Strain gradients in epitaxial ferroelectrics

G. Catalan,[1,*] B. Noheda,[1] J. McAneney,[2] L. J. Sinnamon,[2] and J. M. Gregg[2]

[1]*Materials Science Center, University of Groningen, Groningen 9747AG, The Netherlands*
[2]*Department of Pure and Applied Physics, Queen's University Belfast, Belfast BT7 1NN, United Kingdom*
(Received 23 May 2005; published 14 July 2005)

X-ray analysis of ferroelectric thin layers of $Ba_{1/2}Sr_{1/2}TiO_3$ with different thicknesses reveals the presence of strain gradients across the films and allows us to propose a functional form for the internal strain profile. We use this to calculate the influence of strain gradient, through flexoelectric coupling, on the degradation of the ferroelectric properties of films with decreasing thickness, in excellent agreement with the observed behavior. This paper shows that strain relaxation can lead to smooth, continuous gradients across hundreds of nanometers, and it highlights the pressing need to avoid such strain gradients in order to obtain ferroelectric films with bulklike properties.

Interest in ferroelectric thin films is rapidly expanding due to the recent development of experimental techniques and calculation tools that allow an exploration of ferroelectric phenomena at the atomic level.[1,2] The incorporation of realistic mechanical and electrical boundary conditions in the first-principles formulations is generating insight into the mechanisms limiting the ferroelectric response in thin ferroelectric layers.[3–5] But while the evidence suggests that ferroelectricity may indeed be stable in films of only a few monolayers,[1–3] the sharp peak in the dielectric constant usually associated with the ferroelectric transition is systematically depressed even in films of hundreds of nanometers in thickness. This obviously limits the technological impact that would arise from the ability to maintain ferroelectricity and large dielectric constants down to the nanoscale in real devices.

Recent theoretical works address this issue. Glinchuk and Morozovska[6] look at the effect of a different polarization of a thin (1–10 Å) surface layer with respect to that inside the film, showing that for very thin films (a few nanometers) a dielectric smearing is predicted. For thicker films, Bratkovsky and Levanyuk[7] have proposed two different mechanisms: a compositional gradient and a difference between work functions when the electrodes are dissimilar.

Strain, caused by lattice mismatch with the substrate, is also an important factor affecting the properties of ferroelectric films. Strain can modify the phase diagram,[8,9] change the order of the transition,[9,10] and shift transition temperatures.[9,11] However, strain alone does not generally account for the observed smearing of the dielectric peak, as a sharp anomaly is still expected at the strain-modified transition temperature. Strain *gradients*, on the other hand, are known to couple to the polarization via the flexoelectric effect,[12–14] and could, in theory, cause significant dielectric peak smearing in inhomogeneously strained films.[15] Unfortunately, to date no direct experimental evidence has provided quantitative insight into such gradients.

In this paper, a set of lattice-mismatched epitaxial thin films of different thicknesses have been examined using x-ray diffraction, revealing that vertical long-range gradients develop in the films. These gradients have been then introduced in a thermodynamic model of the transition, and the predictions of the model have been compared with the actual dielectric properties for the same set of films. The results show that the measured strain gradients account for most of the reduction of dielectric constant. The crystallographic tools described here can also be applied to other material systems with strain gradients, whether caused by dislocations or by distributions of impurities or vacancies. Showing a link between strain relaxation and strain gradients thus has wider implications beyond ferroelectricity and is an important result for thin-film epitaxy.

