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Abstract
Recent experimental measurements of large flexoelectric coefficients in ferroelectric ceramics suggest that strain gradients can affect the polarization and permittivity behaviour of inhomogeneously strained ferroelectrics. Here we present a phenomenological model of the effect of flexoelectricity on the dielectric constant, polarization, Curie temperature (T_C), temperature of maximum dielectric constant (T_m) and temperature of the onset of reversible polarization (T_{ferro}) for ferroelectric thin films subject to substrate-induced epitaxial strains that are allowed to relax with thickness, and the qualitative and quantitative predictions of the model are compared with experimental results for $(Ba_{0.5}Sr_{0.5})TiO_3$ thin films on $SrRuO_3$ electrodes. It is shown that flexoelectricity can play an important role in decreasing the maximum dielectric constant of ferroelectric thin films under inhomogeneous in-plane strain, regardless of the sign of the strain gradient.

1. Introduction

When the thickness of epitaxially grown ferroelectric thin films is decreased, changes in functional properties occur: the anomaly in the dielectric constant around the Curie temperature is progressively suppressed [1, 2]; the absolute magnitude of the dielectric constant collapses [1–3]; the coercive field increases [4]; and the remnant polarization frequently changes [5, 6]. A great deal of work has been done to try and understand the origin of such 'size effects' by considering, for example, the influences of epitaxial strain [6, 7], Schottky barriers [8], size-induced phonon hardening [9], changes in grain size and microstructure [10], field penetration into electrodes [11] and alteration in polarization

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states at the electrode–ferroelectric boundaries [12–16]. However, despite extensive research, a complete understanding of the origin of size effects has not yet been achieved. Here an additional possible contribution is considered, namely, the manner in which stress/strain *gradients* inside the thin film change its functional behaviour.

When a film grows epitaxially on a substrate, the bottom layers of the film are subject to important stresses due to lattice mismatch. Such stresses gradually relax as the thickness of the film increases. This strain relaxation has been partially taken into account in recent literature [6, 17, 18] by introducing a thickness-dependent stress (strain) term which is coupled, through the electrostrictive coefficient (Q_{ij}), to the square of the polarization in the Landau–Ginzburg–Devonshire (LGD) free energy. Ultimately, though, in such models the effect of the strain gradient is equivalent to that of a homogeneous strain whose value is the *average* across the film thickness. This approach is reasonably effective in predicting how the apparent Curie temperature evolves as a function of mismatch strain and thickness [6, 17, 18] and also in describing the strain–thickness–temperature phase diagram [18, 19]. However, it does not generally predict the observed decrease in peak permittivity (the dielectric peak as a function of temperature still presents a singularity at the shifted T_C). This has been noted in recent literature [20, 21], but theoretical attempts to address the issue using homogeneous strain approaches have so far only been able to reproduce the smearing of the dielectric peak under very specific conditions (tensile strain, $\langle 111 \rangle$ out-of-plane orientation), when in fact, the disappearance of the dielectric singularity at T_C and the general decrease of the permittivity of thin films with decreasing thickness are universal features of the size effect.

The importance of the effect of strain gradients on the polarization of perovskite ferroelectric ceramics has been recently evidenced by a series of experimental papers by Ma and Cross [22, 23], who have measured the value of the so-called flexoelectric coefficient. The flexoelectric coefficient measures the amount of polarization induced in a dielectric material by strain gradients alone. Values of the flexoelectric coefficient as large as 20 μC m^{-1} for (Pb, Zr)TiO$_3$ (PZT) or 100 μC m^{-1} for (Ba, Sr)TiO$_3$ (BST) prompted the authors of these works to suggest that the flexoelectric effects could be of major importance in ferroelectric thin films [23]. In this paper the potential impact of flexoelectric coupling on the dielectric and polarization properties of ferroelectric thin films will be analysed using a phenomenological approach, and compared with experimental results for inhomogeneously strained ferroelectric thin films.

