X-ray Scattering from Ultrathin Ferroelectrics

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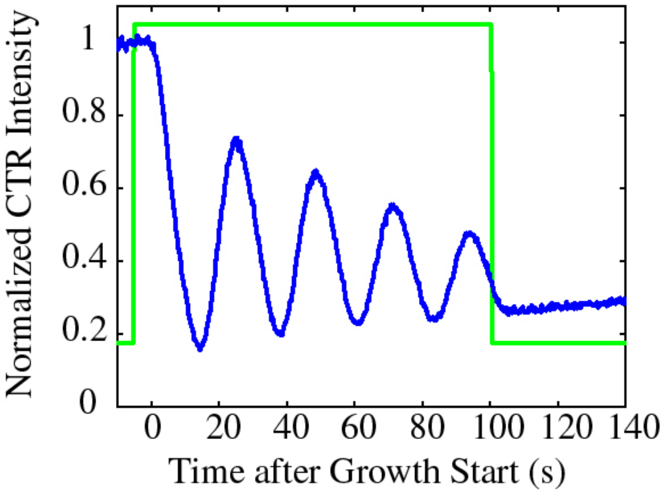
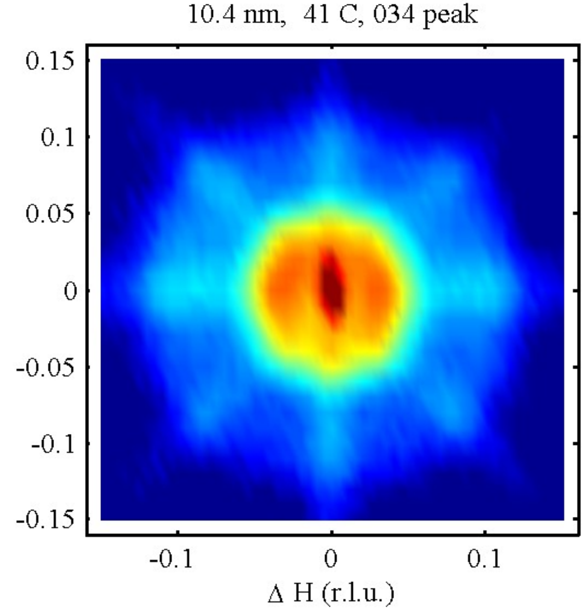
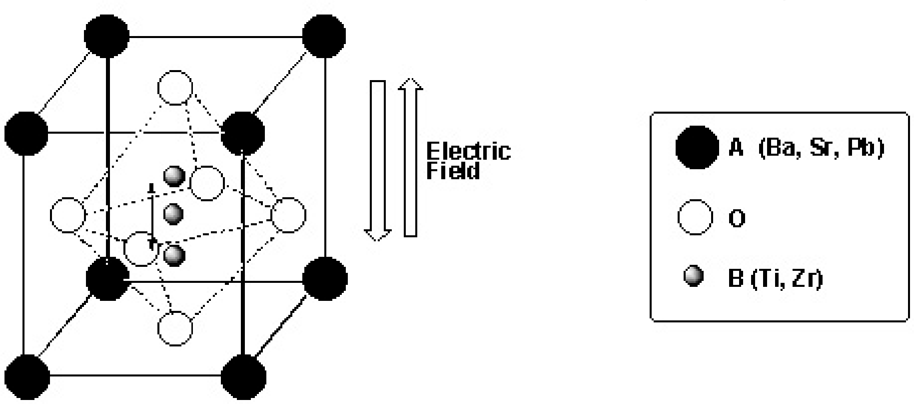


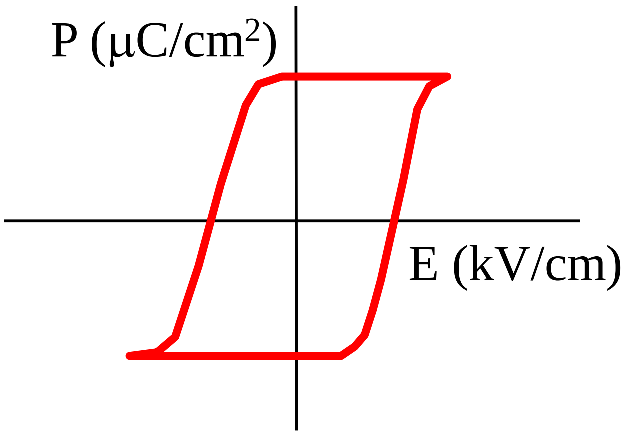


APS User Monthly Ops Meeting
November 18, 2004

Ferroelectrics vs. Ferromagnets

- Ferroelectrics are electric analogue of ferromagnets
- Phase transition with polarization as order parameter
- Below T_C, have spontaneous electric polarization at zero field
- Unit cell of crystal is non-centrosymmetric (charges separated)
- Switchable under application of electric field
- Often form domain structures - polarized regions with different orientations
- Differences with magnets: Polarization strongly coupled to strain; field can be neutralized by charge





