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**Tailoring the Properties of Artificially Layered Ferroelectric Superlattices\*\***   
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and *Jean-Marc Triscone*

Ultra-thin films and fine period superlattices based on di-electric and ferroelectric materials are currently a topic of very active research,[1]in part because of their potential appli-cations,[2,3]but also because the changes in the ferroelectric properties as the thickness of the ferroelectric material is re-duced are of fundamental scientific interest.[4,5]In such artifi-cial ferroelectric-dielectric structures, the key role of the elec-trostatics, which produces a coupling between the materials, has been shown from first principles calculations[6]and experi-ments.[7–9]From these recent developments, it emerges that one can use the ratio of the constituent layer thicknesses as a tuning parameter allowing the electronic properties to be con-trolled and tailored in such artificial systems, which we dem-onstrate in this paper. This approach to tuning and optimizing the properties of ferroelectric materials represents an impor-tant path to new or improved performance applications. While for some time it has been possible to modify ferroelec-tric properties in materials by playing with atomic substitu-tions in solid solutions, which are typically ceramics, (a good example is the Pb1–*x*Zr*x*TiO3 system),[10]it is much less straightforward to do so while maintaining perfect crystal structure and good electrical properties. It is here that epitax-ial superlattices come into their own. As will be shown below, the properties of these heterostructures can be tuned while maintaining materials with a high degree of structural perfec-tion. Additionally, it is found that the designed layering dra-matically reduces the leakage in such structures solving one important material problem for many applications.

Superlattices composed of layers of PbTiO3 (PTO), *n*p unit cells thick, and layers of SrTiO3 (STO), *n*s unit cells thick

