In Situ X-Ray Studies of Ferroelectric Thin Films

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Summary

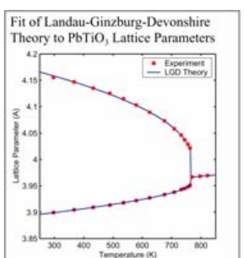
We have used synchrotron x-ray scattering to study the ferroelectric phase transition in coherently strained, epitaxial $PbTiO_3$ thin films grown on $SrTiO_3$, as a function of film thickness [1]. We observe that 180° stripe domains occur below the ferroelectric transition in these films, in order to reduce depolarization field energy. Such domains are known from studies of bulk crystals, arising from a fascinating competition between polarization, strain, and electric field. The 180° stripe domains have been predicted to significantly affect the properties of ferroelectric films [2,3], but have not previously been directly observed in thin films. The dependence of the stripe period on film thickness is in agreement with theory. However, the suppression of the transition temperature as a function of film thickness is significantly larger than that expected solely due to 180° stripe domains, indicating that intrinsic surface effects may also be important. These experiments also confirm that the ferroelectric phase transition occurs above room temperature in coherently-strained epitaxial $PbTiO_3$ films with thicknesses as small as three unit cells.

[1] S.K. Streiffer, J.A. Eastman, D.D. Fong, Carol Thompson, A. Munkholm, M.V.R. Murty, O. Auciello, G.R. Bai, and G.B. Stephenson, *Phys. Rev. Lett.* **89**, 067601 (2002).
[2] A. Kopal, P. Mokry, J. Fousek, and T. Bahnik, *Ferroelectrics* **223**, 127 (1999).
[3] A. M. Bratkovsky and A. P. Levanyuk, *Phys. Rev. Lett.* **84**, 3177 (2000).

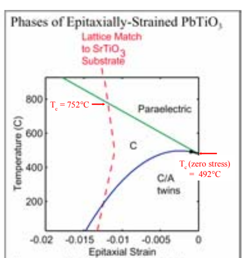
Sample Synthesis

- Synchrotron x-ray measurements were carried out *in-situ* in a MOCVD growth chamber using a dedicated facility on BESSRC beamline 12-ID-D at the Advanced Photon Source.
- The ability to perform x-ray scattering in the MOCVD chamber not only allows us to study $PbTiO_3$ thin films at temperatures above 600°C, where an equilibrium overpressure of PbO must be maintained to preserve film stoichiometry, but also allows us to monitor and control the thickness of the films during growth to sub-unit-cell accuracy.

$PbTiO_3$ on $SrTiO_3$: A Model System for Studying the Effect of Epitaxial Strain on Ferroelectricity



Haun et al., JAP **62**, 3331 (1987)

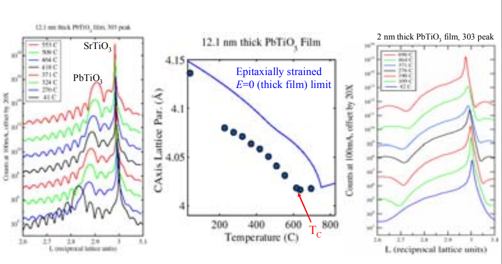


Pertsev et al., PRL **84**, 3722 (2000)

- All parameters in free energy as $f(T,\varepsilon,P,E)$ known.
- $PbTiO_3$ films thinner than ~40nm grow and remain lattice-matched to $SrTiO_3$.
- LGD theory can be used to predict the out-of-plane lattice parameter of $PbTiO_3$ on $SrTiO_3$.
- LGD theory predicts increase of ~260K in T_c due to epitaxial strain for $PbTiO_3$ on $SrTiO_3$.

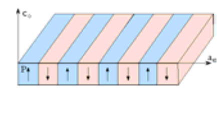
Determining T_c from Lattice Parameter

- Ferroelectric phase transition can be identified by measuring the lattice parameter of the $PbTiO_3$ as a function of temperature.
- Phase transition is continuous, as predicted by LGD theory for an epitaxial film under compression.
- T_c for thick films is very near that of the LGD calculation, but T_c for thinner films is lower than predicted for the given epitaxial strain.
- Problem: very difficult to measure the lattice parameter of ultrathin films!

