

New phenomena at the interfaces of very thin ferroelectric oxides

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 264015

(<http://iopscience.iop.org/0953-8984/20/26/264015>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 13:17

Please note that [terms and conditions apply](#).

New phenomena at the interfaces of very thin ferroelectric oxides

M Dawber^{1,2}, N Stucki¹, C Lichtensteiger¹, S Gariglio¹ and J-M Triscone¹

¹ DPMC, University of Geneva, 24 Quai Ernest Ansermet, 1211 Geneva 4, Switzerland

² Department of Physics and Astronomy, Stony Brook University, Stony Brook, NY 11794-3800, USA

E-mail: matthew.dawber@stonybrook.edu

Received 19 February 2008, in final form 9 April 2008

Published 9 June 2008

Online at stacks.iop.org/JPhysCM/20/264015

Abstract

We present a brief review of the role of interfacial physics in ferroelectric oxides, with an emphasis on the importance of boundary conditions that determine the properties of very thin ferroelectric films and superlattices. As well as discussing the screening problem, and the role of strain and electrostatics in ferroelectrics, we highlight some of the possibilities in fine period superlattices where the high density of interfaces can lead to new and potentially useful phenomena.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The physics of thin film ferroelectric oxides has been a topic of intense and growing interest in recent years. A number of reviews [1, 2] and books [3] have recently been published which build upon the standard texts on ferroelectric materials and applications [4–6] and give a broad overview of the field and the enormous progress recently achieved. The purpose of this article is to focus specifically on recent insights into the problem of interfaces and how they influence the behaviour of very thin ferroelectrics. As with many physical systems with reduced dimensions, the essential physics can often have as much to do with the boundary conditions as with the bulk properties of the material. In this paper we will examine the role of electrostatics and strain, which are the ‘traditional’ boundary conditions of interest for ferroelectrics, but also look at other important effects related to surface and interface reconstructions.

2. Screening at ferroelectric metal interfaces

The electrostatic boundary conditions on a ferroelectric can be easily understood on the basis of continuity of electric displacement. A ferroelectric material possesses a spontaneous polarization. If the material has infinite extent then this polarization can be aligned in the same direction throughout the material, with a uniform electric displacement equal to the

polarization. If, however, the material has an interface, some form of charge distribution must arise at this interface to screen this electric displacement, or alternatively the polarization must be arranged within the material in such a way as to reduce the electric displacement at the interface to zero. This question of how efficiently electric displacement can be screened or minimized by the formation of domains is at the core of the problem of the critical thickness for ferroelectricity, currently a highly active research topic. Just how important this is is highlighted theoretically by the finding that when sufficient image charges are present ferroelectricity can persist in a thin film down to a thickness of three unit cells [7] and indeed experimentally ferroelectricity has been seen down to a thickness of two monolayers in ferroelectric co-polymer PVDF films [8]. ‘Real’ electrodes, by which we mean those with a finite charge density, do a significantly worse job of screening than perfectly placed image charges even in the case where they exist only in first principles calculations and are thus somewhat more perfect than most actual experimental electrodes [9].

Simple models based on the Thomas–Fermi approach [10, 11] can give a fairly good description of the observed behaviour, accounting for the suppression of polarization [12] and the changes in coercive field [13] as the thickness of a film is decreased. The main idea of this model is depicted in figure 1; briefly the charge distributions in the electrodes mean that there is also potential dropped there, giving rise to

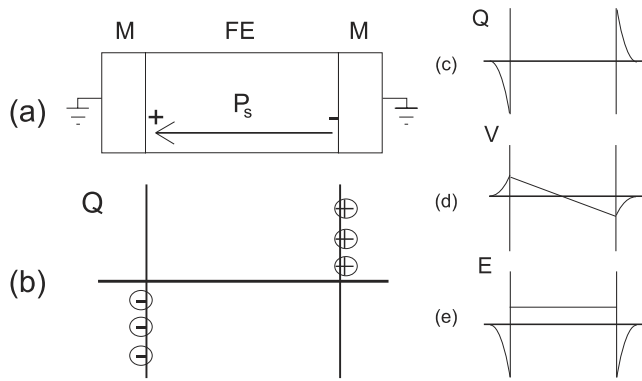


Figure 1. A schematic of (a) a short-circuited electrode–ferroelectric structure with the spontaneous polarization displayed (M = metal, FE = ferroelectric); (b) its charge distribution in the presence of perfect electrodes; its (c) charge distribution, (d) voltage and (e) field profiles in the presence of realistic electrodes. Here the film is taken to be a perfect insulator. Reproduced figure with permission from [13]. Copyright 2003 IOP Publishing.