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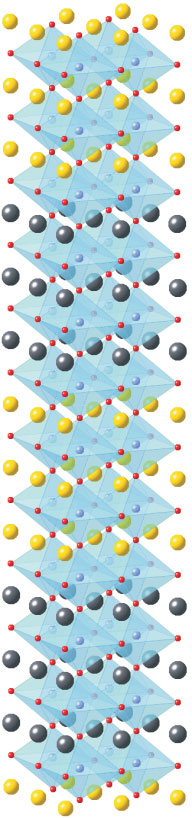
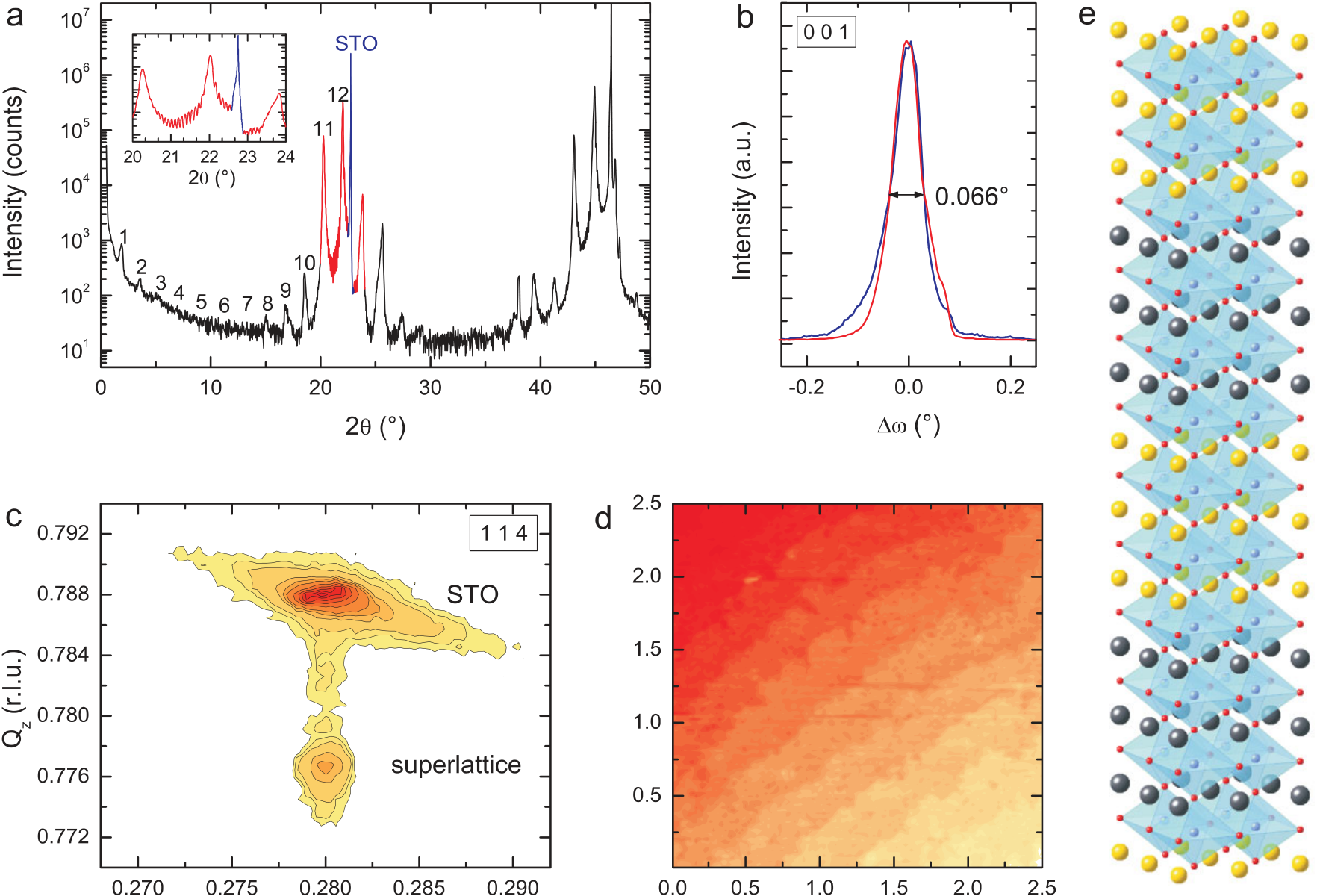
(schematically illustrated in Fig. 1e), hereafter denoted *n*p/*n*s, were prepared by off-axis magnetron sputtering on Nb-doped STO substrates. Here the superlattices were grown at growth temperatures of 510 °C and 460 °C; details of the sputtering process and growth conditions can be found in Ref. [7]. At room temperature, bulk STO is an insulating cubic perovskite with lattice parameter *a* = 3.905 Å[11]and its energy remains minimum for zero polarization at all temperatures. This para-electric material, however, is easily polarizable and a sponta-neous polarization can be induced at room temperature under strain.[12]PTO on the other hand is one of the most studied fer-roelectric materials. Its paraelectric phase is also cubic perov-skite, with lattice parameter *a* = 3.969 Å at the bulk transition temperature.[13]This phase is only stable above ∼ 750 K and, at room temperature, bulk PTO has a tetragonal ferroelectric structure with *a* = 3.904 Å and *c* = 4.152 Å. As can be ex-pected from the lattice parameters of the two systems and in agreement with theoretical phase diagrams,[14]when grown on STO, the compressive misfit strain (*u*m = (*a*substrate – *a*0)/ *a*substrate where *a*substrate is the in-plane lattice parameter of the substrate and *a*0 is the equivalent cubic cell lattice constant of the free standing film) forces PTO to grow *c*-axis oriented with its polarization along the growth direction. The mismatch be-tween the tetragonal a axis of ferroelectric PTO and the cubic lattice parameter of STO is very small and coherent growth of the system is relatively straightforward.

Figure 1a and d shows some X-ray and atomic force micros-copy characterization performed on a 9 unit cell PTO/3 unit cell STO (9/3) x 20 superlattice, and Figure 1b and c shows rocking curves for film and substrate and an X-ray q-space map for a 2 unit cell PTO/5 unit cell STO (2/5) x 36 superlat-tice. These data demonstrate coherent growth, high crystalline and surface quality and establish clearly the induced superlat-tice periodicity which results from the artificial layering in the structure.

A recent study of 20 bilayer PTO/STO *n*p/3 superlattices with *n*p ranging from 53 to 1 revealed at first a progressive de-crease of the average material tetragonality (mean *c*/*a* ratio) when decreasing the PTO layer thickness *n*p and then a sur-prising recovery of tetragonality for *n*p < 3.[7]Since the materi-al tetragonality is related to the material polarization through the strain polarization coupling this behaviour has been taken as signature of a progressive decrease of the polarization in the system as the PTO layer thickness is reduced followed by a recovery of ferroelectricity.

