In Situ X-ray Studies of Ferroelectricity in Ultrathin Perovskite Films

G. B. Stephenson[1,2], D. D. Fong[1], S. K. Streiffer[1,2], R.-V. Wang[1,2], F. Jiang[1],
C. Thompson[3], J. A. Eastman[1], P.H. Fuoss[1]

[1]*Materials Science Division, Argonne National Laboratory, Argonne, Illinois, USA*
[2]*Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois, USA*
[3]*Dept. of Physics, Northern Illinois Univ., DeKalb, Illinois, USA*

Introduction

The paraelectric-to-ferroelectric phase transition in ultrathin films displays complex behavior driven by a fascinating competition between polarization, strain, electric field, domain wall energy, and surface chemistry. For decades, researchers have found that ferroelectric behavior is typically suppressed in films that are sufficiently thin. Various explanations have been put forward: intrinsic suppression of polarization at surfaces, the effect of depolarizing electric fields, or extrinsic effects of composition or strain. As a result, the factors responsible for the size dependence of the paraelectric-to-ferroelectric phase transition remain unresolved, in particular for the technologically important perovskites.

Methods and Materials

We have been using in situ synchrotron x-ray scattering to investigate the ferroelectric properties of ultra-thin, coherently strained epitaxial films of $PbTiO_3$ as a function of film thickness, temperature, vapor ambient, and electrical boundary conditions. The ability to perform x-ray scattering in the film growth chamber allows us to determine optimum growth conditions, to control the thickness of the films to sub-unit-cell accuracy, and to control surface and film stoichiometry during high temperature study [1-3]. X-ray energies of 24 to 30 keV are used to penetrate the 2-mm-thick quartz wall of the deposition chamber.

Results and Discussion

When films are grown on insulating $SrTiO_3$, we find that the ferroelectric phase forms as nanoscale 180° stripe domains [4-7], as shown in Fig. 1. Such equilibrium stripe domains form to minimize the depolarizing field. They produce strong satellites around the $PbTiO_3$ Bragg peaks having non-zero L, as shown in Figures 2 and 3. When films are grown on conducting $SrRuO_3$ layers on $SrTiO_3$, the polar phase forms in a single domain [8] with no satellites. Although we observe a thickness-dependent T_C (Fig. 4), in both cases the polar phase is stable at room temperature in films with thicknesses as small as three unit cells (1.2 nm). The thickness dependence of T_C for $PbTiO_3$ films on $SrTiO_3$ is compared with Landau theory for stripe domains [9] in Fig. 5. Theory predicts a greater suppression of T_C from the residual depolarizing field than actually observed, indicating that any intrinsic surface effect enhances (rather than suppresses) polarization, contrary to some previous models.

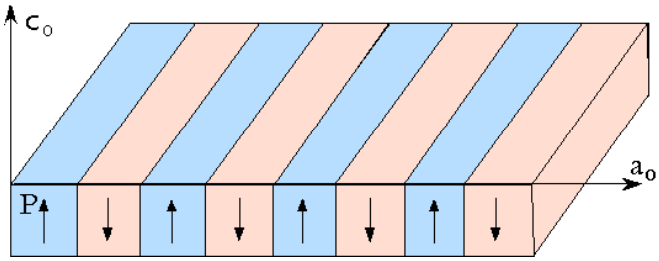

Fig. 1. Schematic of 180 degree stripe domains in a ferroelectric thin film.

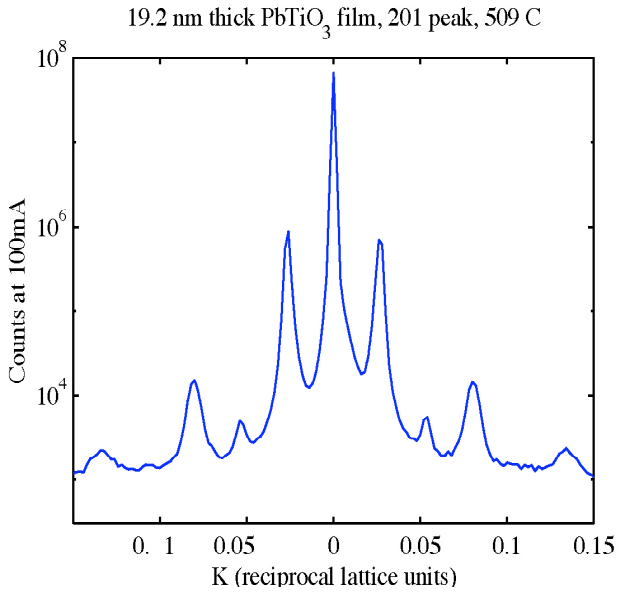

Fig. 2. X-ray scattering from stripe domains.

