Effect of external stress on ferroelectricity in epitaxial thin films

A. Yu. Emelyanov,[1,2] N. A. Pertsev,[1,*] and A. L. Kholkin[2]
[1]*A. F. Ioffe Physico-Technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia*
[2]*Department of Ceramic and Glass Engineering, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*
(Received 10 July 2002; published 20 December 2002)

A nonlinear thermodynamic theory is used to describe the influence of an external mechanical loading on the ferroelectric, dielectric, and piezoelectric properties of epitaxial thin films grown on dissimilar cubic substrates. The calculations are performed for single-domain perovskite films in the approximation of a homogeneous loading of the film upper surface. The ''misfit strain-stress'' and ''stress-temperature'' phase diagrams are developed for epitaxial $PbTiO_3$ and $BaTiO_3$ films. It is shown that the loading may lead to drastic changes of the film polarization state. The most remarkable theoretical prediction is the stress-induced ferroelectric to paraelectric phase transition, which may take place at room temperature in films grown on ''compressive'' substrates that provide large negative misfit strains in the epitaxial system. The small-signal dielectric and piezoelectric constants of single-domain $PbTiO_3$ and $BaTiO_3$ films are also calculated and found to be very sensitive to the external stress under certain misfit strain-temperature conditions. The theory thus predicts that the mechanical loading of ferroelectric films can be employed for the fine tuning of their physical properties. The results of calculations may be also useful for the interpretation of experimental data obtained via scanning force microscopy and the indentation of ferroelectric films.

DOI: 10.1103/PhysRevB.66.214108 PACS number(s): 77.55.+f, 77.80.−e, 77.22.Ch

I. INTRODUCTION

It is well known that ferroelectric, dielectric, and piezoelectric properties of thin films may differ markedly from those of bulk ferroelectrics. These differences are partly due to the straining and two-dimensional clamping of the film by a dissimilar thick substrate. To quantify this mechanical substrate effect, ''misfit strain-temperature'' phase diagrams were developed for epitaxial ferroelectric films using a nonlinear thermodynamic theory.[1–7] In all performed theoretical studies, it was assumed that there are no external mechanical forces acting on the upper surface of the film. This situation is indeed typical of the polarization and dielectric measurements, where the film is practically free to deform in the out-of-plane directions. However, experimental studies of the direct piezoelectric effect require an external loading of the free surface.[8] The microindentation of ferroelectric thin films, which represents a useful technique to study their local depolarization properties,[9] is accompanied by the high mechanical stresses appearing under the metallic indenter.

Moreover, the mechanical loading of the film surface is a characteristic feature of the scanning force microscopy (SFM) operated in the piezoelectric contact mode.[10] The SFM piezoresponse imaging method, which is widely used by many researchers for the characterization of ferroelectric films on the nanometer scale,[11] involves the application of an electric field between the conductive SFM tip and the bottom electrode. The electrostatic attraction (Maxwell force) between this electrode and the tip/cantilever system produces a force pressing the tip to the film surface.[10] An additional mechanical force may be applied to the tip intentionally in order to create high local stresses in the measurement area.[10,12] It was found that the effective piezoelectric coefficient of lead zirconate titanate films appreciably decreases with the increase of the force acting on the tip.[12] Based on SFM studies of $BaTiO_3$ thin films in the piezoresponse mode, the authors of Ref. 10 proposed that the simultaneous application of electric field and compressive stress may induce a ferroelastoelectric switching in the film, resulting in the orientation of spontaneous polarization *antiparallel* to the applied electric field.

The correct interpretation of effects observed via SFM, microindentation, and other stress-inducing techniques requires the development of a *nonlinear* thermodynamic theory of ferroelectric thin films subjected to mechanical loading. Indeed, the order parameters (polarization components) in ferroelectric films may dramatically change with variations of lattice strains.[1–7] The account of strain inhomogeneity in a loaded film, however, will make the nonlinear theory extremely complicated, as can be deduced from the solutions obtained for linear elastic and piezoelectric solids subjected to spherical indentation.[13–16] Therefore, it is worthwhile to study first the case of uniform loading of an epitaxial film.

In this paper, a nonlinear thermodynamic theory is developed for uniformly loaded single-domain ferroelectric films, where the formation of elastic domains (twins) is assumed to be suppressed, e.g., due to kinetic reasons. It is shown that the external loading may lead to drastic changes of the polarization state of the film. Though our solution cannot be directly applied to the interpretation of the SFM data, it provides better understanding of the ferroelectric behavior of loaded epitaxial films and represents a necessary first step in the development of the general nonlinear theory.

II. NONLINEAR THERMODYNAMIC THEORY

Consider a single-crystalline perovskite thin film epitaxially grown in a paraelectric state on a dissimilar cubic substrate. Since changes of the in-plane lattice strains S_1, S_2, and S_6 in the overlayer during cooling or mechanical loading of the heterostructure are controlled by a much thicker substrate, the standard elastic Gibbs function G cannot be used

to determine the equilibrium thermodynamic states of an epitaxial film.[1] (We use the Voigt matrix notation and the rectangular reference frame with the x_3 axis orthogonal to the substrate surface.) When the film/substrate system is subjected to external mechanical forces, the Helmholtz free-energy function F is not appropriate for the thermodynamic description of the film as well. We may assume, however, that the epitaxial single-domain film has three fixed lattice strains (S_1, S_2, and S_6) and three constant internal stresses (σ_3, σ_4, and σ_5). For these mixed mechanical conditions, a modified thermodynamic potential $\tilde{G}$ introduced in Ref. 1 must be used in the theoretical calculations.