a potential in the film under short-circuit boundary conditions. The potential drop in the film is independent of film thickness, which means that the field, antiparallel to the polarization and thus termed the depolarization field, becomes very large in very thin films. There are, however, some clear signs that this is not a sufficiently complete model of the interface. For example, first principles simulations have shown that the charge carrier density in the metal is not the only relevant parameter in evaluating its ability to screen polarization [14–16]; metal states can penetrate into the bandgap [17, 14] and equally there seems to be some evidence that oxide metal electrodes can be partially polarized over a small distance, though on this point there seems to be some disagreement between the first principles simulations of Gerra *et al* [15] and those of Stengel and Spaldin [16]. Also, an interesting new first principles study from Aguado-Puente and Junquera [18] suggests that ionic displacements in the first SrO layer of SrRuO₃ electrodes can promote the formation of domains, adding yet another layer of complexity.

Beyond the first principle results some experimental results also point to the existence of much more efficient screening than can be provided by the electron density in the electrode. Take, for example, the results obtained in Belfast [19] where a rather original approach of producing a BaTiO₃ thin film using a focused ion beam (FIB) (starting from a single crystal and reducing it to a thickness of 100 nm) has been developed. The surprise is that in such samples bulk-like dielectric behaviour was observed, including dielectric constants well above 10 000, implying a remarkably short screening length for the gold electrodes used ($<0.05 \text{ \AA}$). This result thus suggests that there must be some alternative method by which polarization can be screened in this system, perhaps internally by space charge.

Thus far we have mainly discussed the effect of the screening properties of the electrode on the film, but the opposite situation, where the ferroelectric film can be used to modify the properties of a metallic or semiconducting electrode can be equally interesting. There is a long history of trying

to use this effect to produce memory devices, but it can also be used to modify the properties of a superconducting channel [20, 21]. The field effect [22] can also be used to tune magnetic properties [23], of particular interest given the recent attention on multiferroics [24–27].

3. Internal rearrangements; domains and reconstructions

As discussed above, the screening efficiency determines how closely the thin film system can be to its ideal configuration of a uniformly oriented polarization. In many cases ultra-thin ferroelectric films cannot possibly sustain this uniform polarization state and thus end up in a polydomain state. A number of efforts have been made recently to measure and characterize this state [29, 28, 30], and clear experimental evidence now exists for very fine period ‘stripe domains’ forming in very thin films. However, it has also become apparent that changes in external conditions, including those during the growth of the film, can have a large impact on the formation of domains. In a study on PbTiO₃ films on La_{0.67}Sr_{0.33}MnO₃ (LSMO) electrodes, Lichtensteiger *et al* [31] (figure 2) were able to identify three different regimes depending on the thickness of the film using piezoresponse atomic force microscopy (AFM). First for the thicker films the samples were monodomain, for the thinnest, polydomain and for intermediate thicknesses the films are found to be in a mixed state, in which some regions were monodomain and others polydomain, despite the fact that the films were extremely uniform in thickness. One interesting, and not yet explained, point in this experiment is that the LSMO electrodes, counterintuitively, seem not to screen as well as Nb-doped SrTiO₃ electrodes, despite their better metallicity.

Besides domains forming within the bulk of the film there is also the potential for surface rumpling and reconstructions. These effects significantly complicate experimental efforts to study experimentally ferroelectricity in ultra-thin films, as discussed for instance in [32] where surface ferroelectricity has been studied using x-ray photoelectron diffraction techniques. However, besides introducing experimental complications the symmetry breaking at a ferroelectric surface can allow the coexistence of distortions that are usually antagonistic to each other in bulk materials, for example, antiferrodistortive rotations of the oxygen octahedra dominate in SrTiO₃, whereas in PbTiO₃ ferroelectric polar distortions are favoured. In general these distortions do not couple favourably, but at the surface of a PbTiO₃ film these distortions are found to coexist [33, 34], and we will see later that in a superlattice they can couple and lead to a totally new kind of ferroelectricity.