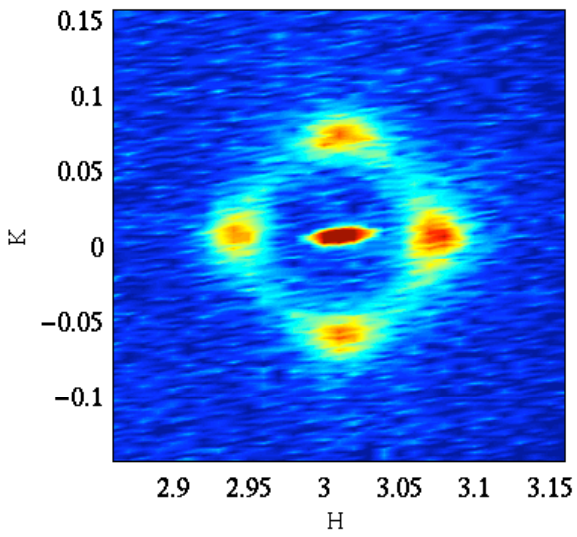

Fig. 3. In-plane map of satellite intensity around the 304 peak for a 3.6 nm thick $PbTiO_3$ film at 370 C.

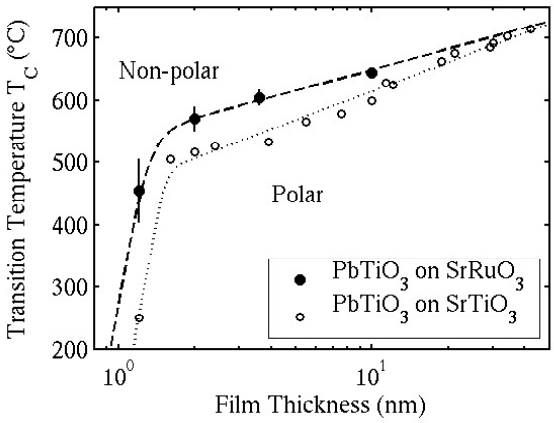

Fig. 4. Thickness dependence of ferroelectric transition temperature for monodomain $PbTiO_3$ films on conductive $SrRuO_3$ and stripe-domain $PbTiO_3$ films on insulating $SrTiO_3$.

Work supported by the U. S. Department of Energy, Office of Science (BES), under Contract No. W-31-109-ENG-38.

Contributing author: Brian Stephenson, stephenson@anl.gov

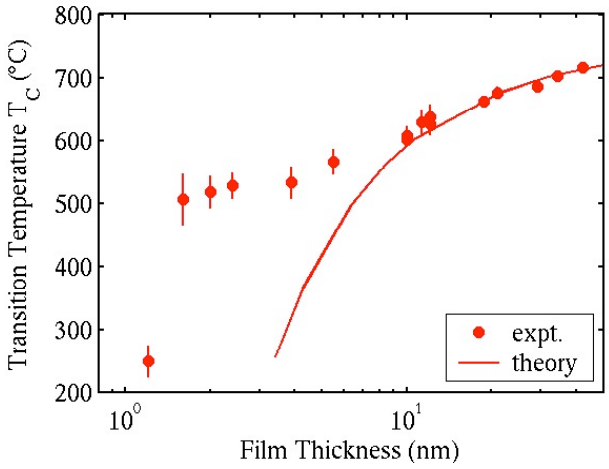

Fig. 5. Comparison of Landau theory prediction to experiment for thickness dependence of T_C in $PbTiO_3$ films on $SrTiO_3$ containing equilibrium stripe domains.

[1] A. Munkholm *et al., Phys. Rev. Lett.* **88**, 016101 (2002).
[2] M.V. Ramana Murty *et al., Appl. Phys. Lett.* **80**, 1809 (2002).
[3] G.B. Stephenson *et al., Physica B* **336**, 81 (2003).
[4] S.K. Streiffer *et al., Phys. Rev. Lett.* **89**, 067601 (2002).
[5] D.D. Fong *et al., Ann. Phys.* (Leipzig) **13**, 27 (2004).
[6] D.D. Fong *et al., Science* **304,** 1650 (2004).
[7] D.D. Fong *et al., J. Synchrotron Rad.* **12**, 163 (2005).
[8] D.D. Fong *et al., Phys. Rev. Lett.* **96**, 127601 (2006).
[9] G.B. Stephenson and K.R. Elder, *J. Appl. Phys.* (in press, 2006)