The potential $\tilde{G}$ of a ferroelectric film may be found in an explicit form using the relation $\tilde{G}=G+S_1\sigma_1+S_2\sigma_2+S_6\sigma_6$ and specifying the Gibbs function G. For perovskite ferroelectrics like $PbTiO_3$ and $BaTiO_3$, this function may be approximated by a six-degree polynomial in polarization components $P_i (i=1,2,3)$.[17,18] In the crystallographic reference frame, which can be directly employed in the case of (001)-oriented films considered in this paper, the function G has a well-known standard form.[1,4,17,18] The resulting expression for the modified potential shows that $\tilde{G}$ is a function of the polarization components P_i, stresses σ_n $(n=1,2,3,...,6)$, and strains S_1, S_2, and S_6. Assuming that the film is grown on a cubic substrate with the surface parallel to the (001) crystallographic plane, we have $S_1=S_2=S_m$ and $S_6=0$, where $S_m=(b^*-a_0)/a_0$ is the misfit strain in the epitaxial system (b^* is the substrate effective lattice parameter,[19] and a_0 is the equivalent cubic cell constant of the free standing film). The stress σ_3 in a single-domain film is governed by the applied load and will be regarded as a given external parameter throughout this paper, whereas the shear stresses σ_4 and σ_5 will be neglected ($\sigma_4=\sigma_5=0$). The remaining components σ_1, σ_2, and σ_6 of the stress tensor depend on the misfit strain S_m, external stress σ_3, and on the polarizations P_i. Explicit expressions for these stresses can be easily derived using the stress-strain relationships[18] $S_n=-\partial G/\partial\sigma_n$ together with the strain conditions $S_1=S_2=S_m$ and $S_6=0$. The substitution of these expressions into the basic formula for the modified thermodynamic potential transforms $\tilde{G}$ into a function of three independent variables: P_1, P_2, and P_3. After some algebraic rearrangement, $\tilde{G}$ can be cast into the form

$$\begin{aligned}\tilde{G}=&\frac{(S_m-s_{12}\sigma_3)^2}{s_{11}+s_{12}}-\frac{1}{2}s_{11}\sigma_3^2+a_1^*(P_1^2+P_2^2)+a_3^*P_3^2\\&+a_{11}^*(P_1^4+P_2^4)+a_{12}^*P_1^2P_2^2+a_{13}^*(P_1^2+P_2^2)P_3^2+a_{33}^*P_3^4\\&+a_{111}(P_1^6+P_2^6+P_3^6)+a_{112}[P_1^4(P_2^2+P_3^2)+P_2^4(P_1^2+P_3^2)\\&+P_3^4(P_1^2+P_2^2)]+a_{123}P_1^2P_2^2P_3^2,\end{aligned}\tag{1}$$

where

$$a_1^*=a_1-\frac{Q_{11}+Q_{12}}{s_{11}+s_{12}}S_m+\frac{Q_{11}s_{12}-Q_{12}s_{11}}{s_{11}+s_{12}}\sigma_3,\tag{2}$$

$$a_3^*=a_1-\frac{2Q_{12}}{s_{11}+s_{12}}S_m-\left(Q_{11}-\frac{2Q_{12}s_{12}}{s_{11}+s_{12}}\right)\sigma_3,\tag{3}$$

$$a_{11}^*=a_{11}+\frac{1}{2}\frac{1}{s_{11}^2-s_{12}^2}[(Q_{11}^2+Q_{12}^2)s_{11}-2Q_{11}Q_{12}s_{12}],\tag{4}$$

$$a_{33}^*=a_{11}+\frac{Q_{12}^2}{s_{11}+s_{12}},\tag{5}$$

$$a_{12}^*=a_{12}-\frac{1}{s_{11}^2-s_{12}^2}[(Q_{11}^2+Q_{12}^2)s_{12}-2Q_{11}Q_{12}s_{11}]+\frac{Q_{44}^2}{2s_{44}},\tag{6}$$

$$a_{13}^*=a_{12}+\frac{Q_{12}(Q_{11}+Q_{12})}{s_{11}+s_{12}}.\tag{7}$$

In Eqs. (1)–(7), a_1, a_{ij}, and a_{ijk} are the dielectric stiffness and higher-order stiffness coefficients at constant stress,[17,18] s_{ln} are the elastic compliances at constant polarization, and Q_{ln} are the electrostrictive constants of the paraelectric phase. The dielectric stiffness a_1 should be given a linear temperature dependence $a_1=(T-\theta)/2\varepsilon_0 C$ based on the Curie-Weiss law (θ and C are the Curie-Weiss temperature and constant, and ε_0 is the permittivity of the vacuum).