4. Strain

Of equal importance to the electrostatic boundary conditions are the mechanical boundary conditions. There is a varying degree of sensibility to strain amongst ferroelectric oxides, with the perovskite titanates showing particularly strong coupling between strain and ferroelectric properties. In the case where a film is constrained in the plane of the lattice

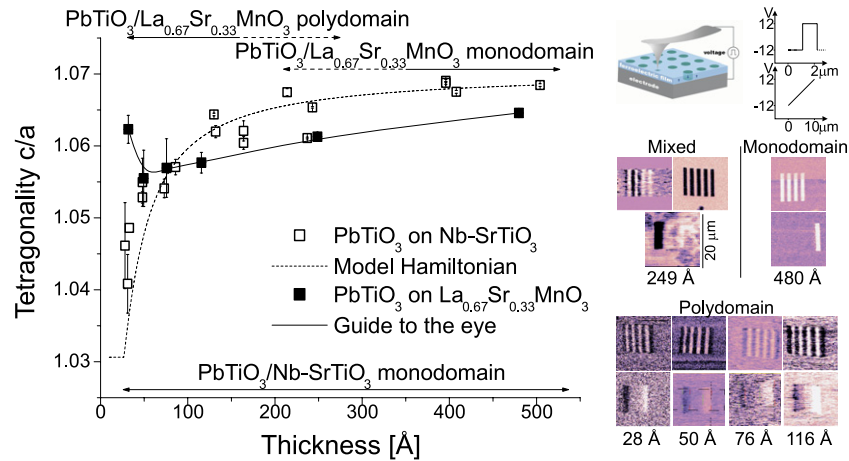


Figure 2. Left: tetragonality as a function of film thickness for thin PbTiO₃ films grown on a thin layer of La_{0.67}Sr_{0.33}MnO₃ on SrTiO₃ substrates (black squares). The behaviour observed here is dramatically different from what was obtained in the case of PbTiO₃ on Nb-SrTiO₃ (open squares). For comparison, the model Hamiltonian prediction with $\lambda_{\text{eff}} = 0.12$ Å is shown as a dotted line (see [12]). The solid line is a guide to the eyes. Right: for each thickness, the topmost figure shows the piezoresponse signal obtained after alternate +12 and -12 V voltages were applied between the metallic tip and the conducting La_{0.67}Sr_{0.33}MnO₃ layer to polarize nine well-defined stripes over a $10 \times 10 \mu\text{m}^2$ area. The lower figure shows the piezoresponse signal obtained after writing a $10 \times 10 \mu\text{m}^2$ square starting with +12 V from one side and finishing with -12 V on the other side, decreasing gradually. Data reproduced from [31].

constant of the substrate the ferroelectric properties can be significantly modified. Compressive strain favours out-of-plane ferroelectricity, while tensile strain favours in-plane ferroelectricity, but even in the case where the substrate does not impose a strain on the film, the lack of freedom in the in-plane direction can change the nature of the ferroelectric phase transition. For example, the first-order bulk phase transition of PbTiO₃ becomes second-order when it is grown as a thin film on SrTiO₃ [29]. Some particularly impressive demonstrations of the power of strain engineering have been made recently, enabled by the development of new scandate substrates, in particular the ferroelectric polarization and transition temperatures of BaTiO₃ [35] have been considerably raised and ferroelectric behaviour at room temperature has been induced in SrTiO₃ [36]. The Landau theory framework presented by Pertsev [37, 38] presents useful guidelines for predicting the relationship between epitaxial strain and ferroelectric properties. Naturally, due to its phenomenological nature, it has limitations, and some recent first principles results, combined with experiment, suggest that in some of the ferroelectric materials, in particular lead zirconate titanate (PZT), the potential for increasing polarization through the application of epitaxial strain is limited [39]. Similarly Gariglio *et al* [40], found in PZT films grown on SrTiO₃ that the transition temperature was quite independent of the strain state of the film. A point well worth making is that we should not expect all ferroelectrics to radically change their behaviour with epitaxial strain, for example in BiFeO₃ with its lone pair driven mechanism for ferroelectricity a large dependence of the polarization on epitaxial strain is neither expected on the basis of first principles calculations [41] nor seen in experiment [42]. Despite these caveats, strain engineering remains one of the most appealing paths to enhanced properties in several ferroelectric materials, and this is especially true in superlattices since in many materials it is much easier to

maintain the structure under a coherent strain state (determined by the substrate) for a large thickness in a multilayer structure than in a single thick layer.