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**Figure 1.** a) *h*–2*h* X-ray diffractogram for a 20 bilayer PTO/STO 9/3 superlattice, b) rocking curves of substrate (blue) and superlattice (red), c) X-ray diffraction q-space map for a PTO/STO 2/5 superlattice around the 114 reflection showing coherent growth of superlattice, d) AFM topography image of typical superlattice surface showing 4 Å high unit cell steps, e) schematic of an ideal 3/3 PTO/STO superlattice structure.

In order to highlight the capacity for tailoring of the ferro-electric properties in such systems, we will mainly focus here on the first region corresponding to high PTO volume frac-tion. Within this region, it has been shown that the energy of the system is appropriately described by:

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| --- | --- | --- | --- | --- | --- | --- | --- |
| *E Pp*� *Ps*� | � | � *xUp Pp*� | � | � 1 � *x*�*Us Ps* | � � *Eelec Pp*�*Ps*� | � | �1� |

where *x* = *n*p/(*n*s + *n*p*)* is the PTO volume fraction and *U*p*(P*p*)* and *U*s*(P*s*)* represent the Helmoltz free energies of PTO and

the most obvious direction for tailoring the properties of these systems is to modify the ratio of the relative thicknesses of the constituent layers rather than the thickness of the materials themselves.[15–17]It is this approach that we take here and show it can be used to effectively tune the ferroelectric prop-erties of the material over a very wide range.

Under the conditions described above the last term in Equation 1 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 PTO volume frac-tion *x* can be written in terms of the polarization *P* as

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| STO estimated at the bulk level under appropriate mechani-  cal constraints of fixed in-plane strain *u*m PTO and *u*m STO im- | *E*�*P*� � *xUP P*� � � 1 � *x*�*US P*� � | �2� |
| posed by the substrate and fixed vanishing out-of-plane stress, |

in terms of their respective polarizations, *P*p and *P*s.

The last term in Equation 1 is an electrostatic energy aris-ing from the possible presence of electric fields within each layer. Inspection shows that this term is always positive and scales as (*P*p – *P*s)2reflecting the fact that, as discussed in a number of references,[5–7,9]a polarization mismatch at the in-terfaces is very costly in energy. Consequently, it is observed that the system will maintain a near uniform polarization with a value intermediate between the optimum values for the par-ent materials.[7]From these considerations we surmise that

In contrast to Ref. [7] which made use of first-principles po-tentials corresponding to zero temperature, here *U*p(*P*) and *U*s(*P*) are estimated within a Landau type approach in order to provide easy access to the finite temperature properties. Standard values of the coefficients were taken from the litera-ture for each compound in order to avoid any fitting proce-dure and test the real predictive power of the model. To re-produce the experimental system, both layers are constrained in plane to the bulk lattice parameter of STO and free to relax

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| along the normal direction. In order to properly take into ac-count the effects of such mixed mechanical constraints (fixed in-plane strain and zero out-of-plane stress), we followed the formulation of Pertsev et al.[14,18]in which the individual Hel-moltz free energy of compound *i* can be expanded in terms of *P* as: | for the lower PTO volume fraction samples, was varied for some samples to give us more flexibility in accessing different PTO volume fraction. A limitation however is that the rela-tively low growth deposition temperatures, required to main-tain the quality of the PTO layers, prevents the growth of STO layers whose thickness is larger that 5 unit cells (above |

this thickness, a degradation in the quality of the superlattices

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| --- | --- | --- | --- |
| *Ui P*� � � *ai*�3*P*2 � *ai*�33*P*4 � *ai* 111*P*6 | | �3� | is noticed). |
| Polarization was measured using an AixAcct TF 2000. The |
| �*ci* 2 11� *ci* 11*ci*  *ci* 11   12� 2*ci* 2 | *ui* 2 *m* | most straightforward way to measure ferroelectric hysteresis |
| loops is simply to apply triangular or sinusoidal voltage pulses |
| and integrate the measured current, which in an insulating |

where the coefficients denoted by \* are those renormalized by the strain constraint and are given by

|  |  |  |  |
| --- | --- | --- | --- |
| *ai*�3� *ai* 1� 2 *ci*�12  11 | *gi* 11� *gi* 12 | �*ui m* | �4� |

sample should be purely displacive and display characteristic hysteresis loops such as those we show in Figure 2a. From the excellent hysteresis results we can conclude that in our super-lattices the leakage current is quite low compared to switching current that arises from the switching of the ferroelectric po-larization.