The films studied in this paper are $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) dielectric layers with thickness between 110 and 660 nm, with $SrRuO_3$ (SRO) bottom electrodes. The films were grown by pulsed laser deposition onto single crystal MgO
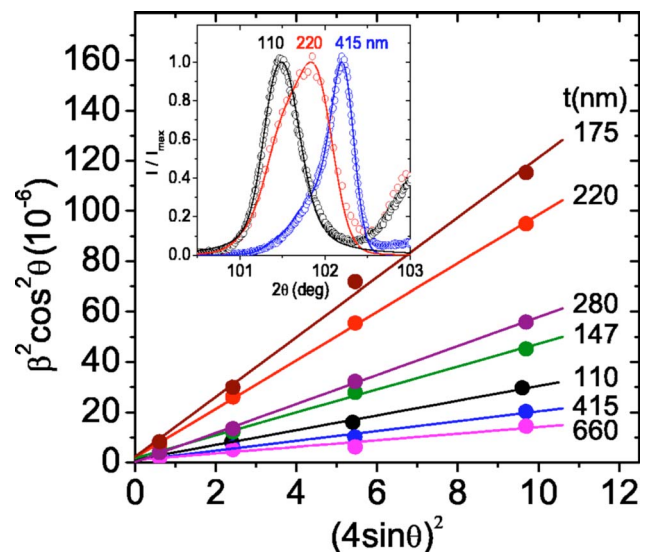

FIG. 1. (Color online) Williamson-Hall plots, showing maximum slope for films of intermediate thickness. Inset: 004 diffraction peaks; peak shapes are well fitted (solid lines) assuming an exponential strain profile. The peaks at ~103° correspond to the SRO electrode.
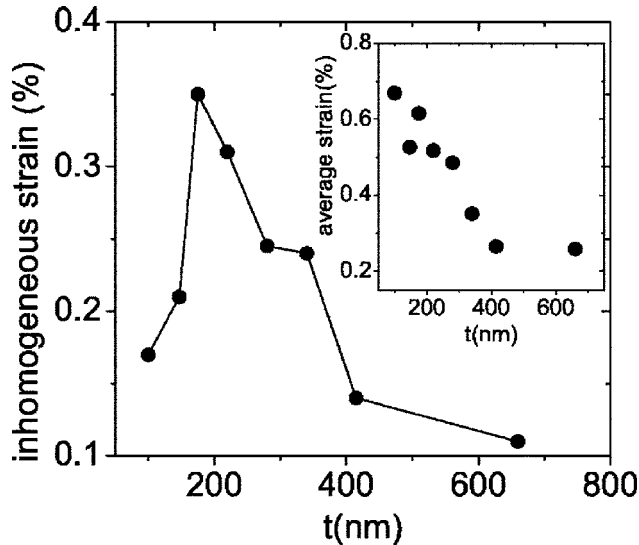
FIG. 2. Inhomogeneous strain as a function of film thickness. The solid line is a visual guide. Inset: average out-of-plane strain.

substrates. Epitaxy was verified by cross-sectional high-resolution transmission electron microscopy (TEM). Details of the growth and TEM characterization are published elsewhere.[11] In the present paper, the crystallographic analysis has been performed using a Philips X'pert MRD diffractometer with Cu $K\alpha_1$ radiation ($\lambda = 1.540$ Å).

The lattice parameters are extracted from the perovskite pseudocubic 00l diffraction peaks (inset of Fig. 1).[16] This allows the calculation of the average out-of-plane strain in each film, given by $\bar{\epsilon}(t) = \bar{c}(t)/c_0 - 1$, where $\bar{c}$ is the average out-of-plane lattice parameter, c_0 is the bulk lattice parameter ($c_{BST} = 3.95$ Å), and t is the film thickness. The average strain for each film is shown in the inset of Fig. 2. There is an out-of-plane expansion for the thinnest films that decreases with thickness, indicating relaxation of the in-plane compression induced by the smaller lattice parameter of the bottom electrode ($c_{SRO} = 3.93$ Å).

Similar to what is known for semiconductor and metallic epitaxial layers, ferroelectric oxides are known to relieve strain as film thickness is increased.[11,17] The strain-relieving mechanism is thought to be mainly the formation of misfit dislocations. It is generally implied that this strain relaxation takes place at or very near the interface, and thus the strain state should be essentially homogeneous across the film (save for the first few monolayers) and depend only on the film's total thickness: $\epsilon = \epsilon(t)$. However, recent work shows that misfit dislocations are associated with strain distributions.[18,19] Furthermore, strain may also be relaxed by other mechanisms, such as vertical segregation of different-sized cations.[20] Thus, rather than a quantity dependent only on the thickness t, strain should be described as an internal profile dependent also on the distance z to the film-substrate interface: $\epsilon = \epsilon(z,t)$. The homogeneous versus inhomogeneous scenarios of strain relaxation have major consequences for the functional properties. Inhomogeneous strain fields around dislocations[18,21] and impurities[22] affect the polarization and critical temperatures of ferroelectric thin films. Cru-

cially, also, inhomogeneous strain is necessarily associated with strain gradients.