5. Superlattices

Having seen that the interfaces of ferroelectric thin films can drastically affect their properties we can expect them to be even more important in systems entirely composed of multiple interfaces. Indeed, ferroelectric-dielectric superlattices emerge as potential model systems where the role of electrostatics and strain can be clearly demonstrated, and where the polar distortions that are governed by these considerations can be forced to interact with non-polar distortions enabled by the symmetry breaking at an interface.

The electrostatic problem in superlattices is related to the screening problem in thin films. Suppose one takes a ferroelectric layer and puts it into intimate contact with a non-ferroelectric material. Provided there is no free charge at the interface then the electric displacement must be continuous in the two materials. This does not of itself guarantee that the polarization is continuous, the system can achieve continuity of displacement even if the polarization is not continuous, but doing so will result in the development of electric fields, and a corresponding electrostatic energy cost.

The electrostatic energy (E_{elec}) of a given layer in a ferroelectric-dielectric superlattice, of thickness l_F or l_D , in the presence of a finite electric field \mathcal{E} , to leading order in the field, is $E_{\text{elec}} = -l\mathcal{E}P^0$. The electric field in the ferroelectric layer, \mathcal{E}_F , and the dielectric layer, \mathcal{E}_D , are determined by the polarizations in the layers, P_F^0 and P_D^0 , respectively, through the condition of continuity of the normal component of the electric displacement field at the interfaces:

$$P_F^0 + \epsilon_0 \mathcal{E}_F = P_D^0 + \epsilon_0 \mathcal{E}_D. \quad (1)$$

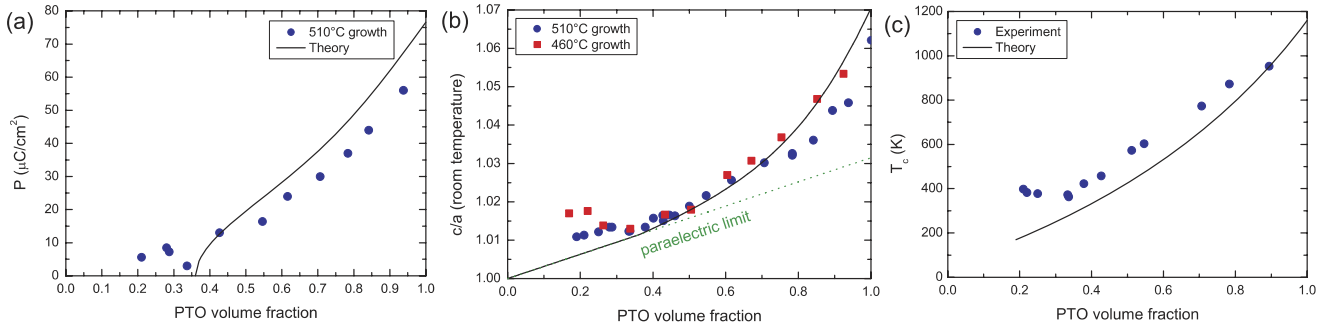


Figure 3. (a) Polarization measured using a PUND technique as a function of PbTiO₃ volume fraction, the solid line shows the prediction from Landau theory, (b) tetragonality of both types of samples, those for which polarization was measured (growth temperature 510 °C) and the samples in [44] (growth temperature 460 °C) plotted against PbTiO₃ volume fraction. The solid line shows the prediction from Landau theory and the dotted line denoted ‘paraelectric limit’ indicates the expected tetragonality when the system is paraelectric, (c) transition temperature determined from x-ray diffraction plotted as a function of PbTiO₃ volume fraction. The solid line shows the theoretical prediction from Landau theory. Data reproduced from [46].