It is interesting to note that the leakage current is reduced

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| *ai*�33� *ai* 11� *gi* 2 11 | �5� | by the insertion of the STO layers into the PTO. In Figure 2b |
| we show the current-voltage measurement obtained during |
| the hysteresis measurement of a 9/3, 9/2 and 9/0 superlattice. |

In the above *g*ij and *c*ij are the electrostrictive constants and elastic stiffnesses respectively. The parameters used in the Landau theory expansions are the same as those used in Ref. [14] for PTO and in Ref. [18] for STO. Note that these two papers use slightly different forms of the starting free energy. Here we have based our work on an expansion of the Hel-moltz free energy in terms of polarization and strain[18]and have converted the parameters of PTO accordingly.[19]The cu-bic lattice parameter of PTO is taken to be 3.969 Å and that of STO 3.905 Å, giving a misfit strain of *u*m PTO = -0.0164 for PTO on STO and trivially for STO on STO *u*m STO = 0. We do not consider evolution of this misfit strain with temperature. Indeed experimentally it is seen that in the high temperature cubic phases the coefficients of thermal expansion of the two materials are very similar.[11]Generalization of the model to other materials where this may not be the case may require at-tention on this point.

For any temperature and composition, the spontaneous po-larization P can be obtained from the condition ∂*E*/∂*P* = 0, i.e., from the solution of the equation:

In each of these superlattices the PTO layer thickness was 9 unit cells. The 9/0 superlattice is essentially a PTO thin film, grown in 9 unit cell steps to ensure that the reduction of leak-age was not in fact simply a result of growing the samples in steps. It seems that the insertion of 2 or more unit cells of STO reduces the leakage dramatically and that it no longer in-terferes with the polarization measurement. One feature of these loops is that the coercive field is very high and also quite asymmetric. We have found that this is due to an interfacial capacitance that arises at the Nb-doped STO/superlattice in-terface. Superlattices grown on SrRuO3 electrodes show much smaller coercive fields, but the essence of the discussion is not modified by this finding.

The direct hysteresis measurement, though appealing, is not in general a very good way of obtaining an accurate measure-ment of the spontaneous polarization. This is because the cur-rent measured contains components due to switching of the ferroelectric polarization, from the linear dielectric response of the material, and, where it exists, a component from leak-age current. In order to separate out only the stable ferroelec-tric polarization a PUND (Positive Up Negative Down)

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| 6*xaPTO*  � 2 *xaPTO*� 111*P*4 � 4 *xaPTO*� � � 1 � *x*� �*aSTO* � 1 � *x* �� 0 �*aSTO*� | � | *P*2 | �6� | measurement[20]was used. A typical result of a PUND mea- |
| surement is shown in Figure 2c. The voltage pulse train that is |
| applied to the sample is shown in the lower right hand corner |
| of the inset. Firstly, a pre-measurement pulse is sent to pole |
| the sample in a defined direction. Then a four pulse train is |

To test to which extent the spontaneous polarization can be tuned and how well this can be predicted from the theoretical model, the electrical properties of a number of superlattices were measured as a function of the PTO volume fraction. To realize these measurements, a series of samples with a total thickness of 100 nm were grown varying the number of bi-layers that were used to make up the superlattices. The STO layer was for most samples 3 unit cells thick but, especially

sent, the first pulse P (Positive) switches the sample into the opposite direction, the next pulse U (Up) is in the same direc-tion and therefore does not switch the sample, and , similarly the N (Negative) and D (Down) pulses measure switching and non-switching current in the opposite direction. This tech-nique allows us to subtract the current from the U cycle from that of the P cycle (and similarly D from N) so as to obtain only that current related to the switching of the ferroelectric

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**Figure 2.** a) P-E loops of a series of ferroelectric superlattices (from 9 PTO/3 STO to 2 PTO/5 STO, the total thickness of each sample is 100 nm), b) measurement of the current-voltage response measured during the hysteresis measurement of superlattices going from 9 PTO/3 STO to 9 PTO/0 STO (corresponding to a PTO thin film grown in 9 unit cell steps), c) result of a typical PUND measurement, as described in the text. d) Po-larization measured using a PUND technique as a function of PTO volume fraction, the solid line shows the prediction from Landau theory.

polarization (upper right hand corner of inset), the magnitude The mean tetragonality of the superlattice, *c*/*a* is found of which is obtained by integrating the current over the from

switching time. We used a pulse rise time of 0.0025 seconds and a 1 second delay time between pulses.

