both symmetrical units yield the same results.

same results as tetragonality (the symmetry of a square, which includes 4 mirror planes perpendicular to the plane apart from the fourth order axis). However, if terms with higher order space derivatives are taken into account the differences between the isotropy and the square symmetry become evident, and one of them is qualitative: in isotropic case, nontrivial inhomogeneous solutions at the stability loss appear simultaneously for all the directions in x–y plane while for the square symmetry there are four such directions, which are parallel either to the sides of the square or to its diagonals. In the case of multilayers with high dielectric constant of the paraelectric layers, which we assume, other effects of the higher order gradient terms are negligible as shown in the supplementary material.[21] It is also mentioned there that one more factor in removing the directional degeneracy of the polarization wave is elastic anisotropy. It seems that for $BaTiO_3$ and $PbTiO_3$ both the higher order gradient terms and the elastic anisotropy dictate that the polarization waves be oriented along the cubic axes in the x–y plane. This allows us to consider polarization inhomogeneities along one direction only, which we choose to be the x-axis. In addition, with the same arguments as in Ref. 14 we omit also the term with the z-derivatives arriving thus at the equation

$$AP_z + BP_z^3 - g\frac{\partial^2 P_z}{\partial x^2} = E_z. \tag{2}$$

For the SD state this equation reads

$$AP_{zs} + BP_{zs}^3 = E_{zs}, \tag{3}$$

where P_{zs} is the polarization in the SD state and E_{zs} is the electric field. It has been shown by many authors (see Ref. 22 and references therein) that the effect of E_{zs} in a short-circuited system reduces to a renormalization of the coefficient A. For the superlattices we are considering, this leads to

$$(A + \varepsilon_0^{-1}(\varepsilon_b + \varepsilon_p)^{-1})P_{zs} + BP_{zs}^3 = 0, \tag{4}$$

i.e.,

$$P_{zs}^2 = -\frac{A + \varepsilon_0^{-1}(\varepsilon_b + \varepsilon_p)^{-1}}{B}, \tag{5}$$

where ε_b is the background dielectric constant.[23] To study stability of the SD state one has to linearize Eq. (2) close to $P_z = P_{zs}$, $E_z = E_{zs}$. For $P_z' = P_z - P_{zs}$, $E_z' = E_z - E_{zs}$ one finds

$$\tilde{A}P_z' - g\frac{\partial^2 P_z'}{\partial x^2} = E_z', \tag{6}$$

where

$$\tilde{A} = -2A - 3\varepsilon_0^{-1}(\varepsilon_b + \varepsilon_p)^{-1}. \tag{7}$$

Comparing with Eq. (1) of Ref. 14 (with $\eta = 0$) we see that the only difference consists of replacing A in this equation by $\tilde{A}$. In addition, the stability problem involves also satisfying the electrostatic equations. However, since the latter are linear, they do not contain P_{zs}, E_{zs} along with P_z', E_z'. Therefore, the boundary of stability of the single-domain state can be obtained from formulas of Ref. 14 (see Eqs. (25) and (30) and comments following Eq. (36) in that paper) just by substitution of $\tilde{A}$ for A. Doing so, we find the value of A corresponding to the stability loss of the single domain state $(A_{lss}(k_c))$

$$A_{lss}(k_c) = A_{ls}(0) - \frac{A_{ls}(k_c) - A_{ls}(0)}{2}, \tag{8}$$

where $A_{ls}(k_c)$ marks the point of instability of the paraelectric state and $A_{ls}(0)$ corresponds to phase transition from paraelectric to SD ferroelectric state. As a result we obtain diagrams in T–l (temperature-layer thickness) plane which are shown in Figures 2(a) and 2(b) that indicate stability regions of the paraelectric phase (already present in Ref. 14) and of the SD ferroelectric state. We emphasize that by stability we mean stability with respect to very small (formally: however small) perturbations, i.e., a stability region may imply both thermodynamically stable (equilibrium) states and metastable ones. Tracing a boundary between the two possibilities requires considerable amount of systematic numerical work which is beyond the scope of the current study. Figure 2(b) illustrates dependence of the stability diagrams on structure of the near electrode regions by plotting the diagrams for the two types of superlattices considered. These stability diagrams are independent of the number of the units in a superstructure which has been commented on to some length in Ref. 14. We use the constants for $BaTiO_3$ in Ref. 24 for the ferroelectric layer and the room temperature

