Soft modes of collective domain-wall vibrations in epitaxial ferroelectric thin films

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Mechanical restoring forces acting on the ferroelastic domain walls displaced from the equilibrium positions in epitaxial films are calculated for various modes of their cooperative translational oscillations. For vibrations of the domain-wall superlattice with the wave vectors corresponding to the center and boundaries of the first Brillouin zone, the soft modes are singled out, which are distinguished by a minimum magnitude of the restoring force. It is shown that, in polydomain ferroelectric thin films, the soft modes of wall vibrations may create enormously high contribution to the film permittivity.

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The formation of multiple patterns of elastic domains (twins) is a characteristic feature of the epitaxial ferroelectric films.[1–6] The experimental data[3,7] and theoretical considerations[8,9] suggest that in perovskite ferroelectrics the 90° domain walls (DWs) may be highly mobile on the microscopic scale even at room temperature.[10] Accordingly, the forced translational vibrations of 90° walls are believed to contribute considerably to the small-signal dielectric and piezoelectric responses of ferroelectric films.[8,11] Up to now, however, only one specific mode of DW vibrations in epitaxial films, i.e., the antiparallel motion of neighboring walls, was described theoretically.[8,11]

In this paper, a general analysis of the cooperative translational vibrations of the ferroelastic walls in epitaxial films is carried out. The calculations are performed in a conventional linear elastic approximation and based on the dislocation-disclination modeling of the sources of internal stresses in polydomain films.[12,13] Forced low-frequency vibrations of 90° walls in epitaxial thin films with a laminar $c/a/c/a$ structure are considered, and soft modes of DW vibrations are singled out, which are characterized by the enhanced collective mobility of the domain walls. It is shown that the excitation of a soft mode in a polydomain ferroelectric film may increase drastically the film dielectric response.

Consider a laminar 90° domain structure with the walls inclined at 45° to the film/substrate interface Σ (Fig. 1). Domain patterns of this type are widely observed in epitaxial thin films of perovskite ferroelectrics grown on (001)-oriented cubic substrates.[3–5] They consist of alternating elastic domains with the polar c axis orthogonal and parallel to Σ (c and a domains). Following Refs. 1 and 8, we shall assume that in equilibrium the $c/a/c/a$ structure has an exact periodicity. Then the initial domain geometry may be described by the width d of the c domains and the domain period D (see Fig. 1). Since c/a and a/c walls create disclinations of opposite sign at their junctions with Σ,[12,13] they should be considered as *physically distinct*. (This approach makes our theory essentially different from the description of twin-wall vibrations in bulk ferroelastic crystals, which was developed in Refs. 14,15.) Therefore, the domain pattern should be regarded as a superposition of two periodic arrays of equivalent DWs, shifted by the distance d from each other. Accordingly, displacements of the c/a and a/c walls from their equilibrium positions will be denoted here as $\delta_m^{(1)}$ and $\delta_n^{(2)}$, respectively, where the integers m and n define initial DW positions in the film. In this work, we assume that $\delta_m^{(1)}, \delta_n^{(2)} \ll \min\{d, D-d\}$.

Let us calculate now the variation ΔU of the energy of a polydomain film/substrate system, which is caused by translational vibrations of 90° walls. Restricting our analysis to the low-frequency range $\Omega \ll c_t/H$ (c_t is the velocity of transverse sound waves, H is the film thickness), we can neglect the kinetic energy of the medium[16] and evaluate ΔU in a conventional quasistatic linear elastic approximation.[8] (This approximation should be valid at frequencies up to $\Omega \sim 100$ MHz at $H \sim 100$ nm.) Then in the absence of external fields the variation ΔU will be reduced to the change ΔW of the elastic energy and can be represented as the following quadratic form:

$$\Delta W = \sum_{m,n} \left\{ \frac{1}{2} \chi[(m-n)D](\delta_m^{(1)}\delta_n^{(1)} + \delta_m^{(2)}\delta_n^{(2)}) - \chi[d+(m-n)D]\delta_m^{(1)}\delta_n^{(2)} \right\}. \quad (1)$$