For a system under short-circuit boundary conditions, the potential drop along the structure must vanish and

$$l_F \mathcal{E}_F = -l_D \mathcal{E}_D. \quad (2)$$

Combining the last two conditions and summing the electrostatic energies of the ferroelectric and dielectric layers gives

$$E_{\text{elec}}(P_F^0, P_D^0) = \frac{l_F l_D}{\epsilon_0(l_F + l_D)} (P_D^0 - P_F^0)^2. \quad (3)$$

For superlattices of PbTiO₃ or BaTiO₃ with SrTiO₃ this term is large compared to the other terms in the equation, and forces the polarization in the system to be practically uniform, which is seen to be the case in a number of first principles calculations [43–45]. In the case of a PbTiO₃/SrTiO₃ superlattice (in moving to this specific case we now denote $P_F = P_p$ and $P_D = P_s$) we can write the total energy of the system as

$$E(P_p, P_s) = xU_p(P_p) + (1-x)U_s(P_s) + E_{\text{elec}}(P_p, P_s) \quad (4)$$

where $x = n_p/(n_s + n_p)$ is the PbTiO₃ volume fraction (n_p and n_s are the number of unit cells of PbTiO₃ and SrTiO₃ in each layer) and $U_p(P_p)$ and $U_s(P_s)$ represent the Helmholtz free energies of PbTiO₃ and SrTiO₃ estimated at the bulk level under appropriate mechanical constraints of fixed in-plane strain imposed by the substrate and fixed vanishing out-of-plane stress, in terms of their respective polarizations, P_p and P_s .

Under the conditions described above the last term in equation (4) effectively *always* vanishes: it can be assumed that $P_s = P_p = P$ and the E_{elec} term can be dropped in practice, meaning that the energy of a superlattice of composition x can be written in terms of the polarization P as

$$E(P) = xU_p(P) + (1-x)U_s(P). \quad (5)$$

A variety of potentials could be used for U_p and U_s , for example in [44] potentials derived from first principles were used. A practical approach to look at the evolution of experimental quantities with temperature is to use Landau

theory, taking parameters obtained from measurements on bulk materials [37, 38], an approach we took in the case of our work on PbTiO₃/SrTiO₃ superlattices [46] where we compared the theoretical predictions given by Landau theory with the evolution of three measurable experimental parameters, namely the polarization, the out-of-plane strain (related to the material tetragonality c/a) and the transition temperature. The polarization can be measured electrically, while the out-of-plane strain and transition temperature can be experimentally measured using x-ray diffraction. Comparison of all three measurements with the theory gives remarkably good agreement (figure 3) for PbTiO₃ volume fractions greater than about 0.4.

The role of the epitaxial strain is also nicely demonstrated in this work, the polarizations and transition temperatures are in close agreement with theory, and we note that for PbTiO₃ on SrTiO₃ one expects a large upwards change in the transition temperature from the bulk value, but not a large increase in the room temperature polarization. This can be understood by realizing that the transition temperature is a function only of the leading P^2 term in the expansion, and the effect of the compressive strain on this term is to raise the transition temperature. At the same time the P^4 coefficient, which effects the polarization, but not the transition temperature, becomes positive due to the fact that the film is constrained on the substrate, at room temperature the combination of these competing effects is that the polarization is not substantially modified from the bulk value. The positive P^4 term also modifies the order of the transition from the first-order behaviour typical of bulk PbTiO₃ to second-order, which is what we experimentally observe in all our superlattices.

Given the fact that the simple electrostatic model does a good job of explaining the important properties of the superlattices with high volume fractions, the recovery of ferroelectricity seen in all three measurements for low volume fractions is particularly intriguing. Due to experimental limitations on the thickness of SrTiO₃ in our superlattices the low volume fraction samples are achieved by making samples with layer thicknesses of only a few unit cells, suggesting that some kind of interfacial effect is responsible for the departure from the expected behaviour.