In order to calculate the vertical strain gradients, x-ray diffraction peak broadening has been analyzed as a function of film thickness. There are three main contributions to peak broadening: the finite thickness of the sample, the inhomogeneous strain, and the instrumental resolution of the diffractometer. When the peak profile is Gaussian, the integral breadth (area of the peak divided by its height) is related to the partial breadths by $\beta_{measured}^2 = \beta_{strain}^2 + \beta_{size}^2 + \beta_{instrument}^2$.[23] The instrumental contribution is calibrated separately using a reference single crystal, and the other two contributions have different angular dependences, so they can be separated by looking at the peak width for different reflections and fitting the results using a Williamson-Hall-type (W-H) relation;[24]

$$(\beta \cos \theta)^2 = \left(K \frac{\lambda}{D} \right)^2 + (4\epsilon_i \sin \theta)^2, \tag{1}$$

where $\beta^2 = \beta_{measured}^2 - \beta_{instrument}^2$, D is the coherence length along the scattering vector (perpendicular to the film's surface in our case), λ is the x-ray wavelength, θ is the diffraction angle, and K is a geometrical constant close to 1.

The inhomogeneous strain ϵ_i is extracted from the slope of linear fits of $(\beta \cos \theta)^2$ vs $(4 \sin \theta)^2$.[25] We have performed least-square fits for the pseudocubic (00l) ($l=1-4$) reflections, finding the linear dependence excellent for all our samples ($r^2 > 0.9$) (Fig. 1). It is nevertheless worth mentioning that, although one of the simplest, the W-H approach is not the only existing strategy to separate size and strain broadening. Quantitative results for ϵ_i may therefore vary somewhat depending on the approach used.[26]

Figure 2 shows the inhomogeneous strain as a function of film thickness. The existence of a maximum in ϵ_i is consistent with the presence of a monotonically decreasing internal strain profile as a function of z in the films: for very thin films there is a small dispersion in lattice parameters; conversely, for very thick films there may be a larger dispersion, but the volume fraction of totally relaxed material is large and dominates the diffraction peak, so that again the variance is small. In between, there must be a thickness where the inhomogeneous strain is maximum.

Extracting quantitative values for the internal strain profile from this analysis requires solving the integral equations for the average ($\bar{\epsilon}$) and inhomogeneous (ϵ_i) strain,

$$\bar{\epsilon}(t) = \frac{1}{t} \int_0^t \epsilon(z,t) dz, \tag{2}$$

$$\epsilon_i^2(t) = \frac{1}{t} \int_0^t [\epsilon^2(z,t) - \bar{\epsilon}^2(t)] dz = \overline{\epsilon^2} - \bar{\epsilon}^2, \tag{3}$$

where $\bar{\epsilon}$, ϵ_i are extracted from peak position and the W-H analysis, respectively, and $\epsilon(z,t) = c(z,t)/c_0 - 1$ is the internal strain profile.

The easiest way to resolve these equations is to assume a certain shape for the internal strain, solve the integrals (2)

and (3), and modify the functional parameters to achieve a good match with the experimental results. This method relies on the correct choice of functional dependence for $\epsilon(z,t)$. Furthermore, since they are integral equations the value of the integrand is very sensitive to errors in the measured strains. As such, the results of the quantitative analysis should be treated as approximations.