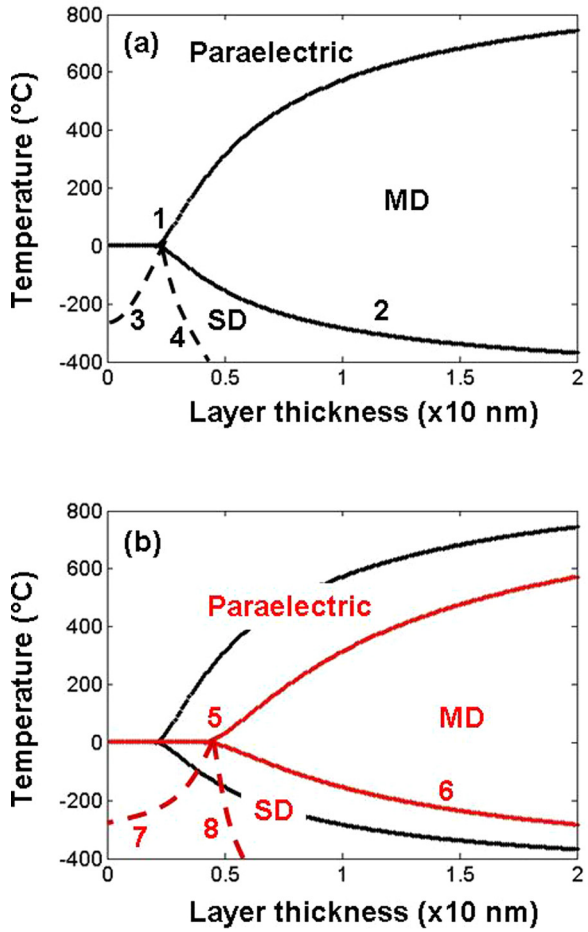

FIG. 2. Stability map of the superlattices in the temperature (T)-layer thickness (l) plane: (a) of the superlattice consisting of bilayer units where 1 indicates the critical thickness and 2 is the single domain-multi domain stability limit curve, 3,4 (dashed curves) are speculated variants for line of single-multi domain first order phase transition. (b) The same for the superlattice consisting of symmetrical units with 5 indicating the critical thickness and 6 the single-multi domain stability limit curve similar to (a). 7,8 is analog of 3,4. In (b), the bilayer case (solid black curve) is given for comparison.

dielectric constant of $SrTiO_3$ for the paraelectric layer ($\varepsilon_p = 300$). Note that, for instance, for a $PbTiO_3/SrTiO_3$ superlattice with equal layer thicknesses, a similar stability diagram is impossible because, according to our calculations using the constants of Ref. 24, $\varepsilon_\perp$ exceeds 500 in the relevant temperature region, i.e., $\varepsilon_\perp > \varepsilon_p$, and a phase transition from paraelectric into SD state does not occur for this system with equal thicknesses of the ferroelectric and paraelectric layers.

In the above analysis of stability of SD state, we did not consider coupling of inhomogeneous polarization and elastic strains, similar to Refs. 20 and 22. Recall that homogeneous strain is fixed by the substrate and determines T_C, which was mentioned above. Pertsev and Kohlstedt[25] have pointed out that neglecting of inhomogeneous polarization-strain coupling is not consistent. They are formally right, but a detailed analysis in Ref. 26 has shown that the effects of this coupling are far less significant than what was claimed. One should keep in mind that our analysis shows that there are significant changes in the stability diagram if configuration of near electrode regions changes and this is a far more stronger effect than corrections to account for inhomogeneous strain effects.

After crossing a line of loss of stability of a state (see the curves in Figures 2(a) and 2(b)), the change can be either continuous or discontinuous. A possibility of a continuous change is evident when one treats the stability of the paraelectric phase. It is perfectly conceivable that the amplitude of the "polarization wave" with respect to which the paraelectric state loses its stability becomes smaller the closer is the system to the stability loss point and is exactly zero at this point. This is a second order ferroelectric phase transition which is realized at positive coefficient B as it takes place for both for $BaTiO_3/SrTiO_3$ and $PbTiO_3/SrTiO_3$ systems (Ref. 24). However, no continuity is possible when crossing the stability line of the SD-MD boundary in the ferroelectric phase. In this case, at the stability loss point there is a finite amplitude of the inhomogeneous polarization distribution (MD state), and this time the stability loss occurs not at a boundary of the MD region (such as at the paraelectric-MD transition) but somewhere inside this region, well below the transition temperature from the paraelectric to the MD state. This means that there will be a jumpwise change of the polarization distribution and, therefore, a finite energy loss. Such a point is a spinodal point of a first order phase transition. This also means that there could exist a lower temperature at which the free energies of the two phases become equal, which could be named as the thermodynamic temperature of the first order transition. Below this temperature the single domain state would have a lower energy than multidomain state, presenting itself as a truly equilibrium state. At the moment this is speculative, of course, and it can well be that the thermodynamic temperature of the first order transition does not exist for some parameters of the system and that the SD state is always metastable though, probably, with a large life time. Unfortunately, we cannot answer this question via analytical calculations and extensive numerical simulations are needed, which are beyond this work. Despite this difficulty, some guesses though can still be made: The broken lines in Figures 2(a) and 2(b) are possible first order transition lines where the free energies of the SD and MD states are equal. Note that the situation here is similar to that in a ferroelectric with dead layers discussed in Ref. 22.

