Prediction of a Giant Dielectric Anomaly in Ultrathin Polydomain Ferroelectric Epitaxial Films

N. A. Pertsev,[1,2] G. Arlt,[2] and A. G. Zembilgotov[3]
[1]*A. F. Ioffe Physico-Technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia*
[2]*Institut für Werkstoffe der Elektrotechnik, Aachen University of Technology, 52056 Aachen, Germany*
[3]*State Technical University of St. Petersburg, 195251 St. Petersburg, Russia*
(Received 24 April 1995)

The amplitudes of electric-field-induced translational vibrations of 90° domain walls formed in a tetragonal ferroelectric thin film grown on a cubic substrate are calculated theoretically. The domain wall contribution to the dielectric response of an epitaxial film is evaluated and shown to be important in common heterostructures. In some special film/substrate systems this contribution must increase rapidly with decreasing film thickness, which may result in a giant dielectric anomaly.

PACS numbers: 77.80.Dj, 77.22.Ch, 77.55.+f

Considerable current interest in ferroelectric thin films is due to their numerous potential applications in electronic devices, which utilize the unique dielectric, pyroelectric, piezoelectric, and electro-optic properties of ferroelectric materials. For many applications, such as dynamic random access memory with very large scale integration, high-frequency transducers, thermistors, and electroluminescent displays, the fabrication of thin films with large electric permittivities is especially important.

Recent experimental studies [1–5] have found that, in tetragonal ferroelectric thin films epitaxially grown on cubic substrate, elastic domains (twins) may form during the preparation of heterostructures. The 90° domain structure of an epitaxial film has a strong impact on the hysteretic polarization behavior of a ferroelectric layer [4,6]. It may be expected that the formation of 90° domain walls in the epitaxial film can also increase markedly its electric permittivity because of the field-induced translational displacements of the walls. Indeed these ferroelastic domain walls, in contrast to the purely ferroelectric 180° walls, have a thickness much larger than the unit cell size (about 100 Å in $BaTiO_3$ [7]) so that the lattice potential barriers hindering their translational motion must be negligible. This supposition is strongly supported by the dielectric measurements on bulk $BaTiO_3$ single crystals with a laminar 90° domain structure [8], which clearly demonstrate that displacements of the 90° wall can be induced even by a weak measuring field $E \sim 1$ kV/m. In addition, it has been shown [9–13] that the vibrational motion of 90° walls must contribute considerably to the dielectric response of tetragonal ferroelectric ceramics.

The above considerations motivated us to perform the first theoretical analysis of the domain wall vibrations in epitaxial ferroelectric thin films. In this Letter, we show that very large permittivities $\epsilon \sim 10^5$ may arise from these vibrations in the heterostructures involving ultrathin films and pairs of materials having lattice misfits near some special value.

Consider a thin tetragonal ferroelectric film epitaxially grown on a cubic substrate with the (001) plane parallel to the surface. Three variants of elastic domains can exist in such a film: c domains with the tetragonal c axis perpendicular to the film surface and a_1 and a_2 domains in which the c axes are parallel to the [100] and [010] axes of the substrate, respectively. In accordance with the observations [1,2,5] we assume that the film contains a laminar 90° domain structure composed of alternating c and a_1 (or a_2) domains as shown in Fig. 1. Following Kwak *et al.* [1,5], we model this $c/a/c/a$ domain pattern by an infinite periodic array of 90° walls. This approximation is justified by the fact that normally 90° domain walls in epitaxial films form regular stacks with the in-plane sizes much larger than the domain widths [2,3,5]. Moreover, for thin films it should be especially good because the screening of internal stress fields by the free surface of a film strongly reduces the long-range elastic interactions between 90° walls.

