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X-Ray Diffraction Studies of 180° Ferroelectric Domains in PbTiO₃/SrTiO₃ Superlattices under an Applied Electric Field

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The dielectric response of PbTiO₃/SrTiO₃ superlattices is studied using electrical and structural measurements. While the dielectric response of paraelectric superlattices is well accounted for by the lattice contribution, superlattices with ferroelectric compositions exhibit an enhanced permittivity. X-ray diffraction allowed the presence of ordered nanodomains in ferroelectric superlattices to be established and their displacement under an applied bias to be directly probed, demonstrating that the enhanced permittivity in these artificial materials is due to domain wall motion.

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The functional properties of ferroic (ferroelectric, ferromagnetic, and ferroelastic) materials are highly influenced by their domain structure. As device dimensions shrink, so do the domains [1], leading to extremely dense domain patterns at the nanoscale. The continuing drive for device miniaturization and progress in thin film synthesis have sparked a new wave of research on nanodomains. Recent theories, for instance, predict rather unusual polarization profiles and domain dynamics in ferroelectric thin films and superlattices [2,3], which are yet to be tested experimentally. At the same time, part of the focus is shifting to domain walls—the boundaries between domains—as new experimental and theoretical work has revealed that they often possess fascinating structural and electronic properties of their own, opening an exciting possibility for novel devices based on the concept of domain wall engineering. Recent examples include the discovery that domain walls in multiferroic BiFeO₃ are conducting and can be used to obtain above-band-gap photovoltaic responses [4].

Probing the electrical properties of nanodomains in ultrathin films is rather challenging. Even local scanning probe techniques, which have been invaluable in studying domain dynamics in thin ferroelectrics [5], do not always have sufficient resolution (limited by the tip radius). Macroscopic techniques, such as x-ray diffraction, have been successfully used to image regular periodic 180° domain patterns in ultrathin ferroelectric films [6], but nonzero field studies are hindered by the conductivity of such thin samples. In this Letter, we show that PbTiO₃/SrTiO₃ (PTO/SrO) ferroelectric-paraelectric superlattices provide an ideal system for studying, using x-ray diffraction, the response of ferroelectric nanodomains to uniform electric fields and that the enhanced dielectric properties observed in such ferroelectric superlattices are linked to nanoscale domain wall motion.

PTO/SrO superlattices have already proven to be an exciting system, offering a way of creating new artificial materials with desirable properties that can be easily tuned by simply changing the various layer thicknesses [7]. Furthermore, the PTO/SrO interfaces were found to host a novel coupling between the ferroelectric mode and antiferrodistortive rotations of the oxygen octahedra, giving rise to improper ferroelectricity [8]. In this Letter we study the nanodomain structure of PTO/SrO superlattices and for simplicity restrict our attention to long-period superlattices where interface effects are less important.

To allow dielectric measurements to be performed, the superlattices were sandwiched between ~30 nm thick conducting SrRuO₃ (SRO) electrodes. The PTO and SrO layers were grown by off-axis radio frequency magnetron sputtering on TiO₂ terminated (001) STO substrates in a 0.18 Torr oxygen/argon atmosphere of ratio 14:32 with a substrate temperature of 520 °C (the corresponding parameters for SRO are 0.1 Torr, 3:40, and 650 °C). Figure 1(a) compares the polarization for different PTO volume fractions x of two series of superlattices: one with SRO top and bottom electrodes (filled circles) and the other (open squares) grown on conducting Nb-doped STO substrates and with Au top electrodes [7]; x is defined as $x = n_{PTO}/(n_{PTO} + n_{STO})$ where $n_{PTO}$ and $n_{STO}$ are the number of unit cells of PTO and STO in a superlattice period. The macroscopic remnant polarization $P_r$, as measured by the PUND (positive up negative down) technique [7], is in good agreement with the Landau-Devonshire (LD) theory prediction (solid line) for superlattices on Nb-STO, whereas samples with SRO electrodes show almost zero remnant polarization for all but the highest PTO volume fractions. In contrast, the structural parameters such as the tetragonality were found to be almost identical for the two series, indicating that the intrinsic microscopic spontaneous polarization ($P_s$) values are the same.