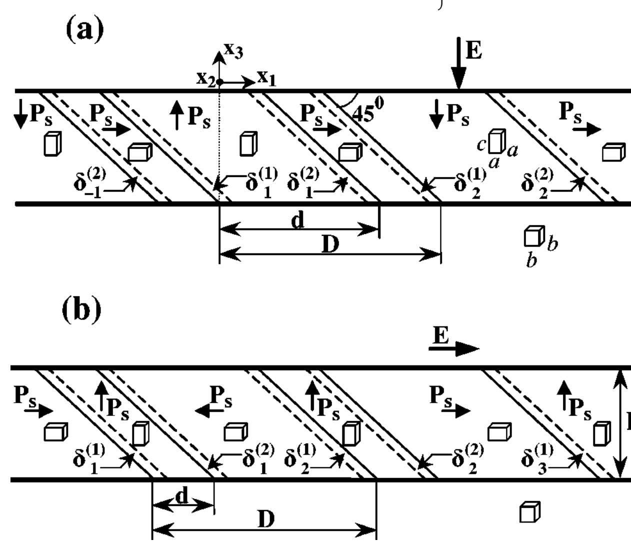

FIG. 1. Soft c mode (a) and a mode (b) of collective vibrations of 90° walls in ferroelectric films with the laminar $c/a/c/a$ structure and special polarization distributions. DW shifts in external electric field **E** are shown by dashed lines.

In deriving Eq. (1) we have taken into account that the elastic interaction between mth and nth walls depends only on the distance l between them, but not on their positions in the film. The negative sign of the second term in curly brackets reflects the fact that displacements of c/a and a/c walls in the same direction result in opposite changes of the sources of internal stresses in the epitaxial system. As shown in Ref. 11, these changes are equivalent to the introduction of additional edge dislocations at the DW junctions with the interface Σ. Dislocations with the Burgers vectors $\mathbf{B}$ normal to Σ allow for shifts of wedge disclinations modeling these junctions.[12,13] In turn, the appearance of defects with $\mathbf{B}$ parallel to Σ is due to changes in the distribution of dislocations modeling the interface, which take place on sections of Σ swept by moving DWs.[11]

The function $\chi(l)$ involved in Eq. (1) can be derived via the calculation of the elastic interaction between two parallel edge dislocations, situated at the distance H from the boundary of elastic half space. Assuming the film/substrate system to be elastically homogeneous and isotropic (with a shear modulus G and Poisson's ratio ν) and using the results of Ref. 17, we obtained the following expression for the function $\chi(l)$ calculated per unit DW length along the x_2 axis:

$$\chi(l)=\frac{G(S_a-S_c)^2}{\pi(1-\nu)}\left[\ln\left(1+\frac{4H^2}{l^2}\right)+\frac{4H^2(l^2-4H^2)}{(l^2+4H^2)^2}\right], \tag{2}$$

where $S_a=(b^*-a)/a$ and $S_c=(b^*-c)/c$ are the misfit strains between the film (having a tetragonal lattice with the parameters a and $c>a$ in the free state) and a cubic substrate with the effective lattice parameter b^*.[18] We have taken into account that the dislocation Burgers vectors are proportional to DW displacements and to $\pm(S_a-S_c)$.[11]

Equation (2) defines the coefficients of all terms in the quadratic form (1), except for the factor $\chi(0)$, which characterizes the restoring force that acts on a displaced wall when all other DWs are kept at their initial positions. Indeed, $\chi(l)$ diverges logarithmically at $l\to 0$ so that our method cannot be used to calculate $\chi(0)$. However, this factor may be found from the condition of elastic-energy invariance with respect to the translation of the DW "superlattice" as a whole. Using Eq. (1), we obtain ($k=\pm 1,\pm 2,\dots$)

$$\chi(0)=\chi(d)-\sum_k [\chi(kD)-\chi(d+kD)]. \tag{3}$$

Let us represent now the displacements of c/a and a/c walls in the form of Fourier series,

$$\delta_n^{(1)}=\sum_q \hat{\delta}^{(1)}(q)e^{iqnD}, \quad \delta_n^{(2)}=\sum_q \hat{\delta}^{(2)}(q)e^{iqnD}. \tag{4}$$

