

Monodomain to polydomain transition in ferroelectric PbTiO_3 thin films with $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ electrodes

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Finite size effects in ferroelectric thin films have been probed in a series of epitaxial perovskite c -axis oriented PbTiO_3 films grown on thin $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ epitaxial electrodes. The film thickness ranges from 480 down to 28 Å (seven unit cells). The evolution of the film tetragonality c/a , studied using high resolution x-ray diffraction measurements, shows first a decrease of c/a with decreasing film thickness followed by a recovery of c/a at small thicknesses. This recovery is accompanied by a change from a monodomain to a polydomain configuration of the polarization, as directly demonstrated by piezoresponse atomic force microscopy measurements.

Recently, both experimental and theoretical studies have suggested that the critical size at which ferroelectricity disappears, traditionally thought to be quite large, may actually be very small.¹⁻⁹ The depolarization field, which results from the imperfect screening of the polarization, has been shown theoretically to play a critical role.^{6,10,11} In uniformly polarized (monodomain) thin PbTiO_3 epitaxial films prepared on Nb-doped SrTiO_3 substrates, it was experimentally shown that the increase of the depolarization field as the film thickness decreases leads to a reduction of the polarization accompanied by a continuous reduction of the film tetragonality c/a .⁸ The direct relation between tetragonality and polarization was also recently experimentally demonstrated in $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices.^{12,13}

In this letter, epitaxial c -axis PbTiO_3 thin films with thicknesses ranging from 480 Å down to 28 Å were grown on epitaxial $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ electrodes (typically 200–300 Å thick) deposited onto (001) insulating SrTiO_3 substrates. It is found that the behavior of the tetragonality is dramatically different from what is observed for PbTiO_3 thin films prepared on metallic Nb-doped SrTiO_3 substrates, with an increase of c/a observed for the thinnest film studied. We show that this behavior is related to a change in the ferroelectric domain structure, with the appearance of domains with 180° alternating polarization (polydomain configuration).

Using off-axis magnetron sputtering, extremely smooth (rms surface roughness of less than 2 Å over $10 \times 10 \mu\text{m}^2$ areas) $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ epitaxial thin films were grown on SrTiO_3 substrates. Their ferromagnetic T_C is around or above 300 K and their resistivity at room temperature typically of 450 $\mu\Omega$ cm. c -axis PbTiO_3 epitaxial thin films of different thicknesses were then deposited on top of the $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ electrodes.

X-ray diffraction measurements were performed on these samples to determine their thickness and lattice param-

eters. Figure 1(a) shows three ϕ -scans around the (101) family of planes obtained on a 248 Å $\text{PbTiO}_3/218$ Å $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ bilayer prepared on a SrTiO_3 substrate, demonstrating the tetragonal symmetry of the different materials and the “cube on cube” growth of PbTiO_3 and $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ on the substrate and on top of each other.

Coherent growth was demonstrated by q -space maps around the (113) reflection, as shown in Fig. 1(b). The three peaks observed correspond, from top to bottom, to the $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ electrode, the substrate, and the PbTiO_3 thin film. As can be seen, the peaks are perfectly aligned in the vertical direction, implying that the a (and b)-axis lattice parameters are identical and equal to the one imposed by the substrate, $a=3.905$ Å. This demonstrates that the strain state of the PbTiO_3 films grown on $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ is similar to the one of the films grown directly on Nb-doped SrTiO_3 substrates. Thus, the main difference between the two PbTiO_3 series is the change of the bottom electrical boundary conditions.

Simulations were then performed to determine the c -axis parameter values, using $\theta-2\theta$ diffractograms around (00 l) reflections for $l=1-5$.¹⁴

Figure 2 shows tetragonality versus thickness for the two series (the average c -axis values and thicknesses obtained along with their standard deviations are used). The model Hamiltonian prediction for monodomain thin films with an effective screening length $\lambda_{\text{eff}}=0.12$ Å is shown as a dotted line⁸ and allows the behavior of the series grown on Nb– SrTiO_3 to be explained. As can be seen, the behavior observed for the thin PbTiO_3 films grown on $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ is quite different from the one observed for PbTiO_3 films directly grown on Nb– SrTiO_3 . For PbTiO_3 films grown on $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$, at large thicknesses where the films are monodomain (as shown below), the tetragonality measured is lower than the one of films prepared on Nb– SrTiO_3 , a possible indication that the depolarization field is higher (implying a larger $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ effective screening length). One would thus expect for this series a