The geometry of the regular $c/a/c/a$ pattern can be described by the period D of the domain structure and the volume fraction $\phi = d/D$ of c domains in the film. In the absence of external fields the configuration is defined by the equilibrium period D^* and the equilibrium fraction ϕ^* of c domains. Obviously the calculation of D^* and ϕ^* is a prerequisite for the analysis of domain

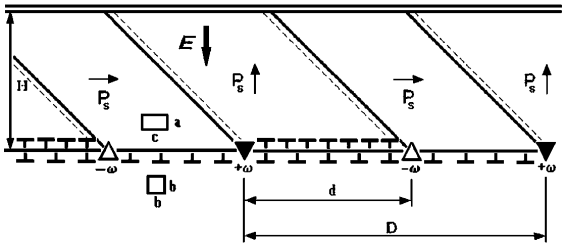

FIG. 1. Epitaxial ferroelectric thin film with a laminar $c/a/c/a$ domain structure sandwiched between the top and bottom electrodes. Dashed lines show how 90° domain walls are displaced by an electric field E from their equilibrium positions. Triangles denote straight wedge disclinations with strengths $\pm\omega$ and symbols $\perp$ denote straight edge dislocations. P_S is the spontaneous polarizations; H is the film thickness; a, $c > a$, and b are the lattice parameters of the tetragonal film and the cubic substrate, respectively.

 0031-9007/96/76(8)/1364(4)$06.00

wall vibrations. The statics of domain configurations in epitaxial ferroelectric and ferroelastic films was studied theoretically in several papers [1,5,14–17]. However, all these studies neglected the influence of the free surface of a film on the internal stresses existing in the strained epitaxy and, thus, on the stored elastic energy which governs the domain configuration.

Recently we have developed a rigorous theory of periodic domain structures forming in tetragonal epitaxial films grown on cubic substrates [18]. Inhomogeneous internal stresses appearing in the film and in the substrate due to a lattice mismatch between them were calculated correctly by the method of fictitious dislocations [19] which enabled us to allow for the effect of a free surface. (The dislocation-disclination model of a laminar $c/a/c/a$ domain structure is shown in Fig. 1. Disclinations here are associated with the junctions of 90° domain walls and the film/substrate interface. Lattice misorientations observed in polydomain epitaxial films [2,3,5] are an experimental evidence for those rotational defects.) On this base the stored elastic energy was evaluated and the equilibrium geometric parameters D^* and ϕ^* were computed for laminar $c/a/c/a$ configurations. It was shown that D^*/H and ϕ^* are functions of the normalized film thickness $HG(S_a - S_c)^2/\sigma(1 - \nu)$ and the relative coherency strain $S_r = (b - a)/(c - a)$ [16] between the film and the substrate having the lattice parameter b. Here $S_a = (b - a)/a$ and $S_c = (b - c)/c$ are the misfit strains, σ is the 90° domain wall energy per unit area, and G and ν are the shear modulus and Poisson's ratio of the film/substrate system which is assumed to be elastically isotropic and homogeneous.

Consider now the influence of a weak ac electric field $E(t) = E_m \sin\Omega t$ with $E_m \sim 1$ kV/m on the $c/a/c/a$ structure formed in the ferroelectric film. We can assume that the film is grown on a lattice matched bottom electrode and covered by a top electrode [4,6]. The external electric field between these electrodes exerts a driving force on the 90° walls because c domains tend to expand or shrink depending on the mutual orientation of the spontaneous polarization $\vec{P}_S$ and the field intensity $\vec{E}$ at the moment t. This force causes reversible displacements $\Delta\ell$ of domain walls from their equilibrium positions. The amplitudes of these displacements are limited by internal restoring forces acting on 90° walls.