The Fourier transforms $\hat{\delta}^{(\alpha)}(q)$ ($\alpha=1,2$) of DW displacements are defined by the relations

$$\hat{\delta}^{(\alpha)}(q)=\lim_{N\to\infty}\frac{1}{N}\sum_n \delta_n^{(\alpha)}e^{-iqnD}, \tag{5}$$

where N is the total number of walls in a DW array. Using Eqs. (4), which represent displacements of individual walls as a superposition of the DW-lattice vibrations having various wave vectors q, we can rewrite the quadratic form (1) as

$$\Delta w=\sum_q \left\{\frac{1}{2}\hat{\chi}_0(q)[\hat{\delta}^{(1)}(q)\hat{\delta}^{(1)}(-q)+\hat{\delta}^{(2)}(q)\hat{\delta}^{(2)}(-q)] -\hat{\chi}_d(q)\hat{\delta}^{(1)}(q)\hat{\delta}^{(2)}(-q)\right\}, \tag{6}$$

where Δw is the change of the elastic energy ΔW calculated per "unit cell" of the DW superlattice (containing two neighboring walls), and

$$\hat{\chi}_0(q)=\sum_n \chi(nD)e^{-iqnD}, \quad \hat{\chi}_d(q)=\sum_n \chi(d+nD)e^{-iqnD}. \tag{7}$$

Equation (6) makes it possible to compare the mobilities of domain walls at different modes of their collective vibrations. (The damping factor may be ignored here because the frictional forces are local and thus independent of the mode of cooperative DW motion.) In this paper we shall consider only the modes with the wave vectors $q=0$ and $q=\pm\pi/D$, which correspond to the center and boundaries of the first Brillouin zone. In this case, $\hat{\delta}^{(\alpha)}(q)$ are real numbers so that the energy Δw becomes a function of only two variables at a fixed q. It is useful to introduce now the new collective coordinates $r(q)$ and $\varphi(q)$ satisfying the relations $\hat{\delta}^{(1)}(q)=r(q)\cos\varphi(q)$ and $\hat{\delta}^{(2)}(q)=r(q)\sin\varphi(q)$. Evidently, the "radius" $r(q)$ defines the deviation of the DW superlattice as a whole from the equilibrium state at the appearance of a mode with the wave vector q. The "polar angle" $\varphi(q)$ shows to which extent the c/a and a/c walls are involved in the vibrations: at $\varphi(q)=0$ or $\varphi(q)=\pi/2$ only the c/a or a/c walls oscillate, whereas at $\varphi(q)=\pi/4$ both walls participate equally in the vibrations.

The mechanical restoring force, which hinders the development of a certain mode of cooperative DW vibrations, is defined by the derivative of the energy Δw with respect to $r(q)$. Using Eq. (6) and taking into account that $\hat{\delta}^{(\alpha)}(q)=\hat{\delta}^{(\alpha)}(-q)$ at $q=0,\pm\pi/D$, we obtain

$$\hat{f}(q)=-\frac{\partial\Delta w}{\partial r(q)}=-r(q)[\hat{\chi}_0(q)-\hat{\chi}_d(q)\sin 2\varphi(q)]. \tag{8}$$

The magnitude of $\hat{f}(q)$ depends on the parameter $\varphi(q)$ and reaches extreme values at $\varphi(q)=\pi/4+\pi k/2$ with $k=\pm 1,\pm 2,\dots$ Therefore, the maximum and minimum DW mobilities correspond to the modes with $\hat{\delta}^{(1)}(q)=\hat{\delta}^{(2)}(q)$ or $\hat{\delta}^{(1)}(q)=-\hat{\delta}^{(2)}(q)$.

Using Eqs. (4), it can be shown that at $q=0$ the modes with extreme magnitudes of the restoring force turn out to be the rigid translation of DW superlattice ($\delta_n^{(1)}=\delta_n^{(2)}=\delta$) and the antiparallel motion[8] of c/a and a/c walls ($\delta_n^{(1)}=-\delta_n^{(2)}=\delta$). In turn, at $q=\pm\pi/D$ the relations defining two "extreme" modes take the form

