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Curie–Weiss-type law for the strain and stress effects on the dielectric response of ferroelectric thin films

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Variations of the dielectric properties of ferroelectric thin films with the misfit strain S_m in the film/substrate system and the associated biaxial stress σ inside the film are analyzed theoretically. Calculations are performed in a mean-field approximation for the dielectric response displayed in a plate-capacitor setup by single crystalline films epitaxially grown on tensile substrates ($S_m>0$). It is shown that, in the absence of misfit-strain-induced phase transitions, the film dielectric susceptibility η_{33} obeys the Curie–Weiss-type law $\eta_{33}(S_m)=\varepsilon_0 K_S/(S_m-S_m^*)$, $\eta_{33}(\sigma)=\varepsilon_0 K_\sigma/(\sigma-\sigma^*)$. Theoretical predictions are compared with the measured stress dependence of the dielectric response of polycrystalline $Ba_{0.7}Sr_{0.3}TiO_3$ films grown on $Pt/SiO_2/Si$. The theory explains the observed dielectric behavior and predicts the existence of in-plane polarization state in this film/substrate system. © *2000 American Institute of Physics.* [S0003-6951(00)03542-7]

For many applications of ferroelectric thin films, such as cells for GBit dynamic random access memories, integrated decoupling capacitors, high-frequency transducers, etc., a high electric permittivity is required.[1] The dielectric properties of a thin film, however, depend not only on the ferroelectric substance itself, but also on the substrate material and other factors. In particular, these properties should be strongly affected by the lattice misfit between the film and substrate.[2–4]

The misfit-strain changes directly manifest itself in the variation of the in-plane lattice parameter, which can be evaluated by the x-ray diffraction.[2] Even in the same film/substrate system, the misfit strain S_m may differ for films of different thicknesses because of the strain relaxation caused by the formation of misfit dislocations.[5] Strong changes of S_m with increasing film thickness are evident in $BaTiO_3/Pt/MgO$ and $BaTiO_3/SrTiO_3$ heterostructures.[2,6] The misfit strain can also be tuned to a certain extent by bending the substrate by an external load. Such a bending test was recently performed by Shaw *et al.* for $Ba_{0.7}Sr_{0.3}TiO_3$ films grown on platinum coated silicon substrates.[7] They evaluated the associated change of the in-plane biaxial stress σ in the film and attributed the observed variation of the capacitance to the stress effect. During the dielectric measurements, however, the film grown on a thick substrate is under a fixed strain, but not at constant stress.[3] Besides, in the presence of spontaneous polarization, the stress is not directly related to the strain.[2] Therefore, the stress effect is not equivalent to the underlying misfit-strain one.

In this letter, we analyze the strain and stress effects on the dielectric response exhibited by perovskite ferroelectric films in a conventional plate-capacitor setup. For clarity, we consider only ferroelectric overlayers grown on cubic substrates providing positive misfit strains in the heterostructure.

To describe the above effects theoretically, we will calculate the dielectric response of a single crystalline epitaxial film using the thermodynamic theory, which was developed recently.[3,4] In contrast with Refs. 3 and 4, a specific feature of the film dielectric properties will be reported here. Namely, our concept is to demonstrate that the reciprocal dielectric susceptibility of a ferroelectric thin film may be a *linear function* of the misfit strain S_m (or internal stress σ) even in the presence of a substantial spontaneous polarization P_s.

Consider a (001)-oriented film grown on a thick (001) substrate above the temperature of ferroelectric phase transition. When the film is in a paraelectric state, the reciprocal dielectric susceptibility χ_{33} in the film thickness direction is a linear function of the misfit strain:[3,4] $\chi_{33}=2a_1-4S_mQ_{12}/(s_{11}+s_{12})$, where a_1 is the dielectric stiffness of a bulk crystal, which linearly depends on temperature T, Q_{12} is the electrostrictive constant of paraelectric phase, and s_{ij} are the film elastic compliances at constant polarization. Therefore, to describe the misfit-strain dependence of the dielectric susceptibility η_{33}, a Curie–Weiss-type law

$$\eta_{33}(S_m)=\frac{\varepsilon_0 K_s}{S_m-S_m^*}, \qquad (1)$$

may be introduced on the analogy of the well-known Curie–Weiss law $\eta_{33}(T)\sim(T-\theta)^{-1}$. Here, $K_S=-(s_{11}+s_{12})/(4\varepsilon_0 Q_{12})$, and $S_m^*(T)=a_1(T)(s_{11}+s_{12})/(2Q_{12})$ is