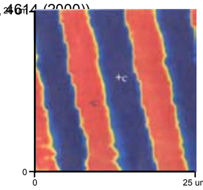


180° Stripe Domains

- Experimentally observed in bulk ferroelectrics (e.g., $BaTiO_3$), but no previous reports of their detection in thin films.
- Their formation is associated with minimization of the depolarization energy.
- The presence of 180° stripe domains in thin films has been invoked to explain properties (e.g., Bratkovsky and Levanyuk, *Phys. Rev. Lett.* **84**, 3177 (2000) and *Phys. Rev. Lett.* **85**, 4614 (2000)).



Periodic c-domains



Scanning nonlinear dielectric microscopy image of $BaTiO_3$, taken from Y. Cho *et al.*, *Jpn. J. Appl. Phys.*, **38**, 5689 (1999)

Theory for 180° Stripe Domains

Competition between Polarization, Strain, Electric Field

Minimize Free Energy:

$$F = \int dV[a(P_i^2) + s(X_i X_j) + \tfrac{\varepsilon_0}{2}E_i^2 + \kappa|\nabla \times P|^2]$$

Polarization — Strain — Electric Field — Domain Wall

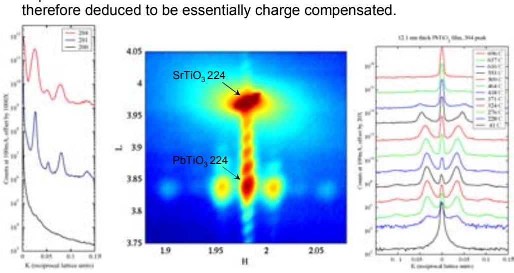
Haun et al., *JAP* **62**, 3331 (1987); Mitsui et al., *Phys. Rev.* **90**, 193 (1953)

Pertsev et al., *PRL* **80**, 1988 (1998); Kopal et al., *Ferroelec.* **202**, 267 (1997)

- 180° domain wall energy of 132 mJ/m² determined from ab-initio calculations (B. Meyer and D.Vanderbilt, Phys. Rev. B **65**, 104111 (2002)).
- All materials parameters are known, allowing comparison of theory and data ***with no adjustable parameters***.

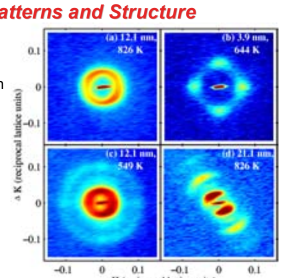
Appearance of 180° Stripe Domains

- Below T_c, satellites with equal spacings in ΔQ are observed at $PbTiO_3$ reflections with $L\neq0$. This indicates that atomic displacements are in the c-axis direction, while the wavevector of the modulation is in-plane ⇒ 180° domains.
- At a lower temperature, the satellite reflections sometimes disappear.
- Modulations are not observed for films on $SrRuO_3/SrTiO_3$, indicating depolarization arises from the film/substrate interface. Film surface is therefore deduced to be essentially charge compensated.

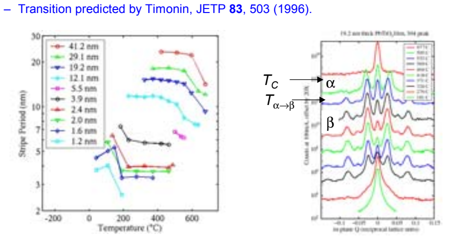


180° Domain Patterns and Structure

- Stripe domain patterns take several different forms, as indicated by differences in reciprocal space maps. Domain orientation can be either:
  - (a), (c): No preferred orientation.
  - (b): Aligned crystallographically (typically for thinner films).
  - (d): Aligned to surface steps due to substrate miscut.
- Under some conditions, see high-order harmonics.
- Odd orders strongest ⇒ 50:50 ratio of up/down.