Figure 2d shows the measured polarization using the PUND measurement plotted as a function of the PTO volume fraction (samples were grown at 510 °C with a total thickness of 100 nm). On the same plot the prediction from the Landau theory is shown. Figure 2d illustrates that the polarization can be tuned in a predictive way and over a wide range (from 0 to 60 lC cm–2) in terms of the PTO volume fraction in the region

*c*�*a* � *x* 1 � *ePTO*

where the in-plane strains *u*i

� 1 � *x*� � 1 � *eSTO*� ��1 � *uPTO*

��1 � *uSTO*�

mof PTO and STO are known� �7�

and the out-of-plane strains *e*i 33are obtained from the condi-

tion of zero out of plane stress (∂*E*/∂*e*i 33= 0), which is guaran-

teed by

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| *x* = 0.4 to *x* = 1. Moreover, the agreement with theory is very | *ei* 1 | |  |  |  | | --- | --- | --- | | *gi* | *P*2 2*ci* | *ui* | |  | 8 |
| good in view of the simplicity of the model and the absence of | 33� 11 | |  |  |  |  | | --- | --- | --- | --- | | � | 11 � | 12 | *m* | | � | �� |
| adjustable parameters. |

As discussed in Refs. [7,21], the measurement of the tetra-gonality through X-ray diffraction allows the polarization to be probed through the strong strain-polarization coupling, a method that has the advantage that it is not limited to samples of a particular thickness.

Equation 8 enables the deduction of a mean c/a depen-dence for the superlattice completely equivalent to the rela-tionship (*c*/*a*)P = (*c*/*a*)para + const *P*2used in Refs. [7,21] in which the polarization was probed through measurement of the tetragonality using X-ray diffraction.

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| Figure 3 compares the average tetragonality predicted from the model to that measured by X-ray diffraction for both the superlattices used for the polarization measurement above and those grown at 460 °C and characterized in Ref. [7]. The | carrying out x-ray diffraction at elevated temperatures which allows one to measure the ferroelectric-paraelectric transition temperature and the critical behaviour associated with it. Some examples of the results of these measurements and the |

transition temperatures extracted are shown in Figure 4.

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| **Figure 3.** Tetragonality of both types of samples, those for which polariza-tion was measured (growth temperature 510 °C) and the samples in Ref. [7] (growth temperature 460 °C) plotted against PTO volume frac-tion. The solid line shows the prediction from Landau theory and the dotted line denoted “paraelectric limit” indicates the expected tetragonal-ity when the system is paraelectric.  data reveal that as the PTO volume fraction decreases the ini-tial behaviour is a concomitant decrease of the average tetra-gonality towards the value expected for a paraelectric materi-al, the films grown at 460 °C exhibiting a slightly larger tetragonality than those grown at 510 °C. We find that, from *x* = 0.4 to *x* = 1, the experimental measurements follow the Landau theory results based purely on the strain-polarization coupling. Together with the evolution of the polarization re-ported in Figure 2, this demonstrates quantitatively that the widely used tetragonality measurement[7,21,23,24]is indeed an efficient technique to probe indirectly the polarization. It also reveals that the use of bulk elastic and electrostrictive con-stants to link both quantities remains a rather good approxi- | Although, with typical Landau parameters, the phase transi-tion of pure PTO at the bulk level is described as first-or-der,[14]due to the fixed epitaxial strain within our superlattice | |
| it becomes second-order (*aPTO*�33 | � 0). Consequently, the |
| **a**        **Figure 4.** a) Three typical examples of the temperature dependent c/a measurements, b) Transition temperature determined from X-ray diffrac-tion plotted as a function of PTO volume fraction. The solid line shows the theoretical prediction from Landau theory. | |

mation down to very small thicknesses.

The present measurements also confirm an anomalous in-crease of the tetragonality in the superlattices with the lowest PTO volume fractions (*x* < 0.4). It is apparent that this anom-alous increase of tetragonality occurs in films grown at both temperatures, though to a much greater extent in films grown at 460 °C. In Ref. [7], due to the lack of electrical measure-ments, it was not definitely established if this increase was a real recovery of ferroelectricity or, instead, a consequence of a modification of the value of *c*ij or *g*ij in ultrathin layers; Figure 2 definitely confirms the existence of a spontaneous polarization and the survival of a strain-polarization coupling qualitatively similar to that observed for higher values of x into the unusual regime.