We shall consider here only prepolarized films which do not contain 180° domain walls. This is a realistic case because 180° walls can be removed from epitaxial films prior to dielectric measurements by an application of a strong dc electric field in contrast to 90° walls, which have much higher coercive fields due to the elastic stabilization of the $c/a/c/a$ structure [17]. In a prepolarized film equivalent domain walls in the $c/a/c/a$ structure are driven by the same force and, therefore, the domain period D^* remains unchanged during the wall motion, as shown in Fig. 1. At the same time neighboring domain walls move in opposite directions so that the volume fraction ϕ of c domains deviates from its initial value ϕ^*. The difference $\phi(t) - \phi^*$ is defined by the domain wall displacements $\Delta\ell(t)$ at the moment t. Assuming that these displacements have the same magnitude $|\Delta\ell(t)|$ for all 90° walls in a film at the same moment, we can describe the field-induced domain wall vibrations by the following equation of motion [9,13,20]:

$$m\,\frac{\partial^2\Delta\ell}{\partial t^2} = f_{\rm res}(t) + P_S E_m \sin\Omega t\,, \tag{1}$$

where m is the self-mass of a 90° domain wall per unit area, $f_{\rm res}$ is the mean internal restoring force acting on displaced walls, and the last term in Eq. (1) gives the effective driving force per unit wall area that is created by the applied electric field $E(t)$. [Displacements $\Delta\ell$ and the forces involved in Eq. (1) are taken to be positive when they are directed into a domains.]

In general, the total restoring force consists of several different components:

$$f_{\rm res} = f_{\rm mh} + f_{\rm el} + f_{\rm lat} + f_{\rm def}\,, \tag{2}$$

where $f_{\rm mh}$ is the mechanical restoring force associated with an increase in the elastic energy $W_{\rm el}(D^*/H, \phi)$ stored in the epitaxial system that is caused by domain wall displacements, $f_{\rm el}$ is the restoring force created by an internal electric field which may be induced by the redistribution of polarization charges during the wall motion, the contribution $f_{\rm lat}$ is due to the pinning of 90° domain walls by the lattice potential relief (Peierls relief) [21], and the term $f_{\rm def}$ allows for the interaction of domain walls with dipolar defects [22] and misfit dislocations. However, the electric restoring force, which plays an important role in ferroelectric ceramics [11,12], is obviously negligible in the case of a thin film sandwiched between two electrodes. The term $f_{\rm lat}$ can also be ignored at not too low temperatures. [In $Pb(Ti_{1-x}Zr_x)O_3$, for instance, this range is above 50 K at frequencies $\Omega < 100$ kHz [9].] The clamping of domain walls by oriented dipolar defects is negligible if the perovskite film is not doped by acceptor ions. The interaction with misfit dislocations may strongly increase the total restoring force [17], but we shall consider only epitaxial systems without these defects, which can be also fabricated [5].

Thus the displacements of 90° walls in our case must be hindered mainly by the mechanical restoring force so that Eq. (2) is reduced to $f_{\rm res} \approx f_{\rm mh}$. By analogy with domain wall vibrations in ferroelectric ceramics [9,13,20], in a wide range of relatively low frequencies $\Omega \ll c_t/H$ (c_t is the velocity of transverse sound waves) this restoring force can be written as $f_{\rm mh} = -k\Delta\ell$. Since the inertial reaction involved in Eq. (1) may be also ignored in this frequency range [9,13,20], we obtain the following solution for the domain wall vibrations induced by a low-frequency measuring field:

$$\Delta\ell(t) = \frac{P_S E_m}{k}\sin\Omega t\,. \tag{3}$$

It can be shown that the mechanical force constant k is defined by the second derivative of the elastic energy $W(D^*/H, \phi)$ stored in the epitaxial system according to the relation

$$k = \frac{2\sqrt{2}}{HD^*} \frac{\partial^2 W_{el}(D^*/H, \phi)}{\partial \phi^2} \bigg|_{\phi=\phi^*} . \quad (4)$$