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the critical misfit strain, at which the paraelectric phase loses its stability against the appearance of the *out-of-plane* polarization P_3. Since in the absence of spontaneous polarization the in-plane biaxial stress σ equals $\sigma = S_m/(s_{11}+s_{12})$, the dependence $\eta_{33}(\sigma)$ obeys the relation

$$\eta_{33}(\sigma) = \frac{\varepsilon_0 K_\sigma}{\sigma - \sigma^*} \tag{2}$$

similar to Eq. (1), with $K_\sigma = -(4\varepsilon_0 Q_{12})^{-1}$ and $\sigma^* = a_1/(2Q_{12})$. This corresponds to a linear relationship for $\chi_{33}(\sigma)$ discussed by Shaw *et al.*[7] However, as follows from the misfit strain-temperature phase diagrams of ferroelectric thin films,[3,4] Eqs. (1) and (2) are valid only at misfit strains not exceeding the second critical value $S_m^{**} = a_1(s_{11}+s_{12})/(Q_{11}+Q_{12})$, at which the paraelectric state loses its stability against the appearance of the *in-plane* polarization.

Since the ferroelectric phase transition in thin films is of the second order, just below the transition temperature the sixth-order polarization terms in the free-energy expansion may be neglected. In the resulting P^4 approximation, the Curie–Weiss-type law [Eqs. (1) and (2)] remains valid, despite the appearance of a nonzero spontaneous polarization $\mathbf{P_s}$. Indeed, the polarization correction to the reciprocal susceptibility χ_{33} is proportional to P_s^2, which linearly depends on the strain S_m in the discussed case. However, the parameters involved in Eqs. (1) and (2) now differ from those characterizing the paraelectric state. For single-domain $BaTiO_3$ (BT) and $PbTiO_3$ (PT) films, where the ferroelectric transition at $S_m > 0$ results in the formation of the orthorhombic *aa* phase with in-plane orientation of $\mathbf{P_s}$,[3,4] we obtain

$$S_m^* = \frac{a_1(1-2r)(s_{11}+s_{12})}{2[-Q_{12}+r(Q_{11}+Q_{12})]}, \tag{3}$$

$$K_s = \frac{s_{11}+s_{12}}{4\varepsilon_0[-Q_{12}+r(Q_{11}+Q_{12})]}, \tag{4}$$

where $r = a_{13}^*/(2a_{11}^*+a_{12}^*)$, a_{ij}^* are the energy-function coefficients introduced in Ref. 3, and Eq. (1) with these parameters is valid at $S_m > S_m^{**}$. Since the in-plane stress σ in the *aa* phase equals $\sigma = [S_m - (Q_{11}+Q_{12})P_s^2/2]/(s_{11}+s_{12})$, similar relations can be derived for σ^* and K_σ.

Well below the transition temperature, the sixth-order terms in the free-energy expansion also become important. Formally, the Curie–Weiss-type law [Eqs. (1) and (2)] is not valid anymore. In the *aa* phase, P_s^2 now has a square root dependence on S_m so that both linear and square root terms are involved in the explicit expression for $\chi_{33}(S_m)$ given in Ref. 8. In order to evaluate deviations from the Curie–Weiss-type law at room temperature, we computed $\chi_{33}(S_m)$ for BT and PT films numerically.[9]

Surprisingly, the dependence $\chi_{33}(S_m)$ was found to be practically linear within the stability range of the *aa* phase, as shown in Fig. 1 for BT. The plot $\chi_{33}(\sigma)$, computed with the aid of the above relation between σ and S_m, also deviates from the linear one only slightly (Fig. 2). Therefore, the observed variations of the film dielectric response with the misfit strain and internal stress may follow the Curie–Weiss-type law [Eqs. (1) and (2)] closely even in the presence of substantial spontaneous polarization. (We recall that, at the same time, χ_{33} is a nonlinear function of temperature.)