To calculate precisely the free energy loss at crossing SD-MD transition, one has to deal with a highly non-linear problem which is well beyond the scope of this work. However, it is fairly easy to formally show that this energy loss does indeed exist. First assume that the polarization distribution in the MD state has the same form as at the stability loss of the paraelectric phase, i.e., the x-dependence of the polarization is described by $\cos k_c x$ while the z-dependence is described by $\cos q_c z$. Second we find variationally the amplitude of the supposed polarization distribution by minimizing the free energy with respect to this amplitude and finding both the amplitude and the corresponding minimum of the free energy. Since this polarization distribution is not precisely the one which should exist in the reality, the computed minimum of the free energy is higher than the equilibrium free energy. Therefore, if the approximately calculated energy of MD phase is lower than the free energy of SD state (which is easy to calculate), then the difference between the exact energies will be of the same sign and larger.

It is convenient to find coefficients of the free energy depending on the aforementioned polarization amplitude by an indirect method from the governing equation. Recall that the stability analysis in Ref. 14 provided the form of the potential and the polarization distributions but not their amplitudes which are coupled so that there remains only one undefined amplitude. We considered the amplitude of potential as undefined, but now we shall consider the polarization amplitude instead and express with the help of it the amplitude of the "electric field wave." Similar to Ref. 14, for a multilayer consisting of many such bilayers the amplitudes of the polarization waves, P_{pw}, in any ferroelectric layer can be obtained from the amplitude in the layer contacting the metallic electrode, i.e., from the amplitude which we calculate next.

It is straightforward to see that the results of the stability analysis of Ref. 14 for the bilayer can be presented in the form

$$\begin{aligned} P_z &= P_{pw}\cos q_c z \cos k_c x, \\ E_z(x,z) &= P_{pw}(A_{ls}(k_c) + gk_c^2)\cos q_c z \cos k_c x. \end{aligned} \tag{9}$$

Substituting into Eq. (2) we get

$$\begin{aligned} &\left[(A - A_{ls})P_{pw} + \frac{9}{16}BP_{pw}^3\right]\cos q_c z \cos k_c x \\ &+ BP^3\left[\frac{3}{16}\cos 3q_c z \cos k_c x + \frac{3}{16}\cos q_c z \cos 3k_c x\right. \\ &\left.+ \frac{1}{16}\cos 3q_c z \cos 3k_c x\right] = 0, \end{aligned} \tag{10}$$

where the cosines with triple arguments arose due to the non-linear term. As it was explained above, our approximation consists in neglecting the higher harmonics. In addition, we neglect changes of the polarization across the ferroelectric layer, i.e., along the z-axis because in the non-Kittel and in quasi-Kittel regimes these changes are indeed small: $q_c l \ll 1$. Then we obtain

$$(A - A_{ls}(k_c))P_{pw} + \frac{3}{4}BP_{pw}^3 = 0. \tag{11}$$

From this equation we immediately find the amplitude of polarization wave

$$P_{pw}^2 = -\frac{4(A - A_{ls}(k_c))}{3B}, \tag{12}$$

but one can recover the free energy by whose minimization Eq. (11) has been obtained only up to an unknown numerical factor. To find this factor one can trace the contribution of a term in the free energy density, e.g., of the term $(A/2)P_z^2$, to $F(P_{pw})$

$$\frac{1}{2}\int AP_z^2 dxdz = \frac{A}{2}P_{pw}^2\int \cos^2 q_c z \cos^2 k_c x dxdz \simeq V\frac{A}{4}P_{pw}^2. \tag{13}$$

Then the free energy density has the form

$$F(P_{pw}) = \frac{A - A_{ls}(k_c)}{4}P_{pw}^2 + \frac{3}{32}BP_{pw}^4, \tag{14}$$

and the free energy density of the equilibrium MD state is

$$F_{md} = -\frac{(A - A_{ls}(k_c))^2}{6B}. \tag{15}$$

Using Eq. (8) one finds this free energy at the stability loss point of the SD state $(A = A_{lss}(k_c))$

$$F_{md}^{lss} = -\frac{3(A_{ls}(0) - A_{lss}(k_c))^2}{8B}. \tag{16}$$

For the SD state one has

$$F_{sd} = -\frac{(A - A_{ls}(0))^2}{4B}, \tag{17}$$

and at $A = A_{lss}(k_c)$ we have

$$F_{sd}^{lss} = -\frac{(A_{ls}(0) - A_{lss}(k_c))^2}{16B}. \tag{18}$$

Comparing with Eq. (16) we see that at the stability loss point of the free energy of the single domain state is definitely higher than that of the multi domain state, i.e., the transition is definitely discontinuous and what we have found is the spinodal line for the SD state. Since the system is in metastable state before reaching the spinodal line, at least in some range of the system parameters the SD is not thermodynamically stable. Metastability with short live-time is equivalent to instability from practical point of view, and we acknowledge that we found only the upper limit of stability of SD state. Finding the reliable practical limits of SD stability for a given material system is a question of further investigation.

In summary, for ferroelectric-paraelectric superlattice with equal layer thicknesses, we have found, at the temperature-layer thickness plane, a line beyond which absolute instability of single domain state occurs, and it converts into multi-domain state. This line is spinodal of the single domain state, i.e., one may expect existence of a thermodynamic first order phase transition whose location remains to be further explored. The structure of the near electrode region has a dramatic impact on position of the spinodal as shown here considering two different units comprising the superlattices.

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