2. Phenomenological theory of flexoelectricity

The first phenomenological description of the flexoelectric effect is due to Kogan [24], who proposed the inclusion of a coupling term between the strain gradient and polarization in the thermodynamic potential. His work was explored by Tagantsev for the case of crystalline dielectrics, and an estimation of the order of magnitude of the flexoelectric coefficient was suggested as $\mu \approx e/a$, where e is the charge of the electron and a is the lattice parameter of the crystal. Phenomenological arguments indicated that this value for normal dielectrics should be multiplied by the relative permittivity for the case of high permittivity materials, including ferroelectrics [25].

The role of the dielectric constant in enhancing the flexoelectric coefficient was indeed confirmed by the experiments of Ma and Cross, who measured the flexoelectric coefficient as a function of temperature for BST [22], and observed the flexoelectric coefficient to reach a maximum near the dielectric peak associated with the ferroelectric phase transition.

Here we are concerned specifically with the phenomenological description of flexoelectricity in relation with its impact on the dielectric behaviour of thin films. We will start with the expression for the Landau–Ginzburg–Devonshire (LGD) free energy (ΔG) of an

infinitesimally thin single-domain perovskite ferroelectric single crystal, epitaxially clamped onto a cubic substrate, with in-plane elastic stresses due to lattice mismatch between the film and substrate. We shall add to the conventional free energy expression a flexoelectricity term to account for the coupling between the polarization and stress gradient, and a converse flexoelectricity term to account for the coupling between the stress and polarization gradient. Polarization is only allowed along the z axis (P_3), and Voigt notation is used:

$$\Delta G = \tfrac{1}{2}aP_3^2 + \tfrac{1}{4}\beta P_3^4 - \tfrac{1}{2}s_{ij}\left(\sigma_i\sigma_j\right) - Q_{i3}\sigma_i P_3^2$$
$$- \gamma_{i3}\frac{\mathrm{d}\sigma_i}{\mathrm{d}z}P_3 - \eta_{i3}\sigma_i\frac{\mathrm{d}P_3}{\mathrm{d}z} + G\left(\frac{\mathrm{d}P_3}{\mathrm{d}z}\right)^2 + K\left(\frac{\mathrm{d}\sigma_i}{\mathrm{d}z}\right)^2 - E_3 P_3 + \sigma_i\varepsilon_j \qquad (1)$$

with γ_{i3} being the stress-related flexoelectric coupling coefficient, η_{i3} being the converse flexoelectric coefficient and T_C being the Curie temperature. We consider that only in-plane stresses arise from the mismatch, and that these are thickness dependent, so $\sigma_1 = \sigma_2 = \sigma(z)$ is the mismatch-induced stress and all other stress components are 0; likewise $\varepsilon_1 = \varepsilon_2 = \varepsilon(z) =$ in-plane strain. In this treatment only the out-of-plane polarization is considered. Both the correlation term $G(\mathrm{d}P/\mathrm{d}z)^2$ and the flexoelectric coupling mean that the polarization is, in principle, thickness dependent, so $P_3 = P(z)$. To find the actual total free energy we integrate equation (1) with respect to z; thus

$$\Delta G = \int \left(\tfrac{1}{2}aP(z)^2 + \tfrac{1}{4}bP(z)^4\right)\mathrm{d}z - \tfrac{1}{2}(s_{11} + s_{12})\int \sigma(z)^2\,\mathrm{d}z$$
$$- Q\int\sigma(z)P(z)^2\,\mathrm{d}z - \gamma\int P(z)\frac{\delta\sigma(z)}{\delta z}\,\mathrm{d}z - \eta\int\sigma(z)\frac{\delta P(z)}{\delta z}\,\mathrm{d}z$$
$$+ \frac{1}{2}G\int\left(\frac{\delta P(z)}{\delta z}\right)^2\mathrm{d}z + \frac{1}{2}K\int\left(\frac{\delta\sigma(z)}{\delta z}\right)^2\mathrm{d}z - E\int P(z)\,\mathrm{d}z$$
$$+ \int\sigma(z)\varepsilon(z)\,\mathrm{d}z. \qquad (2)$$