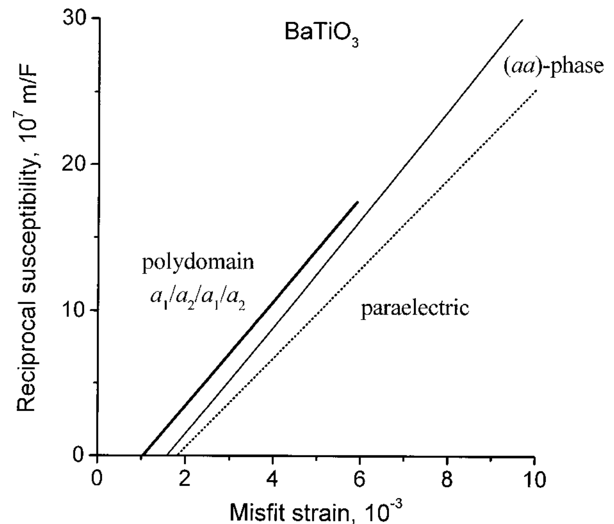

FIG. 1. Misfit-strain dependence of the reciprocal dielectric susceptibility χ_{33} computed for single domain and polydomain $BaTiO_3$ epitaxial thin films at 25 °C.

To investigate the applicability of Eqs. (1) and (2) further, we have performed similar calculations for polydomain epitaxial thin films. Domain widths were assumed to be much smaller than the film thickness, and the thermodynamic theory of dense laminar domain structures[10] was used for numerical computations. For BT and PT films grown on tensile substrates, the formation of the so-called $a_1/a_2/a_1/a_2$ domain structure[11] was found to be energetically favorable at the ferroelectric phase transition.[12] The calculations showed that at room temperature the dependencies $\chi_{33}(S_m)$ and $\chi_{33}(\sigma)$ are almost linear in polydomain BT and PT films as well (see Figs. 1 and 2), which again demonstrate the validity of Eqs. (1) and (2). (It should be emphasized that the domain-wall contribution to the film permittivity equals zero in our case.)

Consider now the parameters involved in the Curie–Weiss-type law well below the transition temperature. The critical misfit strain S_m^*, at which the in-plane polarization

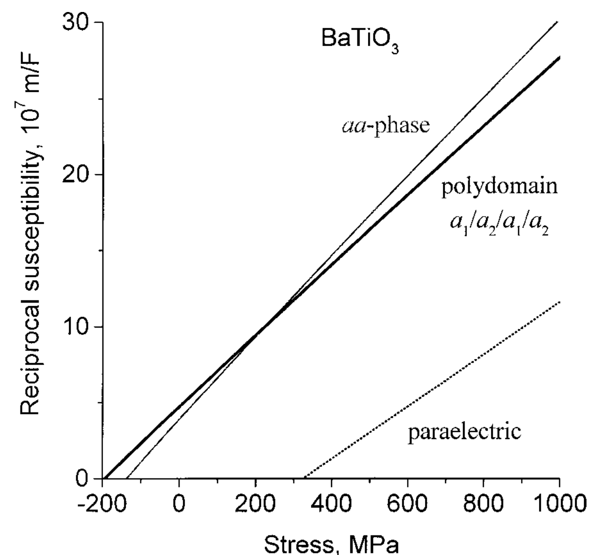

FIG. 2. Theoretical relationships between the in-plane biaxial stress σ and the reciprocal dielectric susceptibility χ_{33} in single domain and polydomain $BaTiO_3$ epitaxial thin films at 25 °C.

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TABLE I. Parameters of the Curie–Weiss-type law for the strain and stress effects on the dielectric response of ferroelectric thin films at 25 °C.

Film	State	S_m^*, 10^{-3}	K_S	σ^*, MPa	K_σ, GPa
$BaTiO_3$	$a_1/a_2/a_1/a_2$	1.03	3.16	−195	490
	aa phase	1.57	3.05	−138	428
	paraelectric	1.80	3.68	322	657
$PbTiO_3$	$a_1/a_2/a_1/a_2$	−0.76	3.27	−1550	448
	aa phase	9.88	6.2	126	816
	paraelectric	18.2	5.98	3310	1086

state (*aa* or $a_1/a_2/a_1/a_2$) loses its stability against the appearance of P_3, should be calculated from the equality $\chi_{33}=0$, which reduces to a quadratic equation for S_m^*. The critical stress σ^* is the root of a similar quadratic equation. In turn, K_S and K_σ should be regarded as fitting parameters, which can be extracted from the dependence computed numerically. For BT and PT films at room temperature, the calculated numerical values of S_m^*, σ^*, K_S, and K_σ are listed in Table I. The values characterizing the prototypic paraelectric state are given here for comparison. It can be seen that the presence of $\mathbf{P_s}$ may strongly influence the parameters of the Curie–Weiss-type law.