A general model for the strain profile, independent of the actual relaxation mechanism, reflects that strain relaxation should be proportional to the strain itself, which yields an exponential dependence on z,[27]

$$\frac{\partial \epsilon}{\partial z} = -\frac{\epsilon}{\delta} \Rightarrow \epsilon(z) = \epsilon_0 e^{-z/\delta}, \qquad (4)$$

where ϵ_0 is the strain at the film-substrate interface and δ is a measure of the penetration depth of the strain. If misfit dislocations are considered as the main relaxation mechanism, a recent strain-gradient theory[19] predicts the vertical profile in the layers to be given by

$$\epsilon(z,t) = \epsilon_0 \left[\cosh \frac{z}{\delta} - \tanh \frac{t}{\delta} \sinh \frac{z}{\delta} \right]. \qquad (5)$$

It is worth noticing that Eq. (4) is a limiting case of (5) when the film thickness is larger than the strain penetration depth ($t \gg \delta$).

Either of these expressions can be integrated to yield $\bar{\epsilon}(t)$ and ϵ_i. In principle, though, the fitting parameters ϵ_0 and δ may depend on the total thickness of the film, so one cannot directly use a single value of these parameters to fit all the results. In order to calculate the thickness dependence of $\epsilon_0(t)$ and $\delta(t)$ we note that there are two parameters and two equations to describe $\bar{\epsilon}$ and ϵ_i, so it is possible to calculate ϵ_0 and δ for each film separately. We have done this for the exponential strain profile (4). Combining the Eqs. (2) and (3) we can eliminate ϵ_0

$$\frac{t}{2\delta} \frac{\bar{\epsilon}^2}{(\epsilon_i^2 + \bar{\epsilon}^2)} = \tanh\left(\frac{t}{2\delta}\right). \qquad (6)$$

This is solved for each film in order to find $\delta(t)$, which is then used to calculate $\epsilon_0(t)$.

Another way to calculate the strain profile consists of using a convolution of the exponential distribution of lattice parameters with the instrumental peak shape in order to fit the measured diffraction peaks (for other approaches see Refs. 29 and 30). We have done this (solid lines in the inset of Fig. 1) and found values for $\epsilon_0(t)$ and $\delta(t)$ similar to those extracted from the W-H approach, with $\delta(t)$ between 100 and 200 nm and $\epsilon_0(t)$ decreasing with thickness from about 1% to 0.6%. In practice, peak fitting is more precise for very thin films displaying thickness fringes in the diffraction pattern (Laue oscillations). When the films are relatively thick, like ours, the W-H strategy is more robust.

Once the internal strain profile $\epsilon(z,t)$ is known, the strain-gradient contribution to the functional properties can be calculated using an elastodielectric free energy expansion incorporating the flexoelectric contribution[15]
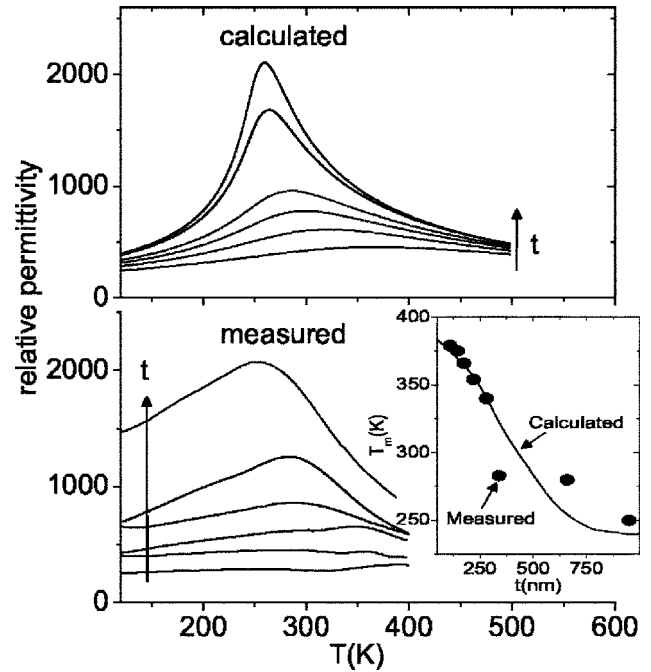