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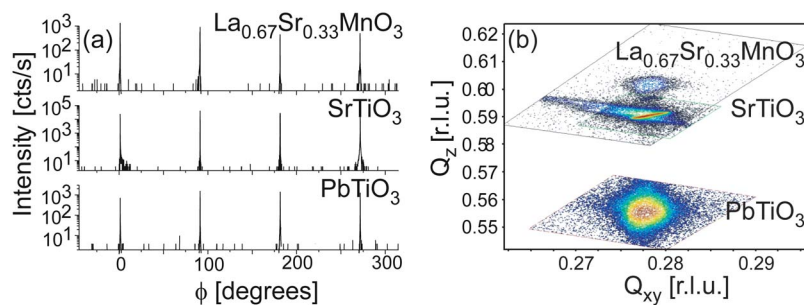


FIG. 1. (Color online) X-ray diffraction measurements on a 248 Å PbTiO₃/218 Å La_{0.67}Sr_{0.33}MnO₃ bilayer. (a) ϕ -scans demonstrating the “cube on cube” growth of La_{0.67}Sr_{0.33}MnO₃ and PbTiO₃ on SrTiO₃. (b) q -space map corresponding to scans in the (113) reciprocal-space region. Q_{xy} and Q_z are in reciprocal lattice units (rlu), with $Q_{xy}=\lambda/2\sqrt{(h/a)^2+(k/b)^2}$ and $Q_z=(\lambda/2)(l/c)$ [$\lambda=1.5406$ Å and $(hkl)=(113)$ here]. The vertical alignment of the three peaks demonstrates that the whole structure is coherent.

substantial decrease of the tetragonality as the film thickness is reduced, with a larger critical thickness. However, as can be seen, the tetragonality is initially only weakly affected by the thickness reduction, with a striking recovery of the tetragonality for the thinnest film. This nonmonotonic behavior may be a signature of a switching from a ferroelectric monodomain structure at large thicknesses to a polydomain configuration as the film thickness is reduced. In a monodomain configuration, when the film thickness decreases, the depolarization field increases and the polarization of the monodomain film will decrease (this is what we observe on Nb–SrTiO₃). However, another solution for the system to reduce its energy is to switch to a polydomain configuration as predicted by Nagarajan *et al.* for ultrathin epitaxial PbTiO₃/SrRuO₃ heterostructures on SrTiO₃ substrates.¹⁵

To test this idea and to probe the domain structure of the different films prepared on La_{0.67}Sr_{0.33}MnO₃, we used piezoresponse atomic force microscopy (PFM).^{2,16} In Fig. 3 are shown the piezoresponse of the different samples after alternate -12 and $+12$ V voltages were applied between a metallic atomic force microscopy 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 (Fig. 3, top) and a gradual ramp from -12 V up to $+12$ V was applied to another area of the sample (Fig. 3, bottom). By comparing the background signal (unwritten area) to the one of the written areas, one can deduce whether the sample is mono- or polydomain. For the PbTiO₃ thin films of 28, 50, 76, and 116 Å, the background in Fig. 3 gives a signal corresponding to the average of the signal given by the areas written with positive and negative voltages. This strongly suggests that these samples are poly-

domain, with domains smaller than the tip resolution (leading to a signal corresponding to the average over the different up and down domains). In contrast, for the thicker sample (480 Å), only the lines written with a positive voltage applied to the tip can be seen. This means that the background signal is identical to the signal given by the lines written with a negative voltage, strongly suggesting that the sample is monodomain with an up-polarization¹⁸ (and thus application of a negative voltage has no effect). Interestingly, the 249 Å thick sample gives a different response depending on the tip location, one corresponding to a monodomain background, the other to a polydomain one. In the image obtained after gradually writing with a ramp from -12 V up to $+12$ V, one sees that, in the background, some large regions appear with different polarizations. This sample is most probably in a mixed state with some large areas being monodomain, and others being polydomain. We note that in contrast to the “pinned” polydomain state of Nagarajan *et al.*,¹⁵ the polydomain state that we find can be switched with an electric field, and large domains remain stable for at least 24 h.

