Observation of 180° Stripe Domains in Ferroelectric PbTiO$_3$ Thin Films

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Introduction

Periodic domain patterns in ferroelectric materials result from a competition between polarization, strain, and electric fields [1]. In particular, 180° stripe domains, which consist of lamella with alternating signs of polarity (Fig. 1), form in bulk ferroelectric single crystals in order to minimize the energy of the depolarizing field. With the present trend of integrating ferroelectric materials into microelectronic devices, there has been increased interest in 180° domain formation in ferroelectric thin films because of the potential effects on ferroelectric properties [2-5]. However, there has been no direct experimental evidence for 180° stripe domains in ferroelectric thin films thus far.
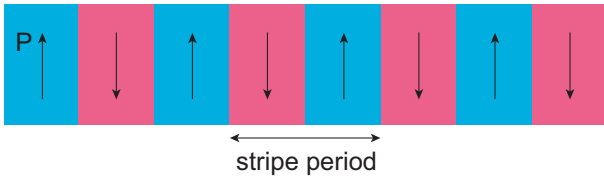

FIG. 1. Schematic of 180° stripe domains.

This activity report summarizes highlights of our recent results [6] on the observation of 180° stripe domains in thin films of the prototypical perovskite ferroelectric, PbTiO$_3$, using *in situ* synchrotron x-ray scattering. This work is part of an ongoing program to understand and control the structure of ferroelectric thin films grown by metal-organic chemical vapor deposition (MOCVD).

Methods and Materials

The experiments were carried out at beamline station 12-ID-D at the APS by using an apparatus specially designed for *in situ* grazing-incidence x-ray scattering measurements both during and after film growth by MOCVD [7]. PbTiO$_3$ films ranging from 2 to 42 nm in thickness were grown on SrTiO$_3$(001) substrates under conditions described previously [8]. Within this thickness range, the films are coherently, compressively strained to the substrate, which causes polarization to occur preferentially along the surface normal direction [9]. An x-ray energy of 24 keV and an incidence angle of 1° were used. The ability to perform x-ray studies in the growth chamber allows us to control the film thickness to sub-unit-cell accuracy for systematic studies of thickness effects and also allows us to study phase transitions at high temperatures immediately after growth, thereby avoiding any irreversible relaxation that can occur upon cooling. Furthermore, the growth system can be used to control the PbO vapor pressure over the film and therefore maintain film stoichiometry as well as an equilibrium surface structure [10].

Results

The ~1.2% compressive epitaxial strain is expected to elevate the ferroelectric transition temperature T_C above the unstrained value of 492°C. We observe that T_C approaches the theoretically predicted value of 752°C [9] for thicker films. However, T_C decreases with film thickness, as expected if the polarization at the interfaces is intrinsically suppressed relative to its equilibrium value in the bulk.

When a film is cooled below T_C, we observe satellite peaks in the diffuse x-ray scattering adjacent to the PbTiO$_3$ Bragg peaks. As the film is cooled further, the satellites shift closer to the Bragg peaks, and higher, odd-order satellites appear. An example of the satellites is shown in Fig. 2, which was taken at 509°C for a 19.2-nm film. The nature of this satellite scattering indicates that it comes from well-ordered 180° stripe domains with alternating polarity (Fig. 1). The satellites show thickness fringes in the out-of-plane direction with the same spacing as those along the crystal truncation rod, indicating that the stripe structure extends through the film. The lack of even-order satellites is consistent with the expected 1:1 ratio of positive and negative domains, as required for electric field energy minimization. We note that at a given temperature, the positions and intensities of the satellites do not change with time and are very reproducible, provided that the temperature is lowered monotonically from above T_C.

The shift in the position of the satellites that occurs at a temperature that is about ~200°C below T_C corresponds to an increase in the stripe period. We interpret this to be a transition from a high-temperature stripe domain phase (F_α) to a low-temperature phase (F_β) with a larger stripe period. Higher-order satellites typically occur only in the F_β phase, indicating that the
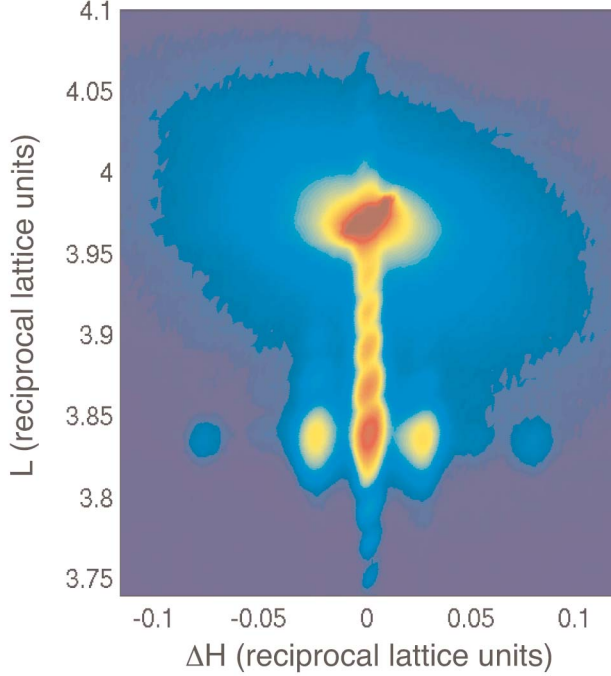
FIG. 2. Satellites in the diffuse x-ray scattering around the $PbTiO_3$ 224 peak. Redder hues indicate higher intensity. The upper intense peak is from the $SrTiO_3$ 224, while the lower intense peak is from the $PbTiO_3$. The fringes along the L-direction are due to the finite film thickness. Satellites from 180° stripe domains are displaced horizontally from the $PbTiO_3$ Bragg peak.