This expression is essentially the same as obtained in previous works [26, 27], the only difference being the inclusion of the flexoelectric and converse flexoelectric terms. The equilibrium solution is found by minimizing with respect to the order parameters. In order to solve this equation we must know the boundary conditions. It is useful to assume a symmetric system with zero boundary conditions so that we can then simplify minimization using the Euler–Lagrange variational method. The physical validity of this approximation is arguable and may depend, among other things, on the type of electrode used. If we did not impose zero boundary conditions, the free energy would have to include the surface term $+1/2D\delta^{-1}(P_{s1}^2 + P_{s2}^2)$, where D is a constant, P_{si} are the polarizations at the two surfaces and δ is the extrapolation depth [26–28]. For the purpose of the present analysis, though, we shall simplify the problem and consider a zero boundary condition[4]. Under these conditions we get, for the derivative with respect to P,

$$E = aP(z) + bP(z)^3 - 2Q_{13}P(z)\sigma(z) - \gamma_{13}\frac{\delta\sigma(z)}{\delta z} - \frac{\mathrm{d}}{\mathrm{d}z}\left[-\eta_{13}\sigma(z) + G\frac{\delta P(z)}{\delta z}\right]. \qquad (3)$$

And minimization with respect to the stress yields

$$-\varepsilon(z) = -(s_{11} + s_{12})\sigma(z) - Q_{13}P(z)^2 - \eta_{13}\frac{\delta P(z)}{\delta z} - \frac{\mathrm{d}}{\mathrm{d}z}\left[-\gamma_{13}P(z) + K\frac{\delta\sigma(z)}{\delta z}\right]. \qquad (4)$$

Hence,

$$\sigma(z) = \frac{Y}{1-\nu}\left(+\varepsilon(z) - Q_{13}P(z)^2 - \eta_{13}\frac{\delta P(z)}{\delta z} - \frac{\mathrm{d}}{\mathrm{d}z}\left[-\gamma_{13}P(z) + K\frac{\delta\sigma(z)}{\delta z}\right]\right) \qquad (5)$$

[4] A constant term can be added to the stress variable so that it is 0 at the boundary.

where we have related the elastic compliances to the Young's modulus Y and the Poisson's ratio ν. We can now substitute (5) into (4) and calculate the polarization. In order to simplify the analysis, we shall consider a situation where $\frac{d}{dz}[K\frac{\delta\varepsilon(z)}{\delta z}]$ is ignored. We then obtain the following equation:

$$E = P(z)\left[a - 2Q_{13}\frac{Y}{1-\nu}\varepsilon(z)\right] + P(z)^3\left[b + 2Q_{13}^2\frac{Y}{1-\nu}\right]$$
$$- (\gamma - \eta)\frac{Y}{1-\nu}\frac{d\varepsilon(z)}{dz} - \left[G - \frac{Y}{1-\nu}(\gamma-\eta)^2\right]\frac{d^2P(z)}{dz^2}. \tag{6}$$

For conventional (non-relaxor) ferroelectrics we have that

$$a = \alpha(T - T_c) \tag{7}$$

where α is the Curie constant and T_c is the critical temperature for the ferroelectric transition (the Curie temperature); the first coefficient of equation (6) can be conveniently redefined as

$$a^*(z) = \alpha(T - T_C^*(z)) \tag{8}$$

where

$$T_C^*(z) = T_C + \frac{2}{\alpha}\frac{Y}{1-\nu}Q_{13}\varepsilon(z). \tag{9}$$

Thus, given that Q_{13} is negative, the Curie temperature will shift up or down depending on whether the in-plane strain is negative (compressive) or positive (tensile), respectively.

The second coefficient of equation (6) becomes

$$b^* = \left[b + 2Q_{13}^2\frac{Y}{1-\nu}\right]. \tag{10}$$

Here it is worth noting that the bulk phase transition of ferroelectrics such as BaTiO$_3$ or PbTiO$_3$ is first order, which means that b is negative and thus a P^6 term should be included in the thermodynamic potential for the proper description of the ferroelectric transition. However, the addition of the electrostrictive term in equation (10) changes the sign of b^* from negative to positive [7, 19], thus changing the character of the phase transition from first to second order, which allows the P^6 term to be neglected, thereby simplifying the treatment (which is now analytically solvable). Empirically, this has been seen to be the case for BST thin films [6, 7]. In the present work we have therefore focused on the case $b^* > 0$ (second-order transition).