We proceed now to the analysis of the experimental data of Shaw *et al.* on the relationship between the in-plane stress and the dielectric response in $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) thin films.[7] Although the measurements in Ref. 7 were made on polycrystalline films, our approach can be used in this case as well because the straining of a thin film on a thick substrate is a macroscopic phenomenon similar in epitaxial and polycrystalline films.[8]

We first extract the actual permittivity of BST films from the data presented in Ref. 7. The film dielectric constant $\varepsilon_{33}(\sigma)$ may be calculated from the capacitance values $c(\sigma)$ measured in Ref. 7 as $\varepsilon_{33}=t/(c^{-1}-c_i^{-1})$, where $t=96.4$ nm is the film thickness and c_i is the interfacial capacitance caused by the presence of ''dead'' surface layers with a low permittivity. Taking $c_i=0.115\,\mathrm{F/m^2}$ as determined by Streiffer *et al.* for BST films,[13] we calculated the pure film permittivity ε_{33} for various values of σ given in Ref. 7. In the absence of external load (residual stress $\sigma=610$ MPa), the relative permittivity was found to be about 570, which is comparable with other data for $Ba_{0.7}Sr_{0.3}TiO_3$ films on platinized Si substrates.[13,14]

For the reciprocal susceptibility $\chi_{33}\approx 1/\varepsilon_{33}$ plotted versus the in-plane film stress σ, a linear relationship was obtained. This corresponds to a linear dependence $c(\sigma)$ reported by Shaw *et al.*,[7] which the authors regarded as a lack of evidence in favor of the presence of spontaneous polarization in the film. According to our results, the linearity of $\chi_{33}(\sigma)$ itself does not indicate the absence of $\mathbf{P_s}$. The experimental value of $K_\sigma\approx 1260$ GPa has the same order of magnitude as the theoretical value of $K_\sigma\approx 500$ GPa computed for BT films. Since for BT-based heterostructures the effect of $\mathbf{P_s}$ on K_σ is relatively weak (see Table I), it is not possible at the moment to gain evidence in favor or against the presence of $\mathbf{P_s}$ from the measured K_σ.

However, the extrapolation of $\chi_{33}(\sigma)$ to zero inverse susceptibility results in a very large effective critical stress $\sigma^*\approx -1500$ MPa. If $\mathbf{P_s}=0$, the critical stress in Eq. (2) may be calculated as $\sigma^*=a_1/(2Q_{12})=-(T-\theta)K_\sigma/C$, where θ and C are the Curie–Weiss temperature and constant of a bulk material. With $\theta=297$ K, $C=1.18\times 10^5$ K (measured for a bulk ceramic[15]), and the observed K_σ, we find that $\sigma^*\approx -10$ MPa, which is two orders of magnitude smaller than the experimental estimate. In the presence of $\mathbf{P_s}$, the dependence $\chi_{33}(\sigma)$ may be roughly evaluated for BST films numerically by taking the involved material parameters as weighted averages of those known for pure $BaTiO_3$ and $SrTiO_3$.[4,16] The apparent critical stress σ^*, which results from the extrapolation of the part of $\chi_{33}(\sigma)$ located between 600 and 1100 MPa, was found to be about (−200) MPa. This value is in better agreement with the experimental one, which in our view indicates the presence of spontaneous polarization in the films in question.[17]

The existence of the in-plane polarization state in BST films grown on Pt-coated Si substrates is further strongly supported by the observed temperature dependence of the permittivity. Indeed, $\varepsilon_{33}(T)$ deviates from the Curie–Weiss law at about 350 K,[7,13,14] i.e., well above the Curie–Weiss temperature of the bulk material (297 K). This agrees with the behavior described by the thermodynamic theory,[8] which predicts the ferroelectric phase transition at about 415 K in a single crystalline BST film on Si.

Thus, our analysis removes an apparent contradiction between the observed linear variation of the reciprocal susceptibility of BST films with stress and a strong deviation from the Curie–Weiss law in the temperature dependence of the film dielectric response.

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