Equation (1) demonstrates that the dependence of $\tilde{G}$ on the polarization components P_i corresponds to that of the standard Gibbs energy function G of a free bulk crystal. However, the coefficients of the second- and fourth-order polarization terms in these two polynomials differ from each other. Remarkably, both the mechanical film/substrate interaction and the external loading lead to a renormalization of the second-order polarization terms. As can be seen from Eqs. (2) and (3), the renormalized coefficients a_1^* and a_3^* are linear functions of the misfit strain S_m and the applied stress σ_3. In contrast, the introduction of this stress into the theory does not affect the renormalized fourth-order coefficients a_{ij}^*. They are defined by Eqs. (4)–(7), which coincide with the relations derived in Ref. 1 for epitaxial films with a free upper surface.

The analysis of Eqs. (2) and (3) shows that the renormalization of the second-order polarization terms in the presence of stress σ_3 may be described by the introduction of an effective misfit strain S_m^σ and effective temperature T_σ given by the expressions

$$S_m^\sigma=S_m-(s_{11}+2s_{12})\sigma_3,\tag{8}$$

$$T_\sigma=T-2\varepsilon_0 C(Q_{11}+2Q_{12})\sigma_3.\tag{9}$$

If the high-order dielectric stiffness coefficients a_{ij} and a_{ijk} are independent of temperature, Eqs. (8) and (9) provide a simple way for the evaluation of the stress effect on the polarization states of epitaxial films. In this case, the effect of external stress becomes equivalent to the changes of the misfit strain and temperature from their actual values S_m and T to the effective strain S_m^σ and temperature T_σ. Therefore, the stress-induced transformations of polarization states can be

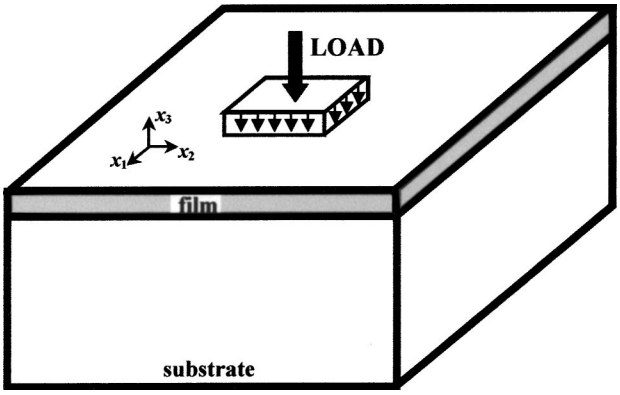

FIG. 1. Schematic of a uniform local loading of an epitaxial thin film.

predicted using the ''misfit strain-temperature'' phase diagrams of unloaded films and evaluating the shift in the (S_m, T) plane, which is caused by loading, from Eqs. (8) and (9). The influence of stress on single-domain states can be also determined directly from Eqs. (1)–(7). For $PbTiO_3$ and $BaTiO_3$ films, quantitative results may be obtained, because all their material parameters involved in the thermodynamic calculations are known to a high degree of precision.[17,18]

At this point it is necessary to emphasize that up to now, for clarity of presentation, we assumed the misfit strain S_m to remain constant during the film loading. However, S_m is generally a function of the applied stress since the substrate is also loaded (via the film). The influence of substrate deformations can be taken into account by adding a stress-induced change $\Delta S_m(\sigma_3)$ to the misfit strain $S_m=(b^*-a_0)/a_0$ of the unloaded epitaxial system. This change may be written as $\Delta S_m=[\beta(s_{11}^{\rm sub}+s_{12}^{\rm sub})+s_{12}^{\rm sub}]\ \sigma_3$, where $s_{mn}^{\rm sub}$ are the elastic compliances of a cubic substrate, and β is a geometric factor depending on the relative size of the loaded area of the substrate. If the whole substrate face is loaded, $\beta=0$ since the in-plane substrate deformations induced by a homogeneous stress σ_3 are equal to $S_1^{\rm sub}=S_2^{\rm sub}=s_{12}^{\rm sub}\ \sigma_3$.[8] In the other limiting case, where the loaded area has dimensions much smaller than those of the substrate face (but much larger than the film thickness, see Fig. 1), the deformations of the surface layer inside the loaded area are given by[13] $S_1^{\rm sub}=S_2^{\rm sub}=(s_{11}^{\rm sub}+2s_{12}^{\rm sub})(s_{11}^{\rm sub}-s_{12}^{\rm sub})\sigma_3/2s_{11}^{\rm sub}$, so that $\beta=(s_{11}^{\rm sub}-2s_{12}^{\rm sub})/2s_{11}^{\rm sub}$. As follows from the above relations, depending on geometry of the experimental setup, the misfit-strain change $\Delta S_m(\sigma_3)$ may be either positive or negative at the same stress σ_3. Therefore, in the rest of the paper we shall consider an intermediate situation, where the stress-induced changes of the misfit strain S_m may be neglected $[\beta\approx -s_{12}^{\rm sub}/(s_{11}^{\rm sub}+s_{12}^{\rm sub})]$. This approach has the advantage of demonstrating *per se* the direct effect of external stress on ferroelectricity in thin films.