FIG. 3. Calculated and measured dielectric constant as a function of temperature for films of thickness 950, 660, 340, 280, 220, and 145 nm. Inset: The temperature of maximum permittivity, experimental (dots) and calculated (solid line).

$$G = \int_0^t \left[\frac{1}{2}aP^2 + \frac{1}{4}bP^4 - \frac{1}{2}(s_{11} + s_{12})\sigma^2 - Q_{13}\sigma P^2 - \gamma P \frac{\partial \sigma}{\partial z} \right.$$
$$\left. - \eta\sigma \frac{\partial P}{\partial z} + \frac{1}{2}E\left(\frac{\partial P}{\partial z}\right)^2 + F\left(\frac{\partial \sigma}{\partial z}\right)^2 \right] dz, \qquad (7)$$

where P is the out-of-plane polarization; s_{ij} the elastic compliances; σ the in-plane stress [related to the measured out-of-plane strain by the Young's modulus and Poisson's ratio: $\sigma = \epsilon Y(-2\nu)$]; Q_{13} is the transverse electrostrictive coefficient, E and F are the constants related to the energy contributions from polarization and stress gradient, and γ and ν are, respectively, the direct and converse flexoelectric coefficients.[31] P is calculated through variational minimization of the thermodynamic potential, while the second derivative of G with respect to P yields the inverse permittivity. This is averaged over the thickness of the film to yield the effective value.

The relative dielectric constants calculated using the strain gradient extracted from our crystallographic analysis are shown in Fig. 3, along with those experimentally measured for the same set of films.[11] The predicted and measured temperatures of maximum permittivity (T_m) are shown in the inset.[28] Clearly, the decrease in the dielectric constant and upward shift of T_m are well reproduced. Quantitatively, the agreement between calculated and measured T_m as a function of thickness is very good, given that the calculations are not a best fit but a prediction using bulk Landau coefficients and the strain gradient extracted from our crystallographic analysis. The calculated dielectric constant is similar to, though somewhat larger than that

experimentally measured. This was expected, as our model does not take into consideration any other permittivity-depressing factors.[6,7] The results nevertheless show that the flexoelectric contribution to the depression in permittivity with decreasing thickness is enormous. This is particularly valid when comparing with the huge permittivities recently measured in gradient-free ferroelectric films.[32]

The dielectric constant is lowest for the thinnest films in spite of the relatively small value of ϵ_i. This is a natural consequence of the fact that the size effect is *not* caused by the inhomogeneous strain itself, but by the strain gradient, which, when the profile is exponential, is largest for the thinnest films. We note also that while compressive in-plane strain can be used to stabilize the ferroelectric state, this can come at the expense of reducing the permittivity if strain gradients are not avoided. Finally, we note that while the methods described here can be used to estimate strain gradients caused by oxygen vacancy distributions,[33] dislocations,[19,21] or cation segregation,[20] they

do not directly allow us to establish which of these mechanisms is actually responsible for the gradient. Further research into the microscopic origin of the gradients is therefore needed.

In summary, x-ray analysis of peak broadening and shape as a function of thickness shows that relaxation of strain in epitaxial films is associated with the appearance of internal strain gradients that, contrary to common belief, can span hundreds of nanometers. The dielectric properties calculated using these strain gradients are close to those experimentally measured, clearly showing the fundamental role played by flexoelectric coupling in decreasing the dielectric constant. This paper highlights the urgent need to avoid strain gradients in order to prevent degradation of the ferroelectric response in thin films.

---

*Electronic address: g.catalan.bernabe@rug.nl

[1] R. Ramesh and D. G. Schlom, Science **296**, 1975 (2002).

[2] C. H. Ahn, K. M. Rabe, and J.-M. Triscone, Science **303**, 489 (2004), and references therein.

[3] J. Junquera and P. Ghosez, Nature (London) **422**, 506 (2003).

[4] I. Kornev, H. Fu, and L. Bellaiche, Phys. Rev. Lett. **93**, 196104 (2004).