The last coefficient of equation (6) is defined as

$$G^* = \left[-\frac{Y}{1-\nu}(\gamma-\eta)^2 + G\right]. \tag{11}$$

This yields the final expression

$$E = a^*P(z) + b^*P(z)^3 - (\gamma-\eta)\frac{Y}{1-\nu}\frac{d\varepsilon(z)}{dz} - G^*\frac{d^2P(z)}{dz^2}. \tag{12}$$

The inverse permittivity is

$$\chi^{-1} = \frac{dE}{dP} = \frac{d^2(\Delta G)}{dP^2} = 3b^*P^2 + \alpha(T - T_C^*) - \frac{d}{dP}\left[G^*\frac{d^2P}{dz^2}\right]. \tag{13}$$

And the effectively measured inverse permittivity will be found by integrating with respect to z and dividing by the thickness of the capacitor. We can now solve these equations to calculate the polarization, and the inverse permittivity as a function of strain, thickness and temperature. In this paper we shall focus on the case of a film subject to externally induced strain arising from lattice mismatch with the substrate.

Before proceeding to calculate the solution, though, it is necessary to relate the flexoelectric coefficients in the model with the value experimentally measured. In order to do this, we note that G^* is of order 10^{-9} J m^3 C^{-2} [15, 27], and thus this term is only important in an ultrathin film regime, where the gradient term associated with the surface depolarization becomes relatively important. For bulk ceramics or single crystals, the $G^* \mathrm{d}^2 P/\mathrm{d}z^2$ term in equations (12) and (13) can therefore be ignored, and the inverse permittivity is

$$\chi^{-1} = 3b^* P^2 + \alpha(T - T_C^*). \tag{14}$$

If this is substituted back into the equation for the polarization, the following expression is obtained:

$$E = \chi^{-1} P(z) - (\gamma - \eta)\frac{Y}{1-\nu}\frac{\mathrm{d}\varepsilon(z)}{\mathrm{d}z} - 2b^* P(z)^3. \tag{15}$$

For small polarizations (i.e., well into the paraelectric state), the P^3 term can also be ignored to a first approximation. Thus, rearranging the terms, and setting $E = 0$, we obtain the following expression for the purely flexoelectric polarization as a function of strain gradient in a bulk ferroelectric:

$$P(z) = \chi(\gamma - \eta)\frac{Y}{1-\nu}\frac{\mathrm{d}\varepsilon(z)}{\mathrm{d}z}. \tag{16}$$

If the flexoelectric coefficient μ is measured as the derivative of the polarization with respect to the strain gradient, it is clear that the flexoelectric coefficient will be proportional to the permittivity, as expected. Equation (16) also allows us to relate the phenomenological coefficients $(\gamma - \eta)$ in our model to the empirically measured coefficient, μ:

$$\mu = (\gamma - \eta)\chi\frac{Y}{1-\nu}. \tag{17}$$

Typical values of μ for BST are of the order of 10^{-4} C m^{-1} [22], so the flexoelectric coefficients in the model would be of the order of $(\gamma - \eta) \sim 10^{-9}$ m^3 C^{-1}.

It must be emphasized that equation (16) is only valid for small values of the polarization; otherwise one has to solve equation (15). This has very important consequences from an experimental point of view: Ma and Cross noted that the linear dependence between the flexoelectric polarization and strain gradient broke down near the dielectric peak, and they tentatively attributed this to the possibility that some small domains of ferroelectric polarization might nucleate above T_c within the ceramic. However, such an appearance of ferroelectricity at temperatures higher than the bulk T_c would be very unlikely for the absolute value of the strains applied in their experiment, as they also correctly noted [22]. We think that, instead, as the flexoelectric polarization becomes large due to the increase in permittivity near T_c, the assumption of a small P breaks down, and thus the flexoelectric polarization departs from the linear dependence on the strain gradient.

3. Thin film ferroelectrics under the effect of epitaxial mismatch strain

Typical values for the flexoelectric coefficient in ferroelectrics are in the range 1–100 μC m^{-1} [22, 23], and Y is of the order of 200 GPa, so the coefficient multiplying the strain gradient term is of order 10^1–10^3 (S.I. units). On the other hand, the correlation coefficient is of order $G^* \sim 10^{-9}$ (S.I. units) [15, 27], so in the presence of external strain, one can generally ignore the last term of equation (12).