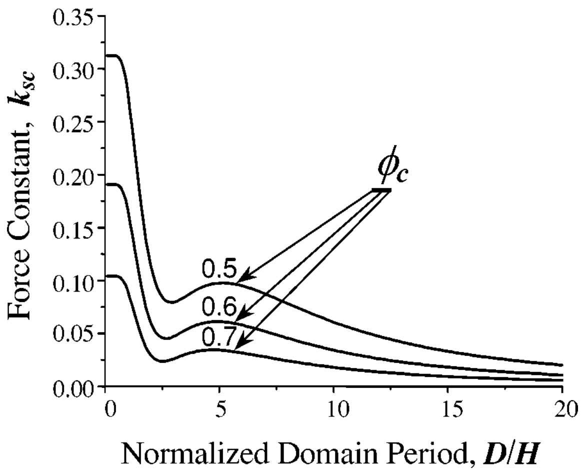

FIG. 2. Normalized force constant $k_{sc}(1-\nu)H/G(S_c-S_a)^2$ of the c mode as a function of the domain-wall periodicity D/H at three different values of $\phi_c=d/D$. Since according to Eqs. (13)–(14) $k_{sc}(1-\phi_c)=k_{sa}(\phi_c)$, these curves can be used to describe the constant k_{sa} of the a mode as well.

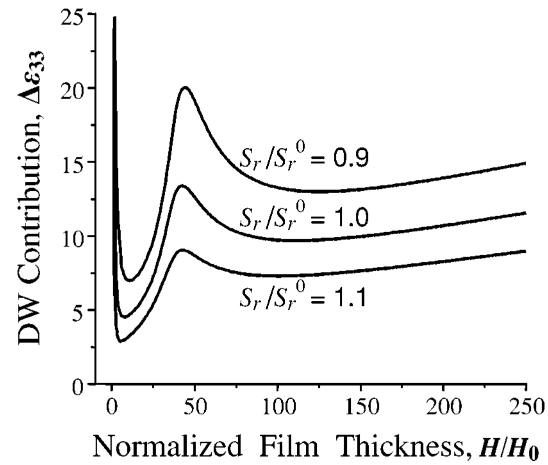

FIG. 3. Normalized c-mode contribution $\Delta\varepsilon_{33}\varepsilon_0 G(S_a-S_c)^2/P_s^2(1-\nu)$ to the electric permittivity as a function of the film thickness H/H_0. The curves are plotted at different values of S_r/S_r^0, where $S_r^0=1/2(1+\nu)$.

$$\delta_n^{(1)}=-\delta_n^{(2)}=(-1)^n\delta, \tag{9}$$

$$\delta_n^{(1)}=\delta_n^{(2)}=(-1)^n\delta. \tag{10}$$

The perturbation of DW superlattice described by Eq. (9) represents the antiparallel motion of neighboring a domains, during which their sizes remain constant [Fig. 1(a)]. The widths of neighboring c domains change in the opposite way so that the vibrations of this type may be termed *c mode*. Equation (10) describes a type of motion pairwise to the c mode (*a mode*), where the widths of neighboring a domains change in opposite phase, whereas the c domains shift as a whole [Fig. 1(b)].

For the revealed extreme modes, it is necessary to calculate the magnitude of the restoring force $f_{res}=-(1/2\sqrt{2}H)\partial\Delta w/\partial\delta$ acting per unit area of a displaced wall. At $q=0$, Eq. (6) gives $\Delta w=[\hat{\chi}_0(0)\mp\hat{\chi}_d(0)]\delta^2$, where the upper sign refers to the rigid translation of DW superlattice, whereas the lower one refers to the antiparallel motion of c/a and a/c walls (h mode). From Eqs. (7) and (3) it follows that $\hat{\chi}_0(0)=\hat{\chi}_d(0)$. Accordingly, in case of the rigid translation the restoring force $f_{res}=-k\delta$ goes to zero. For the h mode, this force is defined by the constant $k_h=(\sqrt{2}/H)\hat{\chi}_d(0)$. Substituting Eq. (2) into Eq. (7) and summing the series at $q=0$, one can calculate $\hat{\chi}_d(0)$ and obtain k_h as

$$k_h=\frac{\sqrt{2}G(S_a-S_c)^2}{\pi(1-\nu)H}\left[R\left(\frac{d}{2D},\frac{H}{2D}\right)+R\left(\frac{d}{2D}+\frac{1}{2},\frac{H}{2D}\right)\right], \tag{11}$$

where the function $R(x,y)$ is given by

$$R(x,y)=\ln\left[\frac{\cosh(4\pi y)-\cos(2\pi x)}{1-\cos(2\pi x)}\right]-8\pi^2y^2\frac{[\cosh(4\pi y)\cos(2\pi x)-1]}{[\cosh(4\pi y)-\cos(2\pi x)]^2}. \tag{12}$$