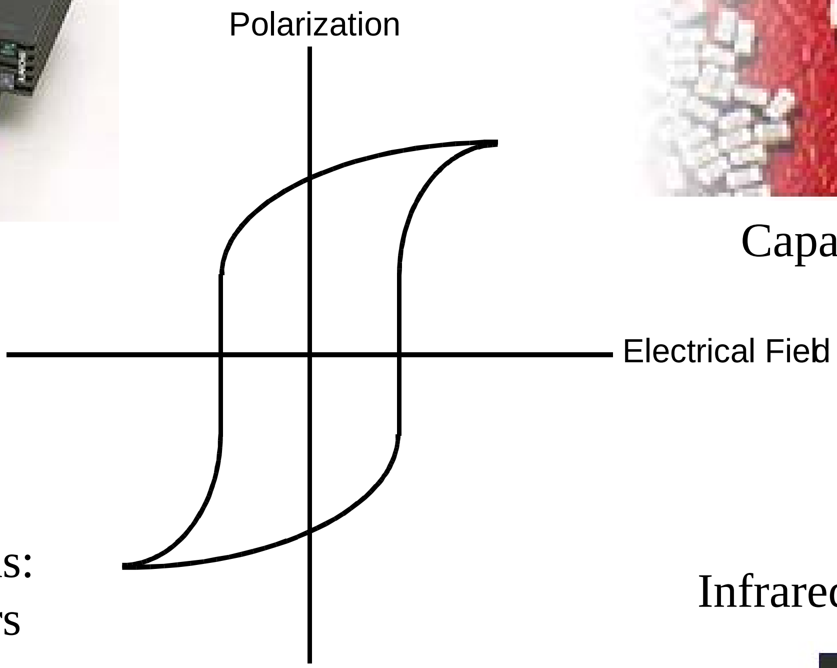
Ferroelectrics and Technology

Sony Corp.