What we then obtain is

$$E = \alpha(T - T_c^*(z))P(z) + b^* P(z)^3 - (\gamma - \eta)\frac{Y}{1-\nu}\frac{\mathrm{d}\varepsilon(z)}{\mathrm{d}z}. \tag{18}$$

The inverse permittivity is

$$\chi^{-1} = \frac{dE}{dP} = \frac{d^2(\Delta G)}{dP^2} = 3b^* P^2 + \alpha(T - T_C^*). \tag{19}$$

And the effectively measured inverse permittivity is found by integrating with respect to z and dividing over the total thickness (t) of the capacitor:

$$\chi_{\text{eff}}^{-1} = \frac{\int_{-t/2}^{t/2} \left(a(T - T_C^*(z)) + 3b^* P(z)^2\right) dz}{t}. \tag{20}$$

First we solve the equation for the polarization. The coefficients can be redefined to simplify the notation:

$$a^*(z)P(z) + b^* P(z)^3 - c = 0 \tag{21}$$

where

$$c = (\gamma - \eta)\frac{Y}{1 - \nu}\frac{d\varepsilon(z)}{dz} - E. \tag{22}$$

Equation (17) has three solutions for the polarization [29]:

$$P_0 = \left(\frac{c}{2b^*} + \sqrt{\left(\frac{a^*}{3b^*}\right)^3 + \left(\frac{c}{2b^*}\right)^2}\right)^{1/3} + \left(\frac{c}{2b^*} - \sqrt{\left(\frac{a^*}{3b^*}\right)^3 + \left(\frac{c}{2b^*}\right)^2}\right)^{1/3} \tag{23}$$

and

$$P = \frac{1}{2}P_0 \pm i\frac{\sqrt{3}}{3}\left(\frac{c}{2b^*}\right)^{1/3}\left(\left(1 + \sqrt{\frac{\left(\frac{a^*}{3b^*}\right)^3}{\left(\frac{c}{2b^*}\right)^2} + 1}\right)^{1/3} - \left(1 - \sqrt{\frac{\left(\frac{a^*}{3b^*}\right)^3}{\left(\frac{c}{2b^*}\right)^2} + 1}\right)^{1/3}\right). \tag{24}$$

Equation (23) is the only real solution when the discriminant inside the square root is positive. Assuming $b^* > 0$ (second-order phase transition), the discriminant is guaranteed to be positive when a^* is positive, i.e., $T > T_C^*$, and hence it is the high temperature paraelectric solution. The solutions given by equation (24) are only real in the low temperature ferroelectric regime. It is important to note that the onset of reversible polarization does not actually happen at T_c (or at the strain-modified T_c^*), but at the temperature T_{ferro} at which the discriminant is 0, which is given by

$$T_{\text{ferro}} = T_C^* - \frac{3b^*}{\alpha}\left(\frac{c}{2b^*}\right)^{2/3}. \tag{25}$$

Thus, the ferroelectric transition will take place at a temperature lower than the Curie temperature. On the other hand, the temperature at which the dielectric constant is maximum will be found by minimizing the inverse permittivity with respect to T, although the analytical expression for this is much more cumbersome, as it involves differentiating P with respect to the temperature, and it is therefore easier to calculate T_m numerically. This splitting of the bulk critical temperature into three important temperatures, namely, the Curie temperature T_C^*, the temperature for the ferroelectric transition T_{ferro} and the temperature of the maximum dielectric constant T_m, has been described before for the case of ferroelectrics under the influence of external fields [16]. Here we note that strain gradients alone can produce the same effect.