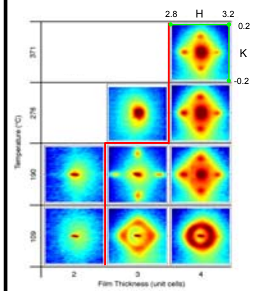


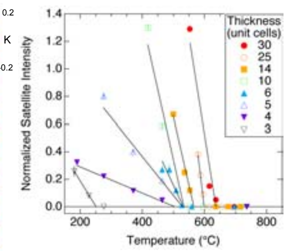
- An abrupt change in domain period occurs at temperature $T_{\alpha\beta}$. We term the high-temperature structure F_α and the lower temperature structure F_β.
- Abrupt change of period is correlated with appearance of higher, odd-order satellites (n = 3, 5, …).
  - Implies a change in polarization profile across domain wall from sinusoidal to "sharp".
  - Transition predicted by Timonin, JETP **83**, 503 (1996).



Determining T_c from Stripe Domains

- Appearance of satellites is another method by which T_c can be determined.

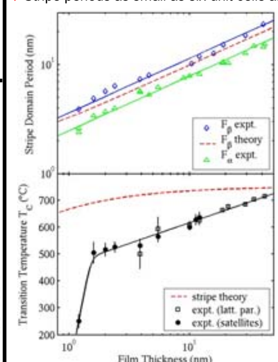




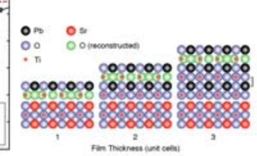
- A three unit-cell-thick film (1.2nm) shows a clear ferroelectric phase transition with T_C of ~250 °C.
- *Ex situ* x-ray measurements down to -153 °C found no ferroelectric transition in a 2 unit cell sample.

Stripe Periods and Transition Temperatures

- Stripe period has parabolic dependence on thickness - agrees with Landau and Lifshitz prediction (1935), trade-off between field and domain wall energies.
- Parabolic dependence holds down to the atomic scale, in both α and β phases.
- Stripe period agrees with linearized macroscopic theory (Kopal et al.) for sharp-wall domains (F_β phase) within a factor of two with *no adjustable parameters.*
- Stripe periods as small as six unit cells are observed in the thinnest films.

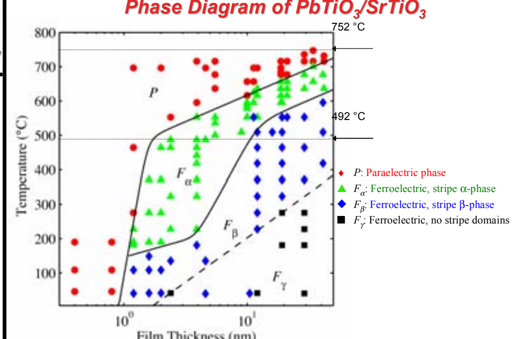


- However, T_c is suppressed with decreasing film thickness ***more*** than predicted by models of stripe domain energetics.



- Three unit cells is the lowest thickness for which a $PbTiO_3$ unit cell has bulk nearest-neighbor coordination - natural cut-off for ferroelectric behavior?

Phase Diagram of $PbTiO_3/SrTiO_3$



- For thick films, T_C approaches theoretical value for epitaxially-strained state.
- T_C is suppressed for thinner films, in a manner that does not follow power-law scaling derived from mean field theory including depolarization and/or an intrinsic surface effect described by an extrapolation length.
- At lowest temperatures, stripes can "disappear" if a film is cooled slowly.

Conclusions

- X-ray satellites observed around all Bragg peaks with L ≠0 indicate the formation of an ordered stripe structure in coherently strained $PbTiO_3$ thin films grown on $SrTiO_3$.
- The stripe domain structure consists of a periodic, 50:50 arrangement of 180° domains, that minimizes the depolarization electric field energy.
- We have measured the paraelectric-to-ferroelectric phase transition to occur as much as 235°C above the bulk transition temperature.
- The suppression of T_c as a function of film thickness is significantly larger than that expected solely based on 180° stripe domains energetics, indicating that intrinsic surface effects may also be important. Nonetheless, a three-unit-cell thick film is found to have a ferroelectric phase transition.

BES - DOE

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