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

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Abstract

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 La$_{0.67}$Sr$_{0.33}$MnO$_3$ epitaxial electrodes. The film thickness ranges from 480 down to 28 Å (7 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.

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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, 2, 3, 4, 5, 6, 7, 8, 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 PbTiO$_3$/SrTiO$_3$ superlattices [12].

In this letter, epitaxial c-axis PbTiO$_3$ thin films with thicknesses ranging from 480 Å down to 28 Å were grown on epitaxial La$_{0.67}$Sr$_{0.33}$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 $180^\circ$ alternating polarization (polydomain configuration).

Using off-axis magnetron sputtering, extremely smooth (RMS surface roughness of less than 2 Å over $10 \times 10$ µm$^2$ areas) La$_{0.67}$Sr$_{0.33}$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 450 $\mu\Omega$·cm. c-axis PbTiO$_3$ epitaxial thin films of different thicknesses were then deposited on top of the La$_{0.67}$Sr$_{0.33}$MnO$_3$ electrodes [8].

X-ray diffraction measurements were performed on these samples to determine their thickness and lattice parameters. Fig. 1 (left) shows three $\phi$-scans around the (101) family of planes obtained on a 480 Å PbTiO$_3$/ 220 Å La$_{0.67}$Sr$_{0.33}$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 La$_{0.67}$Sr$_{0.33}$MnO$_3$ on the substrate and on top of each other.

Coherent growth was demonstrated by q-space maps around the (103) reflection, as shown in Fig. 1 (right). The three peaks observed correspond, from top to bottom, to the La$_{0.67}$Sr$_{0.33}$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
FIG. 1: X-ray diffraction measurements on a 480 Å PbTiO$_3$/220 Å La$_{0.67}$Sr$_{0.33}$MnO$_3$ bilayer. **Left** - $\phi$-scans demonstrating the “cube on cube” growth of La$_{0.67}$Sr$_{0.33}$MnO$_3$ and PbTiO$_3$ on SrTiO$_3$. **Right** - q-space map corresponding to scans in the (103) reciprocal-space region. The vertical alignment of the three peaks demonstrates that the whole structure is coherent.

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 La$_{0.67}$Sr$_{0.33}$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 $l = 1$ to 5 $^{13}$. Fig. 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 $\lambda_{eff} = 0.12$ Å is shown as a dotted line $^{8}$ 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 La$_{0.67}$Sr$_{0.33}$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 La$_{0.67}$Sr$_{0.33}$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 La$_{0.67}$Sr$_{0.33}$MnO$_3$ effective screening length). One would thus expect for this series a 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 non-monotonic behavior may be a signature of a switching from a ferroelectric monodomain structure at
FIG. 2: Tetragonality as a function of film thickness for PbTiO$_3$ films grown on La$_{0.67}$Sr$_{0.33}$MnO$_3$ (black squares). The behavior observed here is different from what was obtained in the case of PbTiO$_3$ films grown on Nb-SrTiO$_3$ (open squares). The model Hamiltonian prediction for monodomain thin films with $\lambda_{eff}=0.12$ Å is shown as a dotted line (details can be found in Ref. [8]).

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-SrTiO$_3$). However, another solution for the system to reduce its energy is to switch to a polydomain configuration as predicted by V. Nagarajan et al for ultrathin epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$/SrRuO$_3$ heterostructures on SrTiO$_3$ substrates [14].

To test this idea and to probe the domain structure of the different films prepared
on La$_{0.67}$Sr$_{0.33}$MnO$_3$, we used the piezoresponse mode of the atomic force microscope (PFM)\cite{2,15}. In Fig. 3 are shown the piezoresponse of the different samples after alternate -12V and +12V voltages were applied between a metallic AFM tip and the conducting La$_{0.67}$Sr$_{0.33}$MnO$_3$ layer to polarize nine well-defined stripes over a $10\times10\mu m^2$ area (Fig. 3 top) and a gradual ramp from -12V up to +12V 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 poly-domain. For the PbTiO$_3$ 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 polydomain, 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-polarization\cite{20} (and thus application of a negative voltage has no effect). Interestingly, the 249 Å thick sample gives different images 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 -12V up to +12V, 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 V. Nagarajan et al\cite{14}, the polydomain state that we find can be switched with an electric field, and large domains remain stable for at least 24 hours.