It is also important to note that c is always different from 0 and hence so is the polarization. The consequence of this is that the inverse permittivity, given by (19) and (20), can no longer be 0, and therefore the singularity in the dielectric constant associated with the paraelectric–ferroelectric transition must disappear for thin films under inhomogeneous strain. The disappearance of the singularity in the dielectric constant is precisely one of the defining
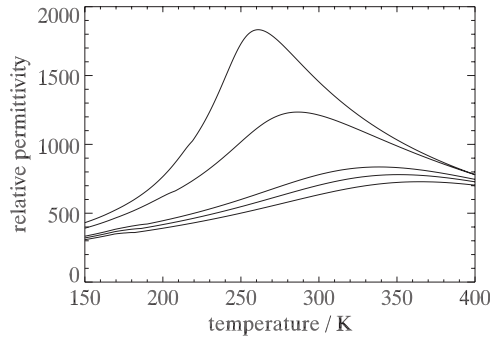
Figure 1. Calculated effective relative permittivity as a function of temperature for BST thin films grown on SRO. The simulated curves correspond to films of thickness $t = 220, 280, 340, 660$ and 950 nm, which are the thicknesses of the films grown in the experiment. The higher dielectric constant corresponds to the thickest film, and vice versa.

features of the size effect. Importantly too, given the dependence of the inverse permittivity on P^2, the sign of the strain gradient is irrelevant: both tensile and compressive strain gradients will result in a smearing of the dielectric peak.

In order to perform the calculations an expression for the strain gradient is needed. Although it is commonly assumed that the in-plane strain is a constant value equal to the lattice mismatch between film and substrate, there is theoretical [17, 30] and empirical [6] evidence that the mismatch strain relaxes with thickness, usually following an exponential law [6, 17]; thus

$$\frac{d\varepsilon}{dz} = -\frac{\varepsilon}{\lambda} \Rightarrow \varepsilon(z) = \varepsilon_m e^{-\frac{z}{\lambda}} \tag{26}$$

where ε_m is the lattice mismatch between substrate and film and λ is the thickness at which the strain has relaxed to $1/e$ of its mismatch value, so it can be viewed as some sort of 'depth of penetration' of the strain into the film.

It is now possible to calculate the expected polarization and dielectric constant as a function of film thickness. Here we have performed the calculations for a $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) film grown on a $SrRuO_3$ (SRO) base electrode. Given that the lattice parameter of SRO is 3.93 Å and that of BST is 3.95 Å, the lattice mismatch strain is -0.5%. T_C, Y, a, b and λ have been obtained from previous literature [31] and are $T_C = 235$ K, $Y = 197.6$ GPa, $v = 0.35$, $a = 9.1 \times 10^5$, $b = 4 \times (796 + 2, 16 \times (T - 273)) \times 10^6$ (both in S.I. units), $\lambda \cong 300$ nm [6]; also the flexoelectric coefficient for BST is $\mu_{12} = 10^{-4}$ C m^{-1} [22]. Introducing parameters in equations (23) and (24) allows the calculation of the polarization, which, substituted in equations (19) and (20), allows the calculation of the effective relative dielectric constant as a function of temperature and film thickness. In order to reproduce typical experimental conditions we have imposed that external stress is only applied at the bottom electrode (SRO) but not at the top one (gold). Likewise, since in (20) we are integrating from $-t/2$ to $t/2$ we have to redefine the thickness variable in the strain relaxation (equation (26)) so that $\varepsilon(z) = \varepsilon_m e^{-(z+t/2)}$.

The permittivity and polarization as a function of temperature for films of different thicknesses are plotted in figures 1 and 2. The results show that as thickness is decreased, the dielectric peak decreases and shifts up in temperature, while the polarization increases due to the flexoelectric contribution.

In figure 3 we have plotted the numerically calculated T_C^*, T_{ferro} and T_m as a function of film thickness for BST films grown under the same conditions. The expected splitting of the
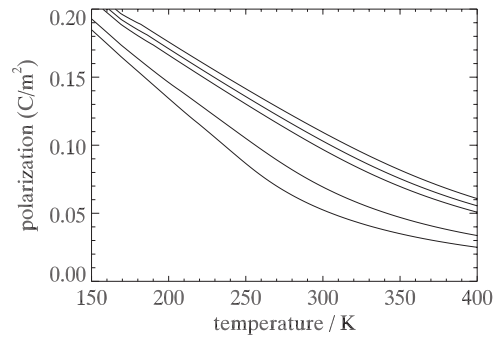
Figure 2. Calculated effective polarization as a function of temperature for BST thin films of various thickness grown on SRO. The films thicknesses are the same as in figure 1. The biggest polarization corresponds to the thinnest film and vice versa.
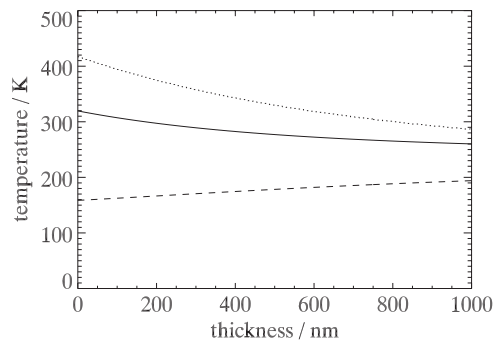