Nonvolatile Memory

AVX

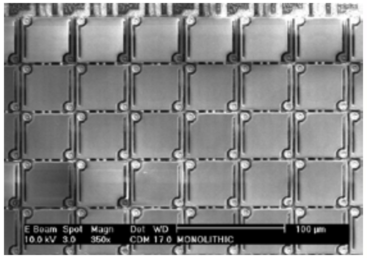
Capacitor Dielectrics



Microelectromechanical Systems:
Micropumps, Sensors, Actuators

G.B. Stephenson, *et al.*

Infrared Imaging



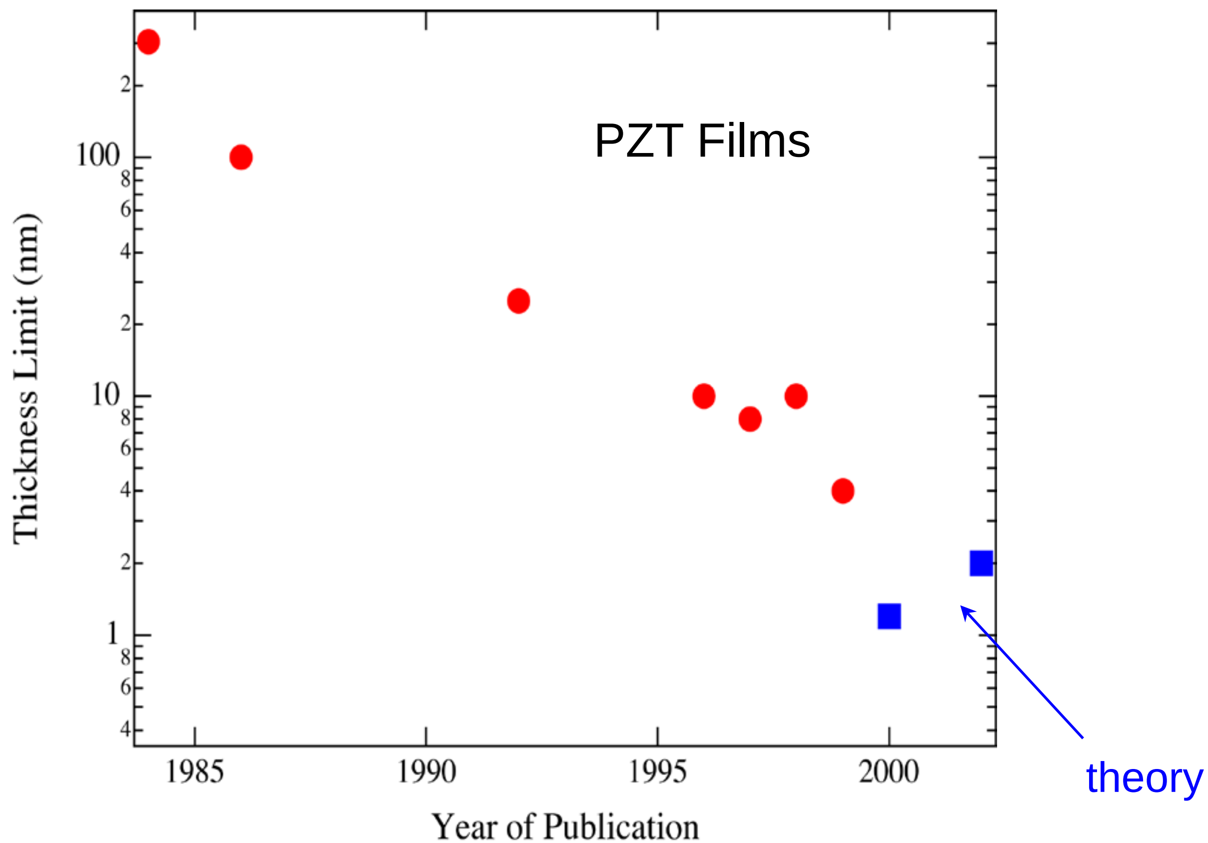
Raytheon Systems

Suppression of Ferroelectricity in Thin Films

- Historically, observed suppression of ferroelectricity in thin films
- What is the cause?
  - extrinsic effects - variable stress, composition, defects
  - “intrinsic” surface effect
  - depolarizing field
- What is the ultimate thickness limit, and why? Is T_c suppressed?

See review by T. M. Shaw et al., Annu. Rev. Mater. Sci. **30**, 263 (2000)

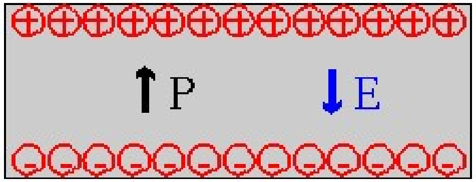
Thickness Limit for Ferroelectricity vs. Year of Publication



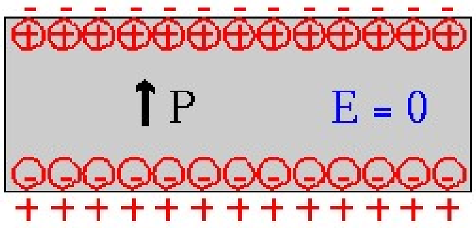
Adapted from Kohlstedt et al., MRS Proceedings **688**, C6.5.1 (2002)

Depolarizing Field

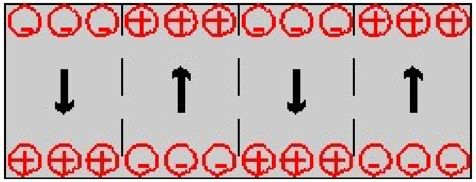
Depolarizing field E_D is the electric field arising from polarization, which can be partially compensated by



- Free charge at surface/interface from
  - Conducting or semiconducting ferroelectric
  - Conducting or semiconducting electrodes
  - Electrodes with "dead layers"
  - Charged surface adsorbates



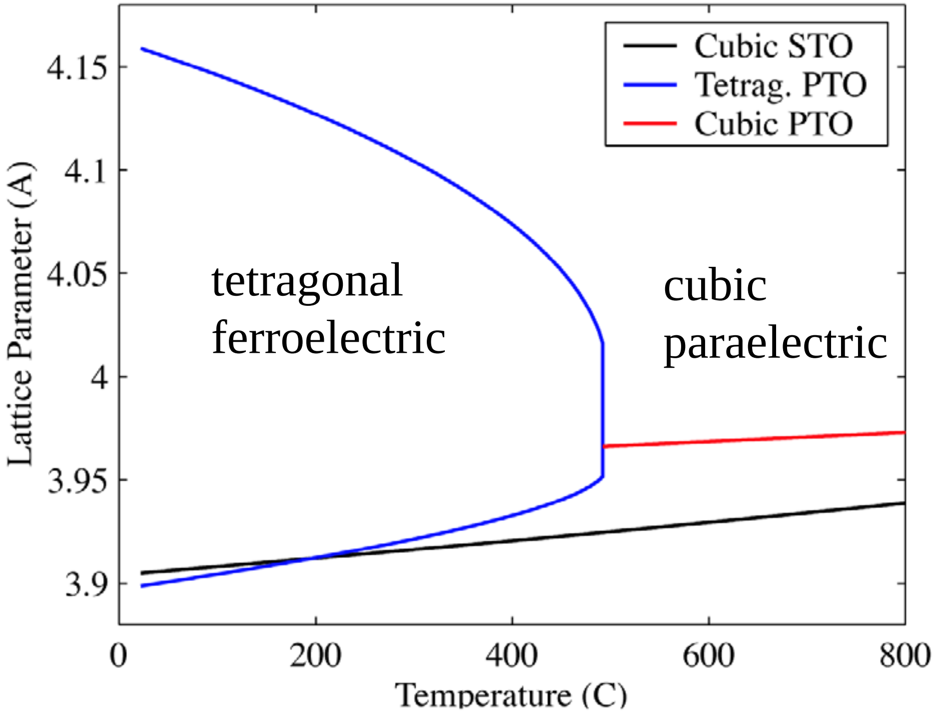
- Domain formation