III. MISFIT STRAIN-STRESS AND STRESS-TEMPERATURE DIAGRAMS OF $PbTiO_3$ AND $BaTiO_3$ EPITAXIAL FILMS

In order to describe the transformations of equilibrium thermodynamic states which may occur in epitaxial films during external loading, it is useful to develop phase diagrams, where the misfit strain S_m and external stress σ_3 are employed as two independent variables, whereas the temperature is assumed to be constant. Using Eqs. (1)–(7) with the numerical values of the involved material parameters listed in Ref. 4, we computed these ''misfit strain-stress'' diagrams for $PbTiO_3$ and $BaTiO_3$ epitaxial films under the short-circuited conditions (electric field $\mathbf{E}=0$ in the film). The equilibrium thermodynamic states of these films were determined by calculating all minima of the potential $\tilde{G}$ with respect to polarization components and then selecting the energetically most favorable phase. In agreement with the results obtained in Ref. 1, the paraelectric phase ($P_1=P_2=P_3=0$), *c* phase (tetragonal with $P_1=P_2=0$, $P_3\neq 0$), *aa* phase (orthorhombic with $P_1=P_2\neq 0$, $P_3=0$), and *r* phase (monoclinic with $P_1=P_2\neq 0$, $P_3\neq 0$) were found to be stable in $PbTiO_3$ and $BaTiO_3$ films.[20] The diagrams showing the stability ranges of these phases at the room temperature ($T=25\,^\circ$C) are presented in Fig. 2.

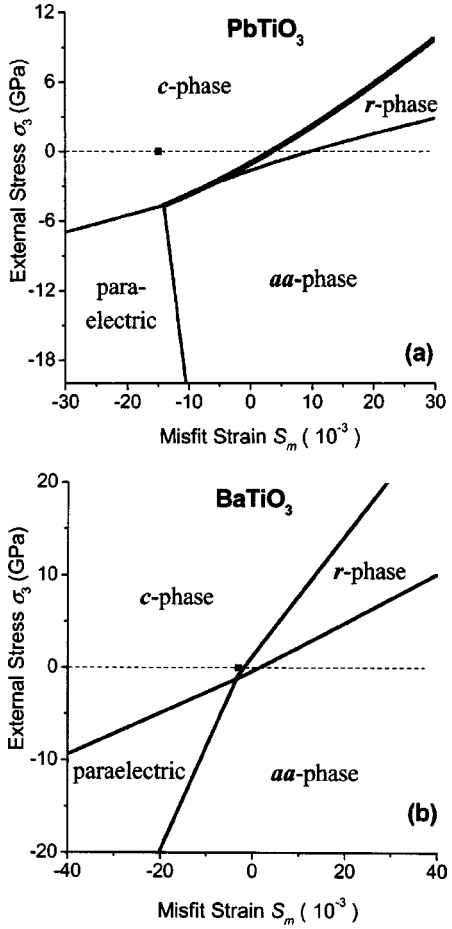

FIG. 2. Misfit strain-stress phase diagrams of single-domain $PbTiO_3$ (a) and $BaTiO_3$ (b) epitaxial films grown on (001)-oriented cubic substrates. The second- and first-order phase transitions are shown by thin and thick lines, respectively. The temperature is taken to be 25 °C. The square indicates the misfit strain, at which the polarization state of unloaded epitaxial film becomes equivalent to that of a bulk crystal due to the disappearance of internal stresses.

phase transitions in ferroelectric thin films. Depending on the misfit strain S_m in the epitaxial system, the initial *c* phase, for instance, may transform into the *r* phase, the *aa* phase, or even into the paraelectric phase under a compressive stress $\sigma_3<0$. Though the *c*-phase/*aa*-phase transition is similar to the 90° polarization switching, it leads to the appearance of an *orthorhombic* lattice in the film, which does not exist in bulk $PbTiO_3$ and $BaTiO_3$ crystals at room temperature.[17,18] The stress-induced formation of the *r* phase is of special interest because in this *monoclinic* phase the spontaneous polarization $\mathbf{P}_s$ has both in-plane and out-of-plane nonzero components. Compressive loading of a film containing the *c* phase may be a convenient technique to create unusual orthorhombic and monoclinic single-domain states in epitaxial ferroelectric films. Indeed, the nucleation of domain (twin) walls, which prevents the formation of these states in $PbTiO_3$ and $BaTiO_3$ films,[4] is expected to be suppressed at low temperatures due to kinetic reasons.

The most remarkable theoretical prediction is the ferroelectric to paraelectric phase transition induced by a compressive stress. This is an unexpected result since only the 90° polarization switching under mechanical stress is usually discussed for thin films in the literature.[9,10] During the *c*-phase/paraelectric-phase transformation, the film out-of-plane polarization P_3 gradually decreases with increasing compressive stress σ_3 in accordance with the relation

$$P_3^2=-\frac{a_{33}^*}{3a_{111}}+\left(\frac{a_{33}^{*2}}{9a_{111}^2}-\frac{a_3^*}{3a_{111}}\right)^{1/2}, \qquad (10)$$

where $a_3^*=a_3^*(S_m,\sigma_3)$ and a_{33}^* are given by Eqs. (3) and (5). This monotonic decrease of P_3 can produce a depolarization current similar to that observed during the microindentation of lanthanum-modified $PbTiO_3$ films.[9] Such a current can be measured if the mechanical load is applied to a film sandwiched between two electrodes, as in a conventional plate-capacitor setup.