Figure 3. Calculated critical temperatures T_m (dotted curve), T_C^* (continuous curve) and T_{ferro} (dashed curve) as a function of z. The bulk Curie temperature is $T_C = 235$ K.
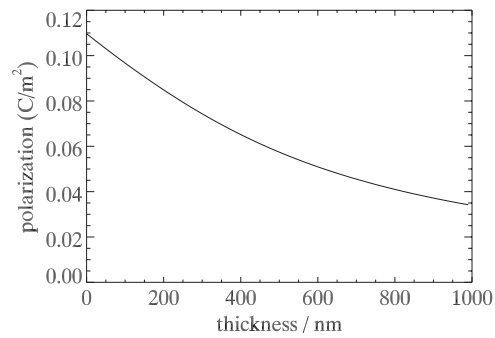

Figure 4. Calculated polarization at room temperature as a function of film thickness.

critical temperature into three different temperatures, with $T_m > T_c > T_{ferro}$, is evident, as is the marked upward trend in T_m with smaller thickness.

Finally, in figure 4 the room temperature polarization has been plotted as a function of thickness, showing the increase in polarization with lowering thickness.

In order to compare the predictions with experimental results, the relative dielectric constant and polarization were measured for BST thin films grown on SRO substrates by
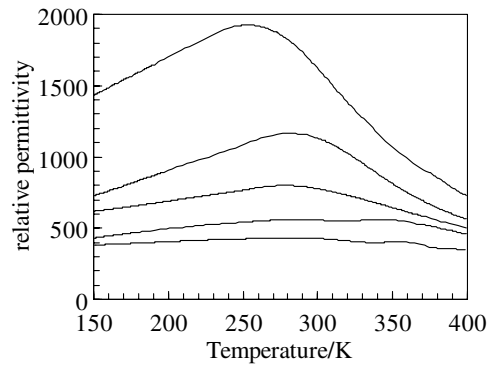
Figure 5. Measured relative dielectric constant as a function of temperature for BST films grown on SRO of thickness $t = 175, 280, 340, 660$ and 950 nm (cf figure 1).
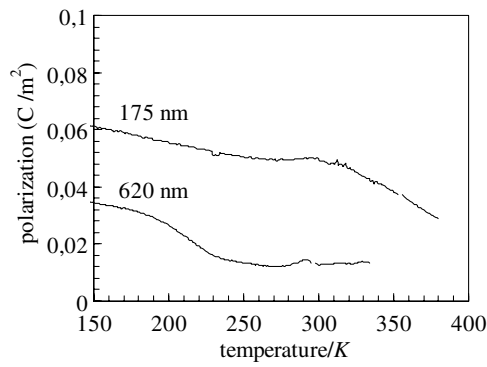

Figure 6. The measured polarization for two BST films grown on SRO, of thickness 175 and 620 nm (cf figure 2).
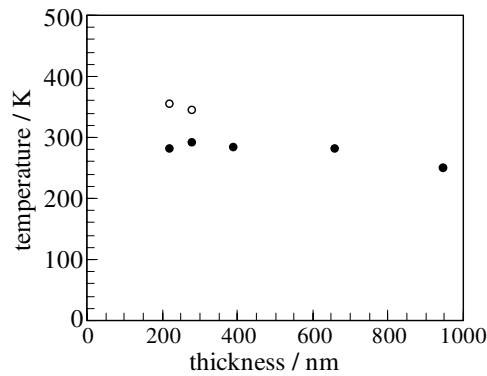

Figure 7. The measured temperature of maximum dielectric constant, T_m, for films of various thicknesses (cf figure 3). Note that for the thinnest films two maxima were observed.