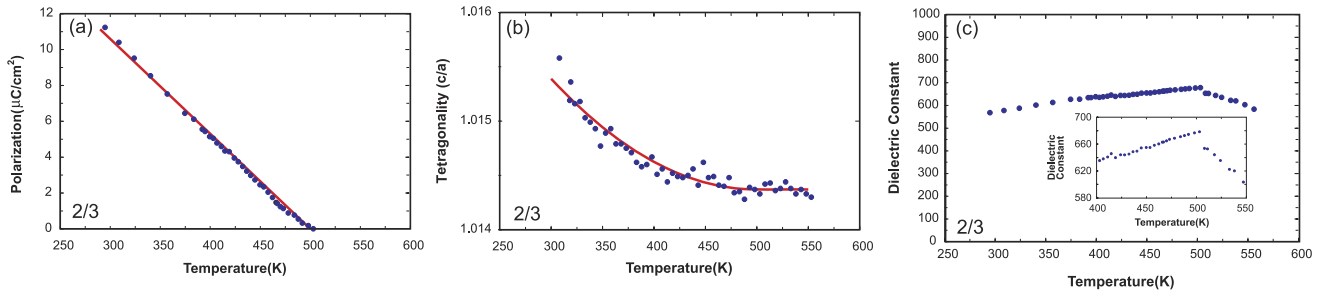


Figure 4. (a) Ferroelectric polarization of a 100 nm thick 2/3 PbTiO₃/SrTiO₃ superlattice as a function of temperature. The line is a fit, $P_z = 0.053(500 - T)$, (b) tetragonality of a 100 nm thick 2/3 PbTiO₃/SrTiO₃ superlattice as a function of temperature. The line is a fit, $c/a = 1.01437 + 2.39 \times 10^{-8}(500 - T)^2$, (c) dielectric constant of a 100 nm thick 2/3 PbTiO₃/SrTiO₃ superlattice as a function of temperature. The inset is a close-up of the same data highlighting the step in the dielectric constant at the transition temperature. Data reproduced from [47].

First-principles simulations of the system allow us to find out on a microscopic level what is occurring. A first-principles study was made on a system that is essentially entirely interfaces, i.e. a 1/1 PbTiO₃/SrTiO₃ superlattice [47]. When made with a sufficiently large supercell to allow antiferrodistortive oxygen rotations the simulations reveal that in addition to ferroelectric instabilities there are also several kinds of antiferrodistortive oxygen rotations. Antiferrodistortive rotations of the oxygen octahedra are not uncommon in perovskite oxide materials, though they typically frustrate rather than enhance the tendency towards ferroelectricity [48]. SrTiO₃ is particularly interesting from this point of view, with both pressure and strain having strong effects on the interplay between the competing distortions [38, 49, 50]. As mentioned previously, in PbTiO₃ the polar distortion suppresses the tendency towards antiferrodistortive oxygen rotations, except at surfaces where the two distortions can co-exist [33, 34]. As an aside, it is interesting to note that in multiferroic BiFeO₃ polar distortions along [111] are accompanied by rotations of the oxygen octahedra around this axis which are linked to the magnetic properties of the material [51].

The two most relevant distortions in the present case of the PbTiO₃/SrTiO₃ superlattice are ones which involve rotation of the oxygen octahedra around the 001 direction. In-plane (in the [100] or [010] directions), nearest neighbour oxygen octahedra are rotated in the opposite sense to each other. From one plane to the next (in the [001] direction) nearest neighbour oxygen octahedra can be rotated in either the same or opposite sense, and these represent two different unstable modes in the system. Further, it is found that the product of the two modes has the same symmetry properties as the polarization mode. The details of these modes, and their symmetry properties can be found elsewhere [47]. Here we emphasize how the coupling of the modes leads to the observed functional behaviour. The symmetry properties of the rotational modes mean that we are able to add an energy term to free energy expansion of the form $\phi_1\phi_2P$, (where ϕ_1 and ϕ_2 are parameters which describe the magnitude of the rotational modes, and play the role of the primary order parameters), which can give rise to an enhancement of the polarization.

Further studies of superlattices with thicker layers show clearly that electrostatics does not lose its primacy at this

short length scale, as the polarization always remains uniform throughout the structure. Rather it is seen that the non-polar distortions are able to arise at the interfaces, in a way that enhances the ferroelectric properties throughout the structure, even though the distortions are larger at the interface than in the middle of layers. When the layers are thick, the contribution of these rotational modes is negligible, but as they become thinner they actually become the driving force for polarization in the material, which becomes a type of improper ferroelectric.

As discussed elsewhere [52, 53, 5], in the case of improper ferroelectricity, which is driven by the coupling of two non-polar order parameters, strikingly different critical behaviour is expected. Notably the polarization is expected to have a modified temperature dependence. As the polarization is produced by the combination of two mean field order parameters with temperature dependence $(T_C - T)^{0.5}$ its evolution with temperature is expected to be linear. In the improper ferroelectric phase there is an additional but temperature independent contribution to the dielectric constant, which disappears above the phase transition temperature without the divergence associated with regular ferroelectrics. Comparison of measurements of polarization, dielectric constant and tetragonality between a ‘normal’ 9/3 sample and an ‘unusual’ 2/3 sample show that while the 9/3 sample shows textbook second-order ferroelectric behaviour the 2/3 sample has characteristics that resemble the behaviour described above (figure 4), thus confirming the first-principles results and demonstrating that the interactions between polar and non-polar modes at the interfaces of the superlattice dominate the behaviour of the entire sample.