To determine the effect of loading on the film polarization states at different temperatures, we also calculated phase diagrams, where the applied stress σ_3 and temperature T are used as two independent variables. Since the misfit strain S_m is a temperature-dependent parameter of the epitaxial system, the ''stress-temperature'' phase diagrams can be developed only for a given substrate. In this work, we have chosen Si as a representative substrate. As usual, it was assumed that the film is fully relaxed ($S_m=0$) at the growth temperature T_g, i.e., $b^*(T_g)=a_0(T_g)$. The variation of the effective substrate lattice parameter b^* during cooling was calculated from the nonlinear temperature dependence of the lattice constant of Si, which was reported in Ref. 21. Temperature dependences of the equivalent cubic cell constants a_0 of $PbTiO_3$ and $BaTiO_3$ crystals were determined using data[18,22] on their lattice constants and thermal expansion coefficients in the paraelectric phase and extrapolating $a_0(T)$ to lower temperatures. Substituting the calculated misfit strain $S_m(T)$ into Eqs. (1)–(3) and taking into account temperature dependences of the involved dielectric stiffnesses,[17,18] we developed the stress-temperature phase diagrams of $PbTiO_3$ and $BaTiO_3$ films grown on Si (see Fig. 3).

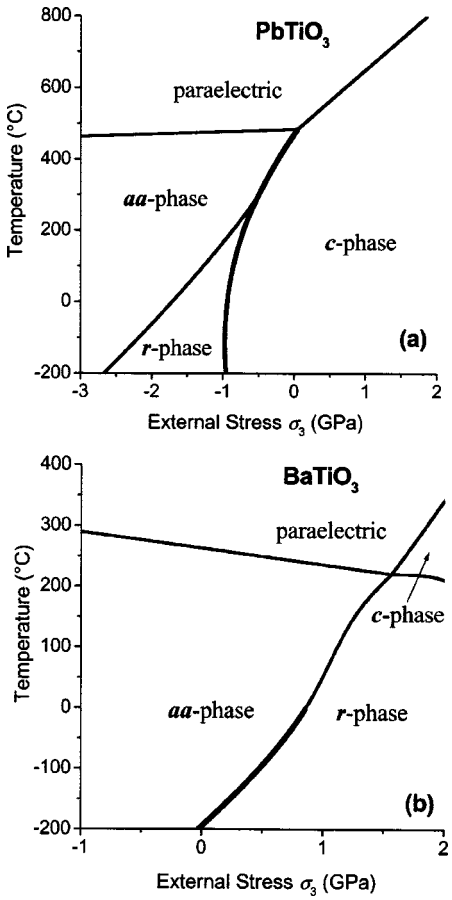

FIG. 3. Representative stress-temperature phase diagrams of single-domain $PbTiO_3$ (a) and $BaTiO_3$ (b) epitaxial films. The misfit strain in the film/substrate system is taken to be fully relaxed ($S_m=0$) at the growth temperature $T_g=800\,°C$. The variation of S_m during the cooling is assumed to be totally controlled by the difference in thermal expansion coefficients of the film and substrate. The dependence $S_m(T)$ corresponds to films deposited on silicon.

The calculations showed that the mechanical loading does not change the order of the paraelectric to ferroelectric phase transition, which remains of second order as in unloaded single-domain films.[1] The ferroelectric transition temperature *decreases* with increasing magnitude of compressive stress $\sigma_3<0$ and rises with increasing tensile stress $\sigma_3>0$ in the case of $PbTiO_3$ films. In contrast, this temperature *increases* with increasing compressive stress and varies nonmonotonically with tensile stress in $BaTiO_3$ films. Accordingly, by creating sufficient tensile stress in the $BaTiO_3$ film at a high temperature (~250 °C for the discussed substrate), it is possible to convert the ferroelectric *aa* phase into the paraelectric one. At low temperatures, the application of a tensile stress may induce the *aa*-phase/*r*-phase transformation [see Fig. 3(b)].

Using the developed nonlinear thermodynamic theory, we also analyzed the possibility of ferroelastoelectric switching[10] in $BaTiO_3$ and $PbTiO_3$ films subjected to both compressive stress σ_3 and electric field **E**. In accordance with the model employed in Ref. 10, it was assumed that the polarization **P** in a film remains oriented along the substrate

normal ($P_1=P_2=0$, $P_3\neq 0$) at all values of the applied stress σ_3. To make this assumption realistic, the misfit strain S_m in the film/substrate system was set negative and large enough to avoid transformations of the initial *c* phase into the *aa* and *r* phases during the loading at room temperature (see Fig. 2). The applied electric field **E** was supposed to be homogeneous and orthogonal to the film surfaces ($E_1=E_2=0, E_3\neq 0$), as in a conventional plate-capacitor setup. To take into account the influence of this field on the film polarization P_3, the latter was calculated from the equation $\partial\tilde{G}/\partial P_3=E_3$. Two possible solutions for the equilibrium polarization $P_3(\mathbf{E})$, i.e., parallel and antiparallel to the applied field **E**, were analyzed, and the corresponding extreme values of the modified thermodynamic potential $\tilde{G}$ were compared. During the calculations, the applied compressive stress was increased from zero up to several GPa, whereas the electric field was varied in a wide range between zero and 10^8 V/m. It was found that the antiparallel orientation of polarization with respect to the electric field **E** *never* appears to be energetically more favorable than the parallel orientation. Moreover, at compressive stresses of several GPa, which were predicted in Ref. 10 to be sufficient for ferroelastoelectric switching, the spontaneous polarization $\mathbf{P}_s(\mathbf{E}=0)$ vanishes in epitaxial films (see Fig. 2). The ferroelectric *c* phase transforms here into the paraelectric one, where the polarization cannot be oriented against the field **E**. Thus, the nonlinear thermodynamic theory does not support the prediction of the stress-induced 180° switching of polarization into the direction antiparallel to the applied electric field, which was made in Ref. 10 using the linear approximation.