While it is straightforward and relatively fast to measure the room temperature tetragonality and compare it to the fer-roelectric polarization, additional insight can be gained by

phase transition of the superlattice at any composition will be second-order and the phase transition temperature can be obtained as that for which the quadratic coefficient in the E expansion the compressive epitaxial strain imposed to the STO layer is�*xaPTO*�3 � 1 � *x*�*aSTO*� vanishes. The role of

to shift the transition temperature to higher temperature. For a pure PTO film (superlattice with *x* = 1), writing

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| --- | --- | --- | --- | --- | --- |
| *aPTO* 1 � *C T* � *Tc*� with *T*c the bulk transition temperature, the strain renormalized transition temperature is: | | | | | |
| *T*�*c*� *Tc*� 2 *C* | �*cPTO*  *cPTO*  12  11 | *gPTO* 11 | � *gPTO* | �*uPTO m* | �9� |

With the parameters used here the misfit strain of –1.6 % imposed by the STO substrate leads to a strain induced up-

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| **COMMUNICATION** |  | k-dielectric capacitors based on ferroelectric materials[29] |
| ward shift of the transition temperature by about 400 K, |
| which is indeed observed experimentally. Beyond the fact that | make use of the divergence of the dielectric constant close to |
| playing with the composition allows the adjustment of *T*c over | the ferroelectric-paraelectric phase transition and therefore in |
| a wide range of temperature (from 300 K to more than | this case a transition temperature not far below room temper- |
| 1000 K), it is also clear that the *T*c curve can be further ad- | ature is desirable. These are just two examples of many, and it |
| justed using strain engineering by an appropriate choice of | is readily apparent that the straightforward tunability of polar- |
| substrate. | ization and transition temperature within an artificial super- |
| As well as seeing that the transition temperatures are in | lattice system that has excellent crystalline properties and re- |
| fairly good agreement with the theoretical prediction (shown | duced leakage across the whole range has enormous potential |

in Fig. 4) it can be seen that, in the samples with high PTO volume fractions, for *T* < *T*c

for many and varied applications.

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| �*c*�*a*�*P*� *c*�*a*�*para*� *Tc* � *T* | � | �10� | Published online: November 12, 2007 |

Provided that *c/a* scales like *P*2(Eq. 8) we can conclude that

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[1] See, for instance, M. Dawber, K. M. Rabe, J. F. Scott, *Rev. Mod.*

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| *P* � *Tc* � *T* | �0�5 | �11� | *Phys.* **2005**, *77*, 1083. |
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This is an experimental proof of the second order nature of the transition and of the appropriateness of the use of the Landau theory in that regime. For samples with lower PTO volume fractions the linear relationship is less obvious, sug-gesting that the present simple model is no longer valid in this region.

To summarize; there are two main points that deserve em-phasis in this work. Firstly, we have provided an extensive ex-perimental demonstration that in ferroelectric multilayers po-larization and transition temperature can be tuned over a very wide range. Additionally, the close link between tetragonality, polarization and transition temperature that has been used in probing the ferroelectric properties of ultra thin films[20]has been shown to be experimentally valid in these samples when *x* > 0.4 (in contrast to some results on PZT thin films where the coupling seems to be less obvious[24,25]). Indeed the recov-ery of ferroelectricity at low volume fractions[7]is here ob-served in all 3 measurements indicating that even when sim-ple electrostatic models break down the relationship between these quantities is at least qualitatively preserved even in this regime. Secondly, it is demonstrated that a simple Landau the-ory approach involving only bulk parameters is rather predic-tive in superlattices with *x* > 0.4 and thus could aid greatly in the design of tailored ferroelectric superlattices for specific applications. This is especially appealing as a large body of work characterizing nearly all known ferroelectrics in their bulk forms on the basis of Landau theory exists, so that our present approach can be readily generalized for a large num-ber of systems. Although there is currently a great deal of in-terest in enhancing polarization and transition temperatures of ferroelectric materials to higher values through strain engi-neering,[13,26]for many applications this is not actually what is required. For example, ferroelectric field effect devices[27,28] require a particular polarization value that matches the prop-erties of the material to which the induced charge effect is applied (which is frequently much lower than the values ob-tained in typical perovskite ferroelectrics). Alternatively, high

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