[5] C. Bungaro and K. M. Rabe, Phys. Rev. B **71**, 035420 (2005).

[6] M. D. Glinchuk and A. N. Morozovska, J. Phys.: Condens. Matter **16**, 3517 (2004).

[7] A. M. Bratkovsky and A. P. Levanyuk, Phys. Rev. Lett. **94**, 107601 (2005). Note that the samples analyzed in this paper were strain-free, which allowed us to neglect the strain gradient term.

[8] O. Dieguez *et al.*, Phys. Rev. B **69**, 212101 (2004).

[9] N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, Phys. Rev. Lett. **80**, 1988 (1998).

[10] C. Basceri *et al.*, J. Appl. Phys. **82**, 2497 (1997).

[11] L. J. Sinnamon, R. M. Bowman, and J. M. Gregg, Appl. Phys. Lett. **81**, 889 (2002).

[12] Sh. M. Kogan, Sov. Phys. Solid State **5**, 2069 (1964).

[13] W. Ma and L. E. Cross, Appl. Phys. Lett. **79**, 4420 (2001); **81**, 3440 (2002).

[14] A. K. Tagantsev, Phys. Rev. B **34**, 5883 (1986).

[15] G. Catalan, L. J. Sinnamon, and J. M. Gregg, J. Phys.: Condens. Matter **16**, 2253 (2004).

[16] Due to the peaks' asymmetry, the average lattice parameters are obtained from the peaks' centers of mass rather than from the maxima.

[17] C. L. Canedy *et al.*, Appl. Phys. Lett. **77**, 1695 (2000).

[18] M.-W. Chu *et al.*, Nat. Mater. **3**, 87 (2004).

[19] L. Nicola, E. Van der Giessen, and M. E. Gurtin, J. Mech. Phys.

Solids **53**, 1280 (2005).

[20] J.-L. Maurice *et al.*, Philos. Mag. **83**, 3201 (2003).

[21] S. P. Alpay *et al.*, Appl. Phys. Lett. **85**, 2044 (2004).

[22] D. Balzar, P. A. Ramakrishnan, and A. M. Hermann, Phys. Rev. B **70**, 092103 (2004).

[23] The addition is quadratic for Gaussian peaks and linear for Lorentzian. For Pseudovoigt peaks the two components must be deconvoluted and analyzed separately.

[24] G. K. Williamson and W. H. Hall, Acta Metall. **1**, 22 (1953).

[25] In general the coherence length D can be extracted from the intercept at the origin. However, we note that since in our case the lattice parameter changes as a function of z, D is not determined by t but by the strain profile.

[26] J. G. M. Van Berkum *et al.*, Acta Crystallogr., Sect. A: Found. Crystallogr. **52**, 730 (1996).

[27] H. Joon Kim, S. Hoon Oh, and Hyun M. Jang, Appl. Phys. Lett. **75**, 3195 (1999).

[28] The tetragonal-orthorhombic transition (~ 50 K below the cubic-tetragonal one in bulk) is visible as a shoulder or small peak in the thinner films. By symmetry our thermodynamic model is restricted to reproduce only the cubic-tetragonal transition, corresponding to the high T_m.

[29] I. Vartanyants *et al.*, Appl. Phys. Lett. **77**, 3929 (2000).

[30] A. Boulle *et al.*, J. Appl. Crystallogr. **36**, 1424 (2003).

[31] The values for the Landau coefficients are $Y = 197.6$ GPa, $\nu = 0.35$, $(\gamma - \nu) = 10^{-9}$ m^3 C^{-1}, $a = 9.1 \times 10^5 (T - T_C)$ (S.I), $b = 4 \times [796 + 2, 16 \times (T - 273)] \times 10^6$ (S.I), $T_C = 235$ K, and E and F can be ignored (Ref. 15).

[32] M. M. Saad *et al.*, J. Phys.: Condens. Matter **16**, 451 (2004).

[33] J. F. Scott, *Ferroelectric Memories* (Springer-Verlag, Berlin, 2000), pp. 158–159.