Figure 1(b) shows the room temperature dielectric constants for the superlattices with SRO electrodes, together with the LD prediction [7] calculated for different applied electric fields as a function of the PTO volume fraction. The vertical dotted line indicates the critical PTO volume fraction $x_c$ separating ferroelectric superlattices ($x > x_c$) from paraelectric ones ($x < x_c$). As can be seen, for com-
positions that are paraelectric, the relative dielectric constants ($\varepsilon_r$) are in good agreement with the values expected for the lattice response (the LD prediction), indicating that extrinsic contributions such as free carrier injection, space charge, or interface effects are not important. The field dependence of $\varepsilon_r$ for the STO rich samples ($x > x_c$) was also found to be in excellent agreement with LD theory predictions. The permittivities of the ferroelectric superlattices, however, are up to an order of magnitude larger than the expected intrinsic dielectric response of the lattice. This, together with the suppression of remnant macroscopic polarization (despite no change in tetragonality), is suggestive of a polydomain state with domain wall motion responsible for the large increase in permittivity. Similar permittivity enhancements were reported for the low temperature rhombohedral phase of $\text{BaTiO}_3$ single crystals, and attributed to domain wall sliding [9].

Domains in superlattices have been inferred by a number of groups, e.g., [10,11], and have already received significant attention from the theoretical community, e.g., [3,12]. The presence of ferroelectric domains in our samples for $x > x_c$ was confirmed by x-ray diffraction measurements. Figure 2 shows satellites around the superlattice Bragg peaks, typical of periodic domain structures [6,13]. The satellites were present around all (00L) and (H0L) Bragg peaks examined and were observed to disappear above the ferroelectric-paraelectric phase transition temperature, confirming that they originate from ferroelectric domains.

Only first order satellites were observed, most likely due to significant variation of domain sizes [14]. For the sample investigated in Fig. 2, with 8 uc PTO and 4 uc STO repeated 100 times, the periodic domain structure has a wavelength equal to about 60 Å.

A detailed analysis of the domain structure will be presented elsewhere. Here we will concentrate on the unique opportunity offered by $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices to study nanodomains under applied electric fields using x-ray diffraction. The small lattice parameter mismatch between these two materials allows coherent growth of structures with total thicknesses of hundreds of nanometers without relaxation, hence keeping a high material perfection. These samples seem thus ideal for x-ray experiments where one wants to apply large voltages to large area electrodes without significant leakage problems. The x-ray measurements were performed using a PANalytical X’Pert PRO diffractometer on approximately $2 \times 2 \text{ mm}^2$ superlattices with SRO electrodes covering the entire top surface (apart from the very edges to avoid electrical shorting). Reciprocal space line scans along the in-plane direction ($Q_x$) were obtained by recording the rocking curves around the superlattice (00L) Bragg peak. The results presented have been reproduced on several other samples.

An Agilent 4284A precision LCR meter was used to apply the dc bias across the sample, while at the same time recording the ac capacitance and dielectric loss tangent (10 mV, 1 kHz signal used). The dc bias produced two
effects on the measured diffraction pattern. First, the superlattice peaks shifted to lower 2θ values, indicative of an increase in the average lattice parameter, while the Bragg peaks from the substrate and SRO electrodes remained unchanged. This was interpreted as a simple piezoelectric effect. By quantifying the changes in the lattice parameter we were able to extract effective piezoelectric coefficients of several tens of pm/V for the samples investigated, comparing quite well with independent measurements using a scanning tunneling microscope on superlattices of the same composition [15]. Second, the peak intensities of the domain satellites were observed to decrease with increasing bias without changes in the peak positions, as shown in Fig. 2(c). The leakage currents were monitored at all times when the field was reduced to zero again. This implies that the domain walls return to more or less their original positions despite the long duration (up to several hours) of the applied voltage, and is consistent with the very small value of the remnant polarization.