FIG. 3. Typical in-plane distributions of diffuse x-ray intensity around the $PbTiO_3$ 304 peak for various film thicknesses and temperatures. Redder hues indicate higher intensity. The elongation of the central Bragg peak is due to an asymmetric resolution function.

180° domain walls are significantly more diffuse in F_α than F_β.

Typical in-plane arrangements of the satellite pattern are shown in Fig. 3. The satellites either form rings (a), are aligned in the crystallographic directions (b, c), or are aligned along a particular azimuth (d), depending on the temperature, film thickness, and substrate miscut. These patterns are consistent with linear stripe domains oriented either randomly or in a specific direction within the illuminated area (1 mm²). The stripe period, Λ, may be determined from these reciprocal space maps by the following equation:

$$\Lambda = a \Big/ \sqrt{(\Delta H)^2 + (\Delta K)^2} \quad ,$$

where a is the reference lattice parameter for the reciprocal lattice units; in this case, the room temperature lattice parameter of $SrTiO_3$ (0.3905 nm).

For both the F_α than F_β phases, the stripe period varies with the square root of film thickness, as shown in Fig. 4. This parabolic thickness dependence is expected from the Landau-Ginzburg-Devonshire theory of ferroelectric 180° stripe domains [3, 11] and results from 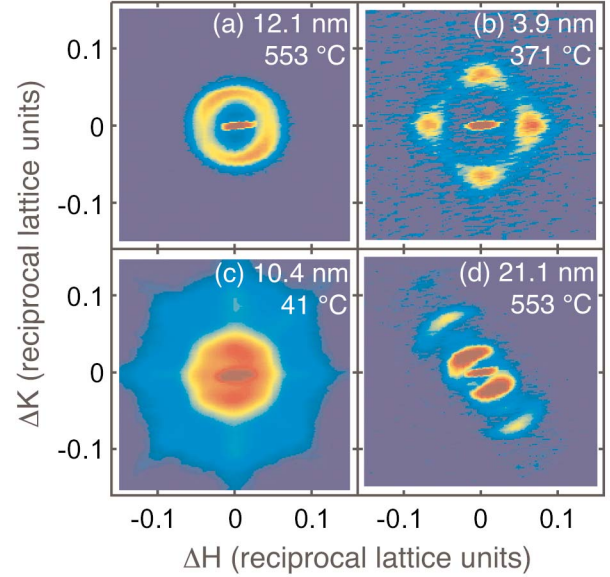a balance between the energy cost of domain walls and the energy gain in reducing the depolarizing field. We note that the stripe period for F_β agrees with theory within a factor of two on an absolute scale, even with no adjustable parameters [6].

Discussion

The qualitative behavior of the stripe domains we observe has been discussed in the theoretical literature. It has been proposed that polarization-wave fluctuations in the paraelectric phase become unstable at T_C, forming a 180° stripe domain phase with diffuse walls [12]. At lower temperatures, the nonlinearity in the free energy function favors sharp domain walls [12]. Both the diffuse and sharp wall theories predict a stripe period proportional to the square root of thickness, with the period for F_α anticipated to be similar to or smaller than that for F_β, as observed.

In summary, we have found the first direct evidence of 180° stripe domain formation in ferroelectric thin films. The stripes change structure while cooling, transforming to a phase having a larger stripe period and sharper walls at a lower temperature. Both stripe phases show a classical square root thickness-dependence. The ferroelectric transition temperatures of the thicker films studied here were significantly elevated above the unstrained bulk value as a result of the compressive epitaxial strain; T_C, however, decreased with film thickness. A more detailed study of the effect of thickness on T_C is currently under investigation.
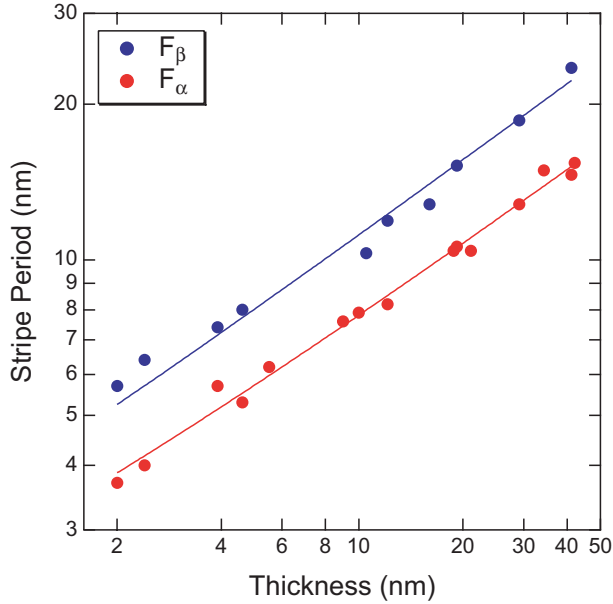
FIG. 4. Stripe period as a function of thickness for the F_α and F_β phases. The lines are fits to the data with a square root thickness-depencence.

References

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