In our calculations we have taken into account that $\partial W_{el}/\partial \phi = 0$ at $\phi = \phi^*$ [18], and $|\phi(E_m) - \phi^*|/\phi^* \ll 1$ at $E_m \sim 1\ \mathrm{kV/m}$ as it follows from the numerical estimates. The second derivative of the elastic energy involved in Eq. (4) can be derived from an expression for $W_{el}(D/H, \phi)$ obtained in our recent work [18]. The calculations finally give the following analytic formula for the force constant k:

$$k = \frac{\sqrt{2}\, G(S_a - S_c)^2}{\pi(1 - \nu)H} \left[\ln \frac{\cosh 4\pi H/D^* - \cos 2\pi\phi^*}{1 - \cos 2\pi\phi^*} - 8\pi^2 \frac{H^2 \cosh 4\pi H/D^* \cos 2\pi\phi^* - 1}{D^{*2}(\cosh 4\pi H/D^* - \cos 2\pi\phi^*)^2} \right]. \quad (5)$$

At very large film thicknesses $H \gg 10^2\sigma(1 - \nu)/G(S_a - S_c)^2$ Eq. (5) reduces to $k = 4\sqrt{2}\, G(S_a - S_c)^2/(1 - \nu)D^*$, with $D^* \sim H^{1/2}$.

The antiparallel motion of domain walls described by Eq. (3) results in a periodic variation $\phi(t) = \phi^* + 2\sqrt{2}\,\Delta\ell(t)/D^*$ of the volume fraction of c domains in a film. This is accompanied by a periodic change $\Delta P(t) = P_S[\phi(t) - \phi^*]$ in the film average polarization measured along the field direction. Since ΔP is proportional to the running value of the field intensity $E(t)$, the domain wall vibrations (3) simply produce an additional contribution ϵ_D to the real part of the film relative permittivity

$$\epsilon_D = \frac{P_S(\phi - \phi^*)}{\epsilon_0 E} = \frac{2\sqrt{2}\, P_S^2}{\epsilon_0 k D^*}, \quad (6)$$

where ϵ_0 is the permittivity of the vacuum. Substitution of Eq. (5) into Eq. (6) shows that ϵ_D can be represented as a product of the ratio $Q = P_S^2(1 - \nu)/\epsilon_0 G(S_a - S_c)^2$ and a dimensionless function of the normalized film thickness $HG(S_a - S_c)^2/\sigma(1 - \nu)$ and the relative coherency strain S_r. This function can be calculated numerically by using in Eqs. (5) and (6) the dependencies of the equilibrium domain period D^*/H and volume fraction ϕ^* on the normalized thickness and the strain S_r which were computed in our recent work [18]. [According to the general theory of domain wall vibrations [13], in a wide frequency range $\Omega < c_t/H$ the wall contribution $\epsilon_D'(\Omega)$ is expected to be almost equal to the static one given by Eq. (6). In this range the domain wall contribution $\epsilon_D''(\Omega)$ to the imaginary part of the film permittivity must be negligible. Strong dispersion in $\epsilon_D'(\Omega)$ and a peak of dielectric losses caused by the emission of sound waves from oscillating walls are expected only at $\Omega \gg c_t/H$.]

We have performed numerical calculations of the domain wall contribution ϵ_D and obtained the two-dimensional plot (see Fig. 2) which shows variations of the normalized permittivity ϵ_D/Q with the film thickness and the relative coherency strain S_r. We note that this plot partly corresponds to metastable $c/a/c/a$ configurations which can be created by cooling the film through the Curie transition in a superimposed electric field [17].

Using the plot shown in Fig. 2, we can estimate ϵ_D for various heterostructures. In the case of comparatively thick films with $H \gg H_0 = \sigma(1 - \nu)/G(S_a - S_c)^2$ we have $\epsilon_D \sim 0.5Q$. Since the difference $S_a - S_c$ at small misfit strains $S_a, S_c \ll 1$ may be replaced by the tetragonality strain $S_T = (c - a)/a$, the Q ratio in fact depends on the properties of the ferroelectric layer only. For $BaTiO_3$ and $Pb(Ti_{0.49}Zr_{0.51})O_3$ at room temperature, with the numerical values of the involved physical parameters given in our previous papers [12,13] we obtain $Q \simeq 2000$. Hence the domain wall contribution $\epsilon_D \sim 1000$ appears to be comparable with the dielectric constants of bulk single crystals [23] and, thus, with possible intrinsic contributions to the permittivity of these ferroelectric films.