IV. DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF UNIFORMLY LOADED $PbTiO_3$ AND $BaTiO_3$ FILMS

Since the stress-induced phase transitions may be accompanied by dielectric and piezoelectric anomalies, we discuss in this section the small-signal dielectric and piezoelectric responses of loaded ferroelectric films. The film dielectric constants ε_{ij} can be calculated from the reciprocal dielectric susceptibilities $\chi_{ij}=\partial^2\tilde{G}/\partial P_i\partial P_j$, which are found by direct differentiation of the modified thermodynamic potential $\tilde{G}$. In general, all components of the matrix χ_{ij} must be determined to compute the dielectric constant $\varepsilon_{kl}=\varepsilon_0+\eta_{kl}$, because the matrix of dielectric susceptibilities η_{ij} is the inverse of χ_{ij}, and the latter is diagonal only in the *c* phase. By substituting the equilibrium values $P_i(\mathbf{E}=0)$ of the polarization components into the expressions derived for χ_{ij} via Eq. (1), it is possible to calculate the small-signal dielectric responses ε_{ij} of epitaxial ferroelectric films as functions of the misfit strain, temperature, and external stress. For the out-of-plane permittivity ε_{33} of the *c* phase, e.g., the calculation yields

$$\varepsilon_{33}=\varepsilon_0+(2a_3^*+12a_{33}^*P_3^2+30a_{111}P_3^4)^{-1}, \qquad (11)$$

where P_3 is given by Eq. (10).

Performing necessary numerical computations, we determined the effect of external loading on the dielectric constants of $PbTiO_3$ and $BaTiO_3$ films. Figures 4 and 5 show

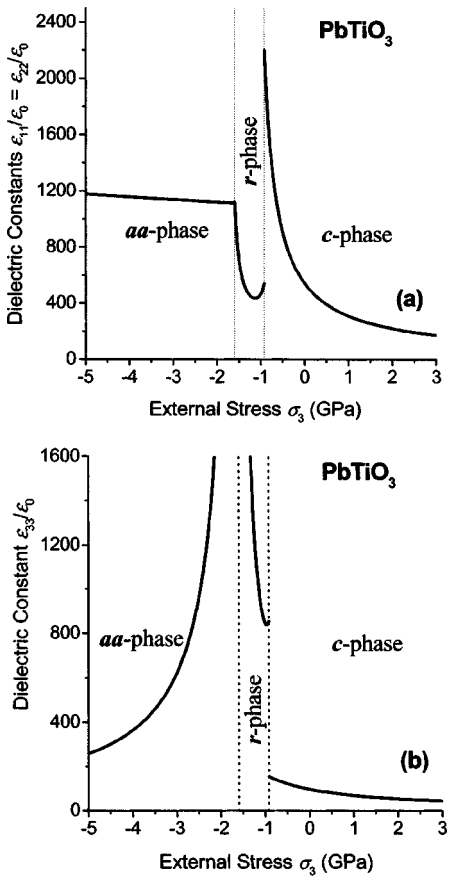

FIG. 4. Dependences of the dielectric constants $\varepsilon_{11}=\varepsilon_{22}$ (a) and ε_{33} (b) of single-domain $PbTiO_3$ films on the external stress σ_3 at $T=25\,^\circ$C. The misfit strain is taken to be $S_m=4.9\times10^{-4}$, which corresponds to the silicon substrate and the deposition at $T_g=800\,^\circ$C.

variations of the diagonal components ε_{ii} ($i=1,2,3$) of the dielectric tensor with the applied stress σ_3 at room temperature. (The misfit strain S_m in the film/substrate system was taken to be 4.9×10^{-4} for $PbTiO_3$ and 5.2×10^{-3} for $BaTiO_3$, which corresponds to the silicon substrate and $T=25\,^\circ$C.) In the case of a $PbTiO_3$ film, the application of a *compressive* stress leads to a strong increase of the in-plane dielectric responses $\varepsilon_{11}=\varepsilon_{22}$ of the *c* phase. They reach values in excess of 2000 at stresses close to $\sigma_3\cong-0.92$ GPa, at which the first-order *c*-phase/*r*-phase transition takes place. The out-of-plane permittivity ε_{33} experiences a jump at this critical stress and then continues to increase at larger stresses, diverging at the second-order *r*-phase/*aa*-phase transition. In contrast, the compressive loading of a $BaTiO_3$ film, which is initially in the in-plane polarization state (the *aa* phase), leads to the reduction of all the dielectric constants ε_{ii}. By creating a strong tensile stress in the film, however, it would be possible to increase the permittivities ε_{ii} significantly (see Fig. 5). This effect is due to the stress-induced second-order phase transitions in $BaTiO_3$ films [Fig. 2(b)]. Theoretically, the permittivities ε_{33} and $\varepsilon_{11}=\varepsilon_{22}$ should diverge at the *aa*-phase/*r*-phase and *r*-phase/*c*-phase transitions, respectively. However, the increase of the film permittivity, which could be observed experimentally, is limited due to extrinsic factors.