The improper ferroelectricity found at the interfaces of PbTiO₃/SrTiO₃ superlattices is one example of the surprises that can be found in ‘interfacially engineered’ materials. Interestingly if one replaces PbTiO₃ with another insulator, LaAlO₃, the result is not ferroelectricity but rather the formation of a conducting layer [54], which has recently been revealed to be in fact superconducting at very low temperatures [55]. These different behaviours are clearly driven by quite different mechanisms, in the case of LaAlO₃/SrTiO₃ it has been suggested that the conducting layer is formed because of the polarity mismatch at the interfaces due to the polar and non-polar nature of the LaAlO₃ and SrTiO₃

(001) planes respectively. In $\text{PbTiO}_3/\text{SrTiO}_3$ it is not the charge of the layers that changes across the interface but rather the tendency for rotational behaviour in the two materials.

These quite different behaviours, both of which appear to be purely interfacial effects, highlight the idea that careful control of oxide interfaces represents a promising approach to induce multiple functionality in a wide range of materials.

6. Conclusions

In this paper we have looked at what are the most important factors that impact on the behaviour of very thin ferroelectrics, and in particular the role that one or many interfaces can play. In doing so we have especially tried to point to some areas where things are not fully understood and where we feel some more attention might be required, from the role of strain, to the finer details of electrostatic screening. Finally and, perhaps most importantly, we have tried to stress some of the possibilities that exist in ferroelectric oxide materials, in particular in superlattice systems where the interfaces can become the majority of the material and drive new, unexpected and fascinating behaviour.