There are a number of possible ways domains can respond to an external field. Pure electrostatic considerations suggest that the thermodynamic ground state under an applied bias corresponds to a domain structure with a period larger than that at zero field [16]. This is not observed experimentally. Such a change in domain period requires the collective motion of domain walls over macroscopic distances, or appropriate creation and annihilation of domain boundaries, and is energetically very costly. A simpler, less costly, response to an electric field is a change in the sizes of oppositely polarized domains without a change in periodicity. This involves only local microscopic motion of domain walls within each domain period. Unlike in bulk crystals or thick films, where switching requires large and generally irreversible domain wall displacements, in the case of nanodomains, large changes in polarization can be obtained from tiny wall displacements. In the sample investigated the domain walls are separated by \( \sim 30 \) Å; hence, each wall need only move \( 15 \) Å (i.e., \( \sim 4 \) uc) to fully saturate the polarization. Pinning of defects is likely to play an important role as the relative changes in domain sizes may be achieved through the reversible bending of domain walls around pinning centers rather than by the displacements of the wall as a whole.

To gain some physical insight into the observed field-induced intensity modulations, we shall consider a simplified model where the domain structure is represented as a rectangular wave of period 2\( l \). This can be expressed as

\[
F(x) = \sum_{n=-\infty}^{\infty} \delta(x - n2l) \otimes T(x, a),
\]

where \( \otimes \) represents the convolution operation, 2\( a \) is the size of (say) the “up” domains, and \( T(x, a) \) is the top-hat function equal to 1 for \(-a \leq x \leq a\) and zero elsewhere. The diffraction pattern of (1) is given by its Fourier transform

\[
\tilde{F}(q) = \frac{1}{\sqrt{2\pi}} \sum_{n=-\infty}^{\infty} e^{-i2\pi nq} \sqrt{\frac{2}{\pi}} \sin a q q
\]

which is a product of two terms. The first term originates from the total domain periodicity (2\( l \)) and hence defines the positions of the satellites, which appear at \( q = \frac{m\pi}{a} \), where \( m \) are integers. The second term modulates the intensities of these peaks according to the volume fraction of the up domains \( f = a/l \). One can see that when \( a = \frac{l}{2} \), i.e., the sample has an equal fraction of up and down domains, all peaks with even values of \( m \) disappear and that the peaks with odd \( m \) have maximum intensity. In the presence of a field, the relative domain sizes change and hence the intensities of the odd \( m \) peaks decrease whereas those of the even peaks increase according to

\[
\frac{I_m(a)}{\max[I(a)]} \equiv \frac{I}{I_0} = \sin^2\left(\frac{ma\pi}{l}\right) = \sin^2(mf\pi).
\]