PLD. Details of the growth methodology and experimental measurements can be found elsewhere [6, 10]. The experimental results are shown in figures 5–8.

The comparison between the experimental results and the simulations is qualitatively good: both the observed decrease in dielectric constant and the increase in polarization as
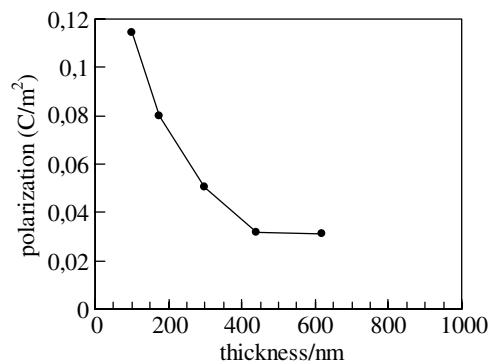
Figure 8. The room temperature polarization for films of various thicknesses (cf figure 4).

thickness is reduced are well reproduced, as is the smoothing of the dielectric curves and the upward trend in the temperature of the maximum dielectric constant with decreasing thickness.

The quantitative similarity between calculations and experiment is also worth noting: although the actual shape of the dielectric peak is sharper in our idealized simulations than in the experiment, the maximum values of the dielectric constant are well reproduced, as are the values for the room temperature polarization. The main quantitative difference lies in the predicted values of T_m, which are noticeably higher than experimentally registered.

As regards the accuracy of these calculations, the formula used for the strain distribution (equation (26)) has been observed to be at least empirically accurate [6, 16], but other equations, such as those based on the Mathews–Blackeslee model [30], may also be used. Although this can affect the quantitative results of the calculations, it should not alter the quantitative order of magnitude, nor would it affect the qualitative aspects of the model.

Other simplifications that we have made are as follows:

 (a) We neglected the surface depolarization and surface tension terms (second derivatives of polarization and strain with respect to z). This approximation is roughly valid whenever there is a dominant external strain term, or for sufficiently thick films compared with the penetration depth of the surface depolarization, which is typically a few nanometres [26–28], or when the choice of electrode prevents or minimizes the surface depolarization effect [16]. It is nevertheless worth noticing that the flexoelectric contribution to G^* is of the same order as the naked surface depolarization term, G, which is one of the sources of the size effect [15, 16], and thus the study of the flexoelectrically modified size effect for ultrathin films is certainly worthy of further attention.
 (b) As stated before, we have limited ourselves to the case of second-order ferroelectric transitions. The extension of the model to describe also first-order transitions remains to be carried out.

4. Conclusions

A phenomenological model of the effect of flexoelectricity on the dielectric constant and polarization behaviour of inhomogeneously strained ferroelectric thin films has been presented. The model was applied to simulate the dielectric properties of a BST thin film epitaxially clamped to a substrate with compressive in-plane stress that relaxes with thickness, and the numerical simulations were compared with our own experimental results for films of the same composition, thickness and lattice mismatch with the substrate.

The conclusions of this study can be summarized as follows:

(i) The flexoelectric coefficient measured in bulk is only a linear function of the strain gradient or the permittivity when the induced polarization is small; near the dielectric peak, the assumption of small flexoelectric polarization is no longer valid and the linear relationship breaks down, and P^3 corrections must be taken into account when measuring the flexoelectric coefficient.

(ii) In the presence of strain gradients, there is a splitting of the bulk Curie temperature into three important temperatures, namely, the strain-modified Curie temperature (T_C^*), the temperature for the onset of reversible polarization (T_{ferro}) and the temperature of the dielectric peak (T_m).

(iii) The disappearance of the singularity in the dielectric constant as a function of temperature is predicted for ferroelectric thin films subjected to inhomogeneous strain, regardless of the sign of the lattice mismatch with the substrate. The dielectric constant of inhomogeneously strained films is always lower than in bulk, in agreement with experimental results.

Acknowledgments

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