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)\cite{9,16}, which was carried out on two samples, 28 Å and 249 Å thick. Curiously (in light of our AFM measurements), 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 PbTiO$_3$ thin film of similar thickness prepared on a Nb-doped SrTiO$_3$ substrate. It appears that during the XPD measurement, the samples are forced to be in
FIG. 3: **Top** - Piezoresponse signals obtained after alternate -12V and +12V voltages were applied between the metallic tip and the conducting La$_{0.67}$Sr$_{0.33}$MnO$_3$ layer to polarize nine stripes over a 10×10 µm$^2$ area. **Bottom** - Piezoresponse signal obtained after application over a 10×10 µm$^2$ square of a voltage gradually ramped from -12V up to +12V. These data also demonstrate ferroelectric switching of the polarization in PbTiO$_3$ films as thin as 28 Å.

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 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. These experiments thus demonstrate in thin films the direct relationship between the tetragonality value and the domain configuration.

To support our experimental observations, we used a simple model solely for the purpose of identifying key thicknesses at which changes in domain structure can be expected. The idea behind this model is that the top surface has a strong preference for one polarization direction over the other, at the very least during the growth process, presumably because of the availability of a particular surface adsorbate. The energy can be written as $U(P) = BP^2 + CP^4 - \frac{1}{2}E_{dep} \cdot P$ with, according to first principles calculations (T=0K) [17], $B = -0.17175279$, $C = +0.16068441$ (U in eV/unit cell) for PbTiO$_3$ constrained in plane to the lattice parameter of SrTiO$_3$. As the film thickness is decreased, the depolarization field increases, which modifies the shape of $U(P)$. When looking at a monodomain scenario, one considers directly the decrease of the polarization to zero as the depolarization field is
increased. A different scenario is to consider for a fixed polarization state how stable this state is against the zero polarization state (which locally the system must pass through to get to a polydomain state). As the thickness decreases and the depolarization field continues to increase, a point is reached at which the local minimum in the as-grown state exists but is at the same or higher energy than the zero polarization state. At this point, domain walls with zero polarization are energetically more favorable than the as-grown polarization direction, but there is still an energy barrier, which means that the polarization may be partially stable. As the thickness is further decreased, eventually the local minimum disappears and the sample must become polydomain. The first field is found to be $E_{\text{dep,1}} = 3.7 \times 10^8 \text{ V/m}$ with a polarization of $P_1 = 60 \mu\text{C/cm}^2$ and the second is $E_{\text{dep,2}} = 5.2 \times 10^8 \text{ V/m}$ with $P_2 = 42 \mu\text{C/cm}^2$. Assuming perfect screening of the polarization on the top surface by the adsorbates, the depolarization field is only due to the bottom electrode and can be written as $E_{\text{dep,1}} = \frac{4\pi P_i}{d_i \varepsilon_0}$ where $\lambda$ is the electrode effective screening length and $d_i$ is the film thickness. Using a screening length of 2 Å, as observed for the La$_{0.67}$Sr$_{0.33}$MnO$_3$ thin films (Ref. [18] [22], these values correspond to critical thicknesses $d_1 = 370 \text{ Å}$ and $d_2 = 185 \text{ Å}$. This predicts that samples above 370 Å can be monodomain, samples between 370 Å and 185 Å might be expected to show either monodomain or polydomain behavior, and that finally any sample below 185 Å must be polydomain, which corresponds remarkably well with our experimental results in view of the simplicity of the model. One finally notes that for a substantially smaller effective screening length (as seems to be the case for the interface between PbTiO$_3$ and Nb-doped SrTiO$_3$), these critical thicknesses will also be much smaller, possibly explaining the different behavior observed between the two series.

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[21] The stability of the polarization against the opposite polarization state cannot be assessed directly, as the energetics of adsorbate screening is difficult to quantify.

[22] Note that the effective screening length appearing in the model Hamiltonian, although related, is not directly the Thomas-Fermi screening length, and includes other contributions than the pure electronic screening, as discussed in Ref. [19].