The domain fraction \( f \) can be estimated from electrical measurements, which were performed on an identical sample but with the top SRO layer patterned into \( 120 \times 120 \) \( \mu \text{m}^2 \) electrodes. The measured dielectric response and polarization-voltage (P-V) loop are shown in Figs. 3(a) and 3(b). Ignoring other possible contributions (e.g., from space charge layers or injected carriers), the increase in polarization from local polarization reversal due to domain wall motion \( P_d \) can be obtained by simply subtracting the nonswitching contribution \( P_{\text{dieel}} \) (i.e., that due to the field-induced intrinsic dielectric response) from the total measured polarization. We estimate the contribution of \( P_{\text{dieel}} \) from LD theory, approximating the intrinsic dielectric response of both the up and down domains with that of a monodomain superlattice having a polarization aligned parallel to the applied field [i.e., the bold part of the red curve in Fig. 3(a)]. The calculated \( P_{\text{dieel}} \) is plotted in red in Fig. 3(b). The up-domain fraction [Fig. 3(c)] can now be calculated using \( f(V) = \frac{1}{2}[(P_d/P_s) + 1] \), where the LD theory value for \( P_s \) is 34.1 \( \mu \text{C/cm}^2 \) for this composition. Further details regarding the calculation of \( P_{\text{dieel}} \) and the approximations involved can be found online [17]. Here we only point out that the LD description of the intrinsic dielectric response is not perfect, as is clear from the fact that a full polarization reversal is not observed in our samples despite exceeding the thermodynamic coercive voltage, indicated by the divergence of \( \varepsilon_c \) in Fig. 3(a). The inadequacy of our simple LD theory model developed for monodomain samples in accurately describing the contribution from the intrinsic dielectric response is in part due to the dense domain structure itself. It was recently shown by Chen and Roytburd [18] that electromechanical con-
In conclusion, we have shown that PTO/STO superlattices present an appealing system for the study of ordered 180° nanodomains under an applied field, enabling simultaneous electrical and structural measurements to be performed on large samples. With the low intensity laboratory x-ray source used here, only static properties could be probed. On the other hand, synchrotron radiation equipped with current detectors that allow nanosecond time resolution opens new exciting possibilities of studying with x-rays the dynamics of periodic domain structures at the nanoscale [20].

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FIG. 3 (color). (a) Measured dielectric response (black) compared with a theoretical curve expected for a monodomain sample of the same average composition x (red); the dielectric loss, tanδ, was below 0.008 over the entire range of biases. (b) Polarization-voltage hysteresis curve (black) and the approximate lattice contribution to the polarization (red) estimated from LD theory. (c) The “up”-domain fraction calculated from the measured P-V loop and the LD predictions for P_{diele} and P_s.

(3) The observed intensities of domain satellite peaks (data points) normalized to the zero bias value and compared with the prediction of Eq. (3). Shaded regions illustrate the effect of a ±5 μC/cm² variation in P_s.

Constrains at domain boundaries lead to interdomain clamping, effectively stiffening the lattice as well as hindering complete switching.

With the above caveats, the calculated f(V) was used to estimate the expected changes in intensity of the first order satellite peaks for different applied voltages using Eq. (3) [red curve in Fig. 3(d)]. For comparison, the actual intensities of the satellite peaks (these are intensities at peak maxima, normalized to the value at zero volts [19]) are plotted as filled circles. The agreement is excellent, implying that the observed intensity changes are consistent with local domain rearrangements which alter only the relative domain sizes but not the domain period (as the latter would show up as a change in the satellite peak positions). A decrease in satellite intensities could also result in part from an increase in domain randomness (domain size variation) [14], a point that should be studied further. These results allow important conclusions to be drawn. While subjected to large electric fields, in excess of the thermodynamic coercive field, for very long times, the system does not reach a monodomain configuration. Instead the relative sizes of oppositely poled domains change with field via domain wall motion but without annihilation of domains walls. When the field is reduced, the original domain structure is restored. The nanoscale domain wall motion (of the order of 10 Å or a few unit cells for the largest applied fields) is at the origin of the enhanced permittivity observed in these artificial materials.

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[19] Integrated intensities show similar behavior but suffer from larger errors due to difficulties in adequate background subtraction.

Here we elaborate on the calculation of the up-domain fraction $f$. Note that positive voltages correspond to the bottom electrode being at a higher potential than the top one, so that the majority domains have a polarization that points up (towards the top electrode) for positive voltages. The field dependence of the polarization within each up and down domain is assumed to follow the Landau theory prediction for a monodomain superlattice of the same average composition ($x=0.67$) as the sample and is shown in Fig. S1b. The polarization within each domain can be divided into two parts: the zero field spontaneous polarization $\pm P_s$, and the non-linear field-induced dielectric response $P_{\text{diele}}$, so that

$$P^\uparrow(E) = +P_s + \int_0^E \chi^\uparrow(E) dE \equiv +P_s + P^\uparrow_{\text{diele}}(E) \quad (1)$$

$$P^\downarrow(E) = -P_s + \int_0^E \chi^\downarrow(E) dE \equiv -P_s + P^\downarrow_{\text{diele}}(E). \quad (2)$$