Another measurement that allows the polarization state to be determined (monodomain up or down or polydomain) and the tetragonality of the top few layers to be measured is x-ray photoelectron diffraction (XPD),^{9,17} which was carried out on two samples, 28 and 249 Å thick. During the XPD measurements, both samples were observed to be monodomain up with a tetragonality that, in the case of the thinner sample, is much smaller than the value determined by x-ray diffraction. However, this low c/a value is found to be in good agreement with the value obtained using XPD on a monodomain PbTiO₃ thin film of similar thickness prepared on a Nb-doped SrTiO₃ substrate. It appears that during the XPD measurement, the samples are forced to be in a monodomain configuration, causing a reduction of the polarization (for very thin films) and a concomitant decrease of the tetragonality. Once the XPD measurements are finished, the

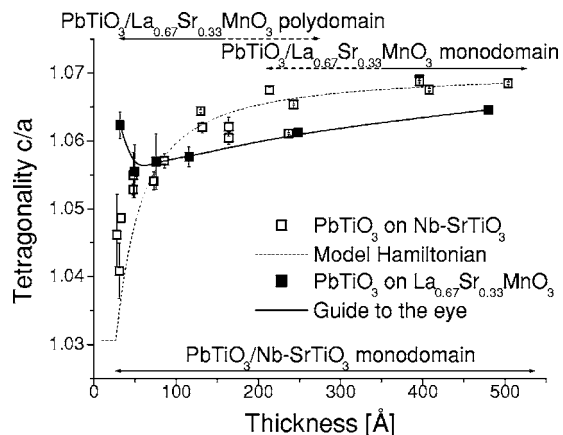


FIG. 2. Tetragonality as a function of film thickness for PbTiO₃ films grown on La_{0.67}Sr_{0.33}MnO₃ (black squares). The behavior observed here is different from what was obtained in the case of PbTiO₃ films grown on Nb–SrTiO₃ (open squares). The model Hamiltonian prediction for monodomain thin films with $\lambda_{\text{eff}}=0.12$ Å is shown as a dotted line (details can be found in Ref. 8).

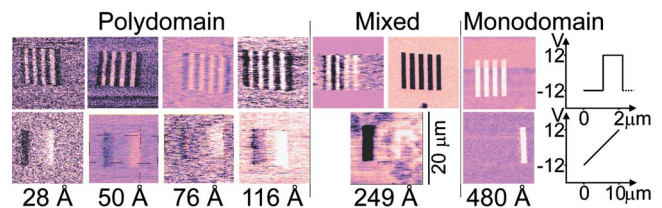


FIG. 3. (Color online) Top: Piezoresponse signals obtained after alternate -12 and $+12$ V voltages were applied between the metallic tip and the conducting La_{0.67}Sr_{0.33}MnO₃ layer to polarize nine stripes over a $10 \times 10 \mu\text{m}^2$ area. Bottom: Piezoresponse signal obtained after application over a $10 \times 10 \mu\text{m}^2$ square of a voltage gradually ramped from -12 V up to $+12$ V. These data also demonstrate ferroelectric switching of the polarization in PbTiO₃ films as thin as 28 Å.

samples return to their more stable state, which for the thinner film is a polydomain state, allowing the recovery of the polarization and therefore also of the tetragonality, as was checked by repeating the x-ray diffraction and PFM measurements. In fact, during the XPD experiment, using a standard x-ray tube with an Al window in front, an electron shower is produced by the x-rays crossing the window. These electrons provide extra negative charges at the surface during the measurements and it is very likely that they induce the “up” state configuration. This effect is discussed in Ref. 9 where experiments varying the x-ray intensity did not reveal any change in the material tetragonality, suggesting that the modification of the domain structure (or switching of the polarization) occurs in the initial stage of the experiments.

The results presented here demonstrate the key role of the electrical boundary conditions on ferroelectricity and on the ferroelectric domain structure of very thin PbTiO_3 films. Additionally, the different behaviors observed for c/a in XPD and x-ray experiments, associated with a different domain structure, reveal the direct relationship between the tetragonality value and the domain configuration in thin films.

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