References

- [1] Dawber M, Rabe K M and Scott J F 2005 *Rev. Mod. Phys.* **77** 1083
- [2] Ahn C H, Rabe K M and Triscone J-M 2004 *Science* **303** 488
- [3] Rabe K M, Ahn C H and Triscone J M (ed) 2007 *Physics of Ferroelectrics, A Modern Perspective (Springer Topics in Applied Physics vol 105)* (Berlin: Springer)
- [4] Jaffe B, Cook W R and Jaffe H 1971 *Piezoelectric Ceramics* (London: Academic)
- [5] Lines M E and Glass A M 1977 *Principles and Applications of Ferroelectrics and Related Materials* (Oxford: Oxford University Press)
- [6] Scott J F 2000 *Ferroelectric Memories* (Berlin: Springer)
- [7] Ghosez Ph and Rabe K M 2000 *Appl. Phys. Lett.* **76** 2767
- [8] Bune A V, Fridkin V M, Ducharme S, Blinov L M, Palto S P, Sorokin A V, Yudin S G and Zlatkin A 1998 *Nature* **391** 874
- [9] Junquera J and Ghosez Ph 2003 *Nature* **422** 506
- [10] Batra I P and Silverman B D 1972 *Solid State Commun.* **11** 291
- [11] Mehta R, Silverman B and Jacobs J T 1973 *J. Appl. Phys.* **44** 3379
- [12] Lichtensteiger C, Triscone J-M, Junquera J and Ghosez Ph 2005 *Phys. Rev. Lett.* **94** 047603
- [13] Dawber M, Chandra P, Littlewood P B and Scott J F 2003 *J. Phys.: Condens. Matter* **15** L393
- [14] Junquera J, Cohen M H and Rabe K M 2007 *J. Phys.: Condens. Matter* **19** 213203
- [15] Gerra G, Tagantsev A K, Setter N and Parlinski K 2006 *Phys. Rev. Lett.* **96** 107603
- [16] Stengel M and Spaldin N A 2006 *Nature* **443** 679
- [17] Heine V 1965 *Phys. Rev.* **138** A1689
- [18] Aguado-Puente P and Junquera J 2007 *Preprint* **0710.1515v1** [condmat]
- [19] Saad M M, Baxter P, Bowman R M, Gregg J M, Morrison F D and Scott J F 2004 *J. Phys.: Condens. Matter* **16** L451
- [20] Ahn C H, Gariglio S, Paruch P, Tybell T, Antognazza L and Triscone J-M 1999 *Science* **284** 1152
- [21] Takahashi K S, Gabay M, Jaccard D, Shibuya K, Ohnishi T, Lippmaa M and Triscone J-M 2006 *Nature* **441** 195
- [22] Ahn C H *et al* 2006 *Rev. Mod. Phys.* **78** 1185
- [23] Hong X, Posadas A and Ahn C H 2006 *Appl. Phys. Lett.* **86** 142501
- [24] Fiebig M 2005 *J. Phys. D: Appl. Phys.* **38** R123
- [25] Spaldin N A and Fiebig M 2005 *Science* **309** 5391
- [26] Eerenstein W, Mathur N D and Scott J F 2006 *Nature* **442** 759
- [27] Ramesh R and Spaldin N A 2007 *Nat. Mater.* **6** 21
- [28] Fong D D *et al* 2004 *Science* **304** 1650
- [29] Streiffer S K *et al* 2002 *Phys. Rev. Lett.* **89** 067601
- [30] Vlooswijk A H G *et al* 2007 *Appl. Phys. Lett.* **91** 112901
- [31] Lichtensteiger C, Dawber M, Stucki N, Triscone J-M, Hoffman J, Yau J-B, Ahn C H, Despont L and Aebi P 2007 *Appl. Phys. Lett.* **90** 052907
- [32] Despont L *et al* 2006 *Phys. Rev. B* **73** 094110
- [33] Bungaro C and Rabe K M 2005 *Phys. Rev. B* **71** 035420
- [34] Munkholm A *et al* 2002 *Phys. Rev. Lett.* **88** 016101
- [35] Choi K J *et al* 2004 *Science* **306** 1005
- [36] Haeni J H *et al* 2004 *Nature* **430** 758
- [37] Pertsev N A, Zembilgotov A G and Tagantsev A K 1998 *Phys. Rev. Lett.* **80** 1988
- [38] Pertsev N A, Tagantsev A K and Setter N 2000 *Phys. Rev. B* **61** R825
- [39] Lee H N *et al* 2007 *Phys. Rev. Lett.* **98** 217602
- [40] Gariglio S, Stucki N, Triscone J-M and Triscone G 2007 *Appl. Phys. Lett.* **90** 202905
- [41] Ederer C and Spaldin N A 2005 *Phys. Rev. Lett.* **95** 25760
- [42] Kim D H, Lee H N, Bieganski M D and Christen H M 2007 *Preprint* **0710.5208v1**
- [43] Neaton J and Rabe K M 2003 *Appl. Phys. Lett.* **82** 1586
- [44] Dawber M, Lichtensteiger C, Cantoni M, Veithen M, Ghosez Ph, Johnston K, Rabe K M and Triscone J-M 2005 *Phys. Rev. Lett.* **95** 177601
- [45] Nakhmansson S M, Rabe K M and Vanderbilt D 2005 *Appl. Phys. Lett.* **87** 102906
- [46] Dawber M, Stucki N, Lichtensteiger C, Gariglio S, Ghosez Ph and Triscone J-M 2007 *Adv. Mater.* **19** 4153
- [47] Bousquet E, Dawber M, Stucki N, Lichtensteiger C, Hermet P, Gariglio S, Triscone J-M and Ghosez Ph 2008 *Nature* **452** 732
- [48] Zhong W and Vanderbilt D 1995 *Phys. Rev. Lett.* **74** 2587
- [49] Lin C H, Huang C M and Guo G Y 2006 *J. Appl. Phys.* **100** 084104
- [50] Vasudevarao A *et al* 2006 *Phys. Rev. Lett.* **97** 257602
- [51] Ederer C and Spaldin N A 2005 *Phys. Rev. B* **71** 060401 (R)
- [52] Levanyuk A P and Sannikov D G 1974 *Usp. Fiz. Nauk.* **112** 561
- [53] Strukov B A and Levanyuk A P 1998 *Ferroelectric Phenomena in Crystals* (Berlin: Springer)
- [54] Ohtomo A and Hwang H Y 2004 *Nature* **427** 423
- [55] Reyren N *et al* 2007 *Science* **317** 1196