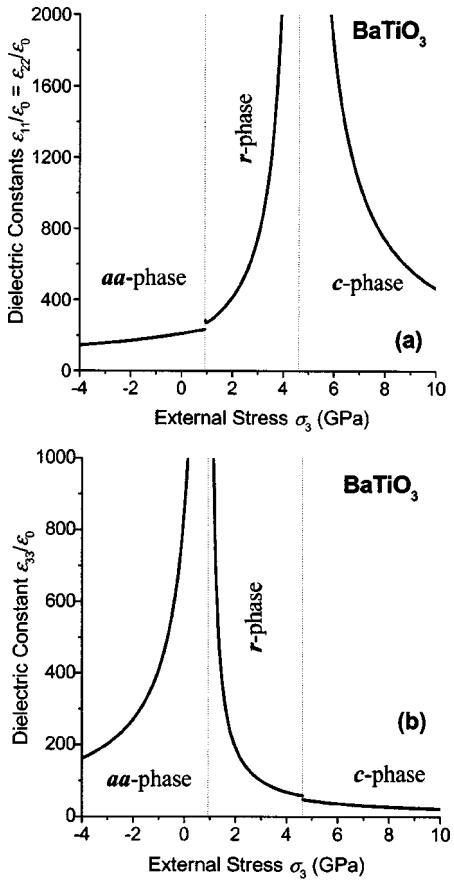

FIG. 5. Dependences of the dielectric constants $\varepsilon_{11}=\varepsilon_{22}$ (a) and ε_{33} (b) of single-domain $BaTiO_3$ films on the external stress σ_3 at $T=25\,^{\circ}\mathrm{C}$. The misfit strain is taken to be $S_m=5.2\times10^{-3}$, which corresponds to the silicon substrate and the deposition at $T_g=800\,^{\circ}\mathrm{C}$.

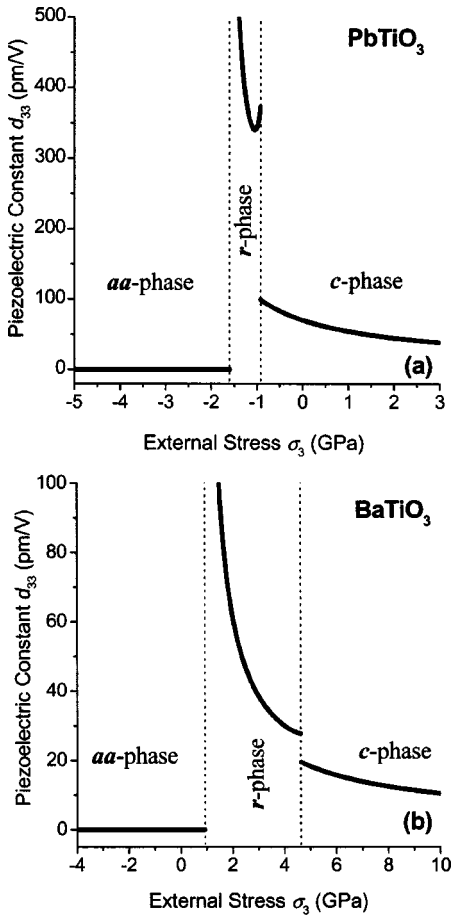

FIG. 6. Dependence of the longitudinal piezoelectric coefficient d_{33} on the external stress σ_3 calculated for single-domain $PbTiO_3$ (a) and $BaTiO_3$ (b) films at $T=25\,^{\circ}\mathrm{C}$. The misfit strain S_m is taken to be 4.9×10^{-4} (a) and 5.2×10^{-3} (b), which correspond to the Si substrate and $T_g=800\,^{\circ}\mathrm{C}$.

Let us now proceed to the theoretical description of the piezoelectric properties of loaded ferroelectric thin films. For simplicity, we shall restrict our analysis to the converse piezoelectric effect displayed by a thin film in a plate-capacitor setup. Since the epitaxial film is rigidly connected with a thick substrate, the application of an electric field E_3 orthogonal to the film surfaces may result only in a change of the film thickness and a tilt of the ferroelectric overlayer relative to the substrate normal. These effects are determined by the piezoelectric coefficients d_{33}, d_{34}, and d_{35}. In general, the constants d_{in} are calculated as $d_{in}=\partial S_n/\partial E_i=b_{kn}\eta_{ki}$, where $b_{kn}=\partial S_n/\partial P_k$. The strains $S_n=-\partial G/\partial\sigma_n$ may be found as functions of the polarization components P_i and stresses σ_n by differentiating the standard Gibbs free energy G. Taking into account the mechanical boundary conditions, we find the variable lattice strains in a loaded epitaxial film as

$$S_3=\frac{2s_{12}}{s_{11}+s_{12}}(S_m-s_2\sigma_3)+s_{11}\sigma_3+\left[Q_{12}-\frac{s_{12}(Q_{11}+Q_{12})}{s_{11}+s_{12}}\right]\times(P_1^2+P_2^2)+\left(Q_{11}-\frac{2s_{12}Q_{12}}{s_{11}+s_{12}}\right)P_3^2,$$

$$S_4=Q_{44}P_2P_3,\quad S_5=Q_{44}P_1P_3. \tag{12}$$

The differentiation of these relations makes it possible to calculate the relevant constants b_{kn} using the known equilibrium values $P_i(\mathbf{E}=0)$ of the polarization components. Since the small-signal dielectric susceptibilities η_{ki} of loaded films are already determined, the piezoelectric constants d_{33}, d_{34}, and d_{35} can be finally calculated as functions of the misfit strain S_m, temperature T, and external stress σ_3.