For the heterostructures which contain very thin films with $H \leq H_0$ and have the relative coherency strain close to the "critical" strain $S_r^* = 1/2(1 + \nu)$, the theory predicts a dielectric anomaly that is clearly seen in Fig. 2. At $S_r = S_r^*$ and $H = 0.42H_0$, e.g., we have obtained $\epsilon_D = 127Q$. With the value of $Q \simeq 2000$ this formally gives the giant permittivity of $\epsilon \simeq 250\,000$. (We note that earlier Clarke and Burfoot [24] predicted a giant local dielectric response inside 180° domain walls in ferroelectrics.) The anomaly shown in Fig. 2 is caused by the drastic weakening of elastic interactions between 90° walls in ultrathin

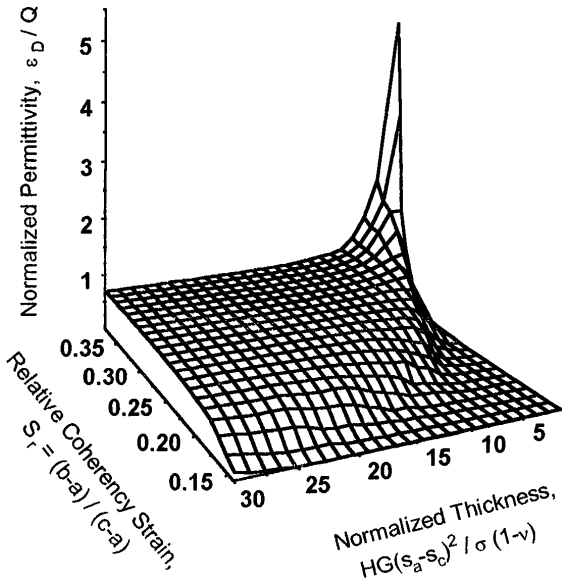

FIG. 2. Two-dimensional plot of the domain wall contribution to the electric permittivity of an epitaxial ferroelectric film.

films where the equilibrium distances between neighboring walls become much larger than the wall size $\sqrt{2}H$ [18]. This softening of domain wall vibrations appears only in the heterostructures with near-critical coherency strains because here the critical thickness H^*, below which films stabilize in a single domain state [14,25], tends to zero as $S_r \rightarrow S_r^*$ [16,18].

Unfortunately in common ferroelectrics the threshold thickness H_0 is expected to be of the order of the unit cell size. For $BaTiO_3$, e.g., with the domain wall energy of $\sigma = 3 \times 10^{-3}$ J/m^2 calculated in Ref. [26] we obtain $H_0 = 10$ Å. Nevertheless, the giant permittivities caused by domain wall vibrations probably can be observed in ferroelectrics with the second order phase transition like $K(Nb_xTa_{1-x})O_3$ with $x < 0.45$ [23]. In these materials the domain wall energy scales as $\sigma \sim P_S^3$ [21]. Using the relation $S_T \sim P_S^2$, we see that here $H_0 \sim P_S^{-1}$ so that the threshold thickness will increase strongly near the Curie temperature. The Q-ratio must also increase very rapidly here since it varies as $Q \sim P_S^{-2}$.

The film average spontaneous polarization P_S is also expected to decrease to zero near some critical film thickness when the ferroelectric with the second order phase transition has a positive extrapolation length δ [27]. In ferroelectrics of this type the giant permittivities caused by domain wall vibrations might be observed even at temperatures far from the Curie temperature.