It should be noted that earlier[8] the force constant k_h was derived as $k_h=[\sqrt{2}G(S_a-S_c)^2/\pi(1-\nu)H]R(d/D,H/D)$. The analysis shows that Eq. (11) can be cast into this form as well.

At $q=\pm\pi/D$, the elastic-energy change Δw caused by the appearance of an extreme mode is given by $\Delta w=[\hat{\chi}_0(\pi/D)\pm\hat{\chi}_d(\pi/D)]\delta^2$, where the upper and lower signs refer to the c and a modes, respectively. By summing the series (7) at $q=\pm\pi/D$ with the account of Eqs. (2)–(3), it is possible to find $\hat{\chi}_0(\pi/D)$ and $\hat{\chi}_d(\pi/D)$. This yields the following expressions for the constants k_{sc} and k_{sa} defining restoring forces for the c and a modes:

$$k_{sc}=\frac{\sqrt{2}G(S_a-S_c)^2}{\pi(1-\nu)H}\left[R\left(\frac{d}{2D},\frac{H}{2D}\right)-R\left(\frac{1}{2},\frac{H}{2D}\right)\right], \tag{13}$$

$$k_{sa}=\frac{\sqrt{2}G(S_a-S_c)^2}{\pi(1-\nu)H}\left[R\left(\frac{d}{2D}+\frac{1}{2},\frac{H}{2D}\right)-R\left(\frac{1}{2},\frac{H}{2D}\right)\right]. \tag{14}$$

Numerical calculations based on Eqs. (13)–(14) show that k_{sc} and k_{sa} are positive at all allowed values of H/D and d/D, which indicates the stability of the initial $c/a/c/a$ structure.

Compare now the constants k_h, k_{sc}, and k_{sa}. The analysis of Eqs. (11)–(14) demonstrates that k_h is considerably larger than k_{sc} and k_{sa} at any domain geometry. This feature is due to the fact that the h mode changes the fraction $\phi_c=V_c/V$ of the film volume occupied by c domains, whereas the c and a modes leave ϕ_c unaltered (see Fig. 1). Thus, the antiparallel motion of c/a and a/c walls appears to be the most *hard mode* of collective DW vibrations.

In turn, the force constant k_{sc} at $d/D>0.5$ is smaller than k_{sa}, whereas at $d/D<0.5$ it is larger than k_{sa}. For the wave vector $q=\pi/D$, therefore, the minimum restoring force corresponds to the c mode at $d/D>0.5$ and to the a-mode at $d/D<0.5$. Accordingly, in the domain structures, where the equilibrium width of c domains is larger than that of a domains, the c mode may be regarded as a *soft mode* of DW vibrations. In the opposite case ($d/D<0.5$), the a mode becomes the soft mode of these oscillations. At $d/D=0.5$, the equality $k_{sc}=k_{sa}$ holds, and all the modes with $q=\pi/D$ have the same restoring force. (In nonperiodic domain structures, similar soft modes of DW vibrations should exist, which do not alter the average widths of c and a domains in the film.)

Equations (11)–(14) show that the force constants given in units of $G(S_a-S_c)^2/[(1-\nu)H]$ depend on the parameters D/H and d/D of unperturbed domain pattern only. For the constant k_{sc}, these dependences are shown in Fig. 2. It can be seen that k_{sc} decreases gradually with increasing volume fraction $\phi_c=d/D$ of c domains in the initial structure, but it is a nonmonotonic function of the normalized domain period D/H.

Let us analyze now how the extreme modes may be excited during the forced vibrations of 90° walls in epitaxial layers. In ferroelectric films, translational domain-wall vibrations can be induced by an external ac electric field $E(t)=E_m\sin(\Omega t)$. In a conventional plate-capacitor setup, the field $\mathbf{E}$ interacts mainly with the spontaneous polarization $\mathbf{P}_s$ in the c domains. When in all c domains the vector $\mathbf{P}_s$ has the same orientation due to poling, the measuring field $E(t)$ induces the h mode.[8] The excitation of the soft c mode appears to be a much more complicated technical problem. To achieve this goal, it is necessary to create a spatially inhomogeneous electric field $\mathbf{E}(x_1)$ in the film. The normal component E_3 of this field must be modulated in the film plane so as to be opposite in sign in the neighboring c domains at the same time. To create such a field, fingered electrodes with a special geometry, which provides the field modulation along the x_1 axis fitting the DW periodicity D, must be deposited on the substrate boundary and the film free surface.

The system of fingered electrodes may be used in two different ways. First, the c mode may be induced in a prepolarized film with the usual spatial distribution of $\mathbf{P}_s$, where the vector $\mathbf{P}_s$ has the same orientation in all c domains. In this case, a strong dc field with a fixed polarity must be applied to the film during its cooling through the Curie temperature in order to promote the formation of c domains under the electrodes and to create uniform polarizations $\mathbf{P}_s$ inside them. After this preliminary poling, a weak ac field $E_3(t)$ should be induced between the upper and lower electrodes having opposite polarities for the neighboring pairs of electrodes at any moment. Second, this system of electrodes may be used to construct a special initial distribution of the polarization $\mathbf{P}_s$ in the film, where $\mathbf{P}_s$ has opposite orientations in the neighboring c domains [Fig. 1(a)]. The application of ac field in the same phase to all pairs of electrodes will induce the soft c mode in this film.

The dielectric response ε_{33} of a film with the above special polarization pattern will contain a DW contribution caused by the c mode of wall vibrations. This contribution $\Delta\varepsilon_{33}$ may be calculated in the same way as it was done for the h mode in Ref. 8. The calculation gives $\Delta\varepsilon_{33}=2\sqrt{2}P_s^2/(\varepsilon_0 k_{sc} D)$. Using Eq. (13) for the force constant k_{sc}, we see that $\Delta\varepsilon_{33}$ can be represented as a product of the material parameter $\eta=P_s^2(1-\nu)/\varepsilon_0 G(S_a-S_c)^2$ and a dimensionless function of the structural parameters D/H and $\phi_c=d/D$. Since the equilibrium values of D/H and ϕ_c are known functions of the normalized film thickness H/H_0 and the relative coherency strain $S_r=(b^*-a)/(c-a)$ in the epitaxy,[13] we can calculate the dependences of $\Delta\varepsilon_{33}$ on these parameters. Some of our results are shown in Fig. 3.

The dependence of $\Delta\varepsilon_{33}$ on the film thickness H is marked by the presence of a local maximum and by the increase of $\Delta\varepsilon_{33}$ at $H\to 0$. The most important feature, however, consists in the fact that the c mode creates enormously large contribution to the permittivity of the ferroelectric films with a conventional thickness of $H=(0.1–1)$ μm. Indeed, at $H\gg H_0$ [$H_0\sim 1$ nm for $BaTiO_3$ and $PbTiO_3$ (Refs. 8,9)] the h mode gives only $\Delta\varepsilon_{33}\sim 0.5\eta$, whereas the c mode provides $\Delta\varepsilon_{33}\sim 10\eta$ and even more in a considerable range of misfit strains S_r. Accordingly, in $BaTiO_3$ and $Pb(Zr_{0.51}Ti_{0.49})O_3$ films, for example, the contribution $\Delta\varepsilon_{33}$ of the c mode at room temperature may be larger than 20 000, since in this case $\eta\approx 2000$.[8]

For the excitation of the a mode, it is necessary to create a spatially inhomogeneous electric field directed in the film plane ($E_1\neq 0$). Theoretically, the soft a mode may give anomalous contribution to the film in-plane permittivity ε_{11}.

Thus, in polydomain ferroelectric films, the measuring electric field may excite a soft mode of translational vibrations of 90° walls, which provides much larger collective DW mobility than the antiparallel motion of neighboring walls. Using a special setup with fingered electrodes, it may be possible to observe a very high dielectric response of an epitaxial film due to appearance of a soft mode of forced DW vibrations.

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