The total polarization in the sample is then

$$P = f P^\uparrow + (1-f) P^\downarrow = (2f-1)P_s + \left( f P^\uparrow_{\text{diele}} + (1-f) P^\downarrow_{\text{diele}} \right). \quad (4)$$

The first term in equation (4) corresponds to the net spontaneous polarization due to the domain structure (called $P_d$ in the main manuscript), which changes with applied field due to the changing $f$. The second term is the extra polarization due to the dielectric response of the domains.

**FIG. S1:** (a) Voltage dependence of the dielectric permittivities $\chi^\uparrow$ and $\chi^\downarrow$ for the up and down domains respectively. (b) The corresponding voltage dependence for the polarizations in the up and down domains. (c) The field-induced dielectric contribution to the polarization within each up and down domain ($P^\uparrow_{\text{diele}} = P^\uparrow - P_s$ and $P^\downarrow_{\text{diele}} = P^\downarrow + P_s$ respectively), as well as the total contribution to the measured polarization from the field-induced dielectric response $P_{\text{diele}} = f P^\uparrow_{\text{diele}} + (1-f) P^\downarrow_{\text{diele}}$. (d) The fraction of up-domains obtained by solving equation (4) (solid lines) as well as the corresponding fraction calculated by approximating the dielectric response of all domains by that of a monodomain sample with polarization parallel to the field (dashed lines).
It is clear from Fig. S1a that for non-zero applied field the intrinsic dielectric response of domains with polarization parallel and antiparallel to the field is quite different, the latter being the larger of the two. Therefore in a ferroelectric with equal fractions of up and down domains the contribution of the antiparallel domains would be more important if the ratio of up and down domains did not change with field. In reality of course, the fraction of antiparallel domains decreases with applied voltage and hence their contribution is reduced. Fig. S1d shows the up-domain fraction \( f \) as a function of voltage obtained from the experimental P-V loops by solving equation (4) with \( P_s \), \( P_{\text{diele}}^\uparrow \) and \( P_{\text{diele}}^\downarrow \) obtained from Landau theory. If this field dependent \( f \) is taken into account we find that, despite \( P_{\text{diele}} \) being significantly larger for the antiparallel domains, the overall \( P_{\text{diele}} = f P_{\text{diele}}^\uparrow + (1-f)P_{\text{diele}}^\downarrow \) (blue curve in Fig. S1c) is actually quite close to that of the domains with polarization parallel to the field. For comparison, the dashed curve in Fig. S1d shows the up-domain fraction calculated by approximating the \( P_{\text{diele}} \) for both kinds of domains with that of parallel domains only, as was done in the main manuscript. One can see that there is very little difference between the full calculation that includes the difference in the up and down domain dielectric responses, and the simplified calculation.

Note that small discontinuities in the calculated \( f \) appear in Fig. S1d at the theoretical coercive voltages. In reality our films do not fully switch even above the thermodynamic coercive voltage (approx. 20 V). For this reason we chose to approximate the dielectric response with that of parallel domains only. The assumption that the individual domains behave in accordance with our simple Landau model is clearly not perfect. The important point however, is that the dielectric response \( P_{\text{diele}} \) is small in comparison with \( P_\parallel \) and hence even a significant error in \( P_{\text{diele}} \) leads to only small errors in \( f \). The maximum value of \( P_{\text{diele}} \) is about 6 \( \mu \text{C/cm}^2 \), hence even completely neglecting the contribution of \( P_{\text{diele}} \) would only lead to errors in \( f \) comparable to those shown by the shaded regions in Fig. 3c of the main manuscript.