Thus, the field-induced translational vibrations of 90° domain walls may result in a giant dielectric anomaly in ultrathin films with $H \leq H_0$ epitaxially grown on appropriate substrates providing the relative coherency strain close to the critical value $S_r^* = 1/2(1 + \nu)$.

The research described in this publication was made possible in part by Grant No. R4J000 from the International Science Foundation. The authors also thank Andrew Zangwill for critically reading the manuscript and for suggestions to improve it and the Deutsche Forschungsgemeinschaft for financial support.

[1] B. S. Kwak, A. Erbil, B. J. Wilkens, J. D. Budai, M. F. Chisholm, and L. A. Boatner, Phys. Rev. Lett. **68**, 3733 (1992).
[2] Y. Gao, G. Bai, K. L. Merkle, Y. Shi, H. L. M. Chang, Z. Chen, and D. J. Lam, J. Mater. Res. **8**, 145 (1993).
[3] A. E. M. De Veirman, J. Timmers, F. J. G. Hakkens, J. F. M. Cillessen, and R. M. Wolf, Philips J. Res. **47**, 185 (1993).
[4] R. Ramesh, T. Sands, and V. G. Keramidas, Appl. Phys. Lett. **63**, 731 (1993).
[5] B. S. Kwak, A. Erbil, J. D. Budai, M. F. Chisholm, L. A. Boatner, and B. J. Wilkens, Phys. Rev. B **49**, 14 865 (1994).
[6] J. S. Speck, A. Seifert, W. Pompe, and R. Ramesh, J. Appl. Phys. **76**, 477 (1994).
[7] T. Malis and H. Gleiter, J. Appl. Phys. **47**, 1595 (1976).
[8] V. A. Borodina, Ferroelectrics **111**, 277 (1990).
[9] G. Arlt, H. Dederichs, and R. Herbiet, Ferroelectrics **74**, 37–53 (1987).
[10] E. I. Bondarenko, V. Yu. Topolov, and A. V. Turik, Ferroelectrics **110**, 53 (1990).
[11] G. Arlt and N. A. Pertsev, J. Appl. Phys. **70**, 2283 (1991).
[12] N. A. Pertsev and G. Arlt, Ferroelectrics **132**, 27 (1992).
[13] N. A. Pertsev and G. Arlt, J. Appl. Phys. **74**, 4105 (1993).
[14] A. L. Roytburd, Phys. Status Solidi A **37**, 329 (1976); Mater. Res. Soc. Symp. Proc. **221**, 225 (1991).
[15] R. Bruinsma and A. Zangwill, J. Phys. (Paris) **47**, 2055 (1986).
[16] W. Pompe, X. Gong, Z. Suo, and J. S. Speck, J. Appl. Phys. **74**, 6012 (1993).
[17] J. S. Speck and W. Pompe, J. Appl. Phys. **76**, 466 (1994).
[18] N. A. Pertsev and A. G. Zembilgotov, J. Appl. Phys. **78**, 6170 (1995).
[19] N. A. Pertsev and G. Arlt, Ferroelectrics **123**, 27 (1991).
[20] G. Arlt, U. Böttger, and S. Witte, Ann. Phys. (Leipzig) **3**, 578 (1994).
[21] Y. Ishibashi, Ferroelectrics **98**, 193 (1989).
[22] U. Robels and G. Arlt, J. Appl. Phys. **73**, 3454 (1993).
[23] F. Jona and G. Shirane, *Ferroelectric Crystals* (Macmillan, New York, 1962).
[24] R. Clarke and J. C. Burfoot, J. Phys. D **8**, 1115 (1975).
[25] S. Little and A. Zangwill, Phys. Rev. B **49**, 16 659 (1994).
[26] L. N. Bulaewski, Sov. Phys. Solid State **5**, 2329 (1964).
[27] W. L. Zhong, B. D. Qu, P. L. Zhang, and V. G. Wang, Phys. Rev. B **50**, 12 375 (1994).