Figure 6 shows the dependence of the longitudinal piezoelectric coefficient d_{33} of $PbTiO_3$ and $BaTiO_3$ films on the applied stress at room temperature. It can be seen that the piezoelectric response of the c phase, which represents the stable single-domain state in $PbTiO_3$ films at the chosen misfit strain $S_m=4.9\times10^{-4}$, increases under compressive loading. The piezoelectric coefficient d_{33} experiences a jump at the critical stress $\sigma_3\cong-0.92$ GPa, at which the c phase transforms into the r phase, and then becomes anomalously high at the r-phase/aa-phase transition. On the other hand, the $BaTiO_3$ film is initially in the aa phase ($S_m=5.2\times10^{-3}$), so that d_{33} remains zero irrespective of the compressive stress. In contrast, a tensile stress applied to the $BaTiO_3$ film might drastically increase the piezoelectric con-

stant d_{33} since at the critical stress $\sigma_3 \cong 0.925$ GPa the *aa* phase transforms into the *r* phase, which displays a strong piezoelectric response near the critical stress.

V. CONCLUSIONS

The nonlinear thermodynamic theory predicts that the external loading may have a strong impact on the polarization state and physical properties of ferroelectric thin films. First and foremost, the compressive loading of thin films grown on ''compressive'' substrates, which provide large negative misfit strains in the epitaxial system, may transform the ferroelectric phase into the paraelectric one even at temperatures well below the Curie temperature of a bulk material (e.g., at room temperature). Second, the external stress may induce the rotation of the spontaneous polarization $\mathbf{P}_s$ relative to the film plane, resulting in the transition from the out-of-plane polarization state to the in-plane one. Third, the dielectric and piezoelectric constants of ferroelectric films may dramatically increase under the influence of applied stress. Therefore, the external loading provides an effective technique for improving the performances of ferroelectric thin films, which are necessary for their applications in microelectronic devices and microelectromechanical systems (MEMS). In addition, the stability of spontaneous polarization under the stresses developed during the device operation represents an important factor in determining the limits of applicability of MEMS, which employ the piezoelectric properties of ferroelectric thin films.

We believe that the phase transformations predicted in this paper can occur during the *nanoscale loading* of ferroelectric thin films via the SFM tip. Indeed, the highly stressed region V_σ under the tip has very small dimensions of the order of the contact radius ($\sim$10 nm). In this case, the stress-induced twinning of the strained subsurface region becomes energetically unfavorable due to the size effect (in $PbTiO_3$, e.g., the threshold size is about 50 nm; see Ref. 23). Therefore, in the absence of preexisting ferroelastic domain walls in the probed volume, only phase transitions between different single-domain states are expected to take place under the tip. It should be emphasized that the phase evolution may involve a continuous rotation of the polarization vector $\mathbf{P}_s$ and a gradual change of its magnitude. This nanoscale behavior is in contrast to the formation and motion of multiple 90° domain walls, which represents the most probable relaxation mechanism in the films subjected to microindentation.[9]

The stresses $\sigma_n(\mathbf{r})$ induced in a thin film by the SFM tip can be estimated using the Hertzian elastic approximation for the spherical indentation.[14] For $BaTiO_3$ and $PbTiO_3$ films loaded via silicon tips with a radius of about 10 nm, the calculation gives the mean stress $\langle \sigma_3 \rangle \sim -10$ GPa in the probed volume $V_\sigma \sim 10^3$ nm^3 under the tip at the applied forces $f \sim 10^{-6}$ N used experimentally.[10,12] As can be seen from Fig. 2, this compressive stress is high enough to transform the out-of-plane polarization state (*c* phase) into the paraelectric phase or into the in-plane polarization state (*aa* phase). Such a transformation will be accompanied by a strong decrease of the nanoscale piezoelectric response d_{33} of a ferroelectric film measured with the aid of the SFM.[24] Since the transformed nanoscale region is surrounded by a different (initial) phase, the decrease of d_{33} at high applied forces f must be reversible, as observed experimentally in Ref. 12.

Finally, it should be noted that the spherical indentation creates not only the normal stress σ_3 in the film, but also the in-plane stresses σ_1 and σ_2.[14] Since just under the tip these stresses are compressive and close to σ_3, their influence on the film polarization state is similar to the introduction of an additional negative misfit strain $\Delta S_m < 0$ into the epitaxial system. Therefore, the stress state just under the SFM tip promotes the ferroelectric to paraelectric phase transition.

ACKNOWLEDGMENT

The research described in this publication was made possible in part by a grant from the Foundation for Science and Technology of Portugal (Project No. POCTI/35502/CTM/2000).

*Corresponding author.
Electronic address: pertsev@domain.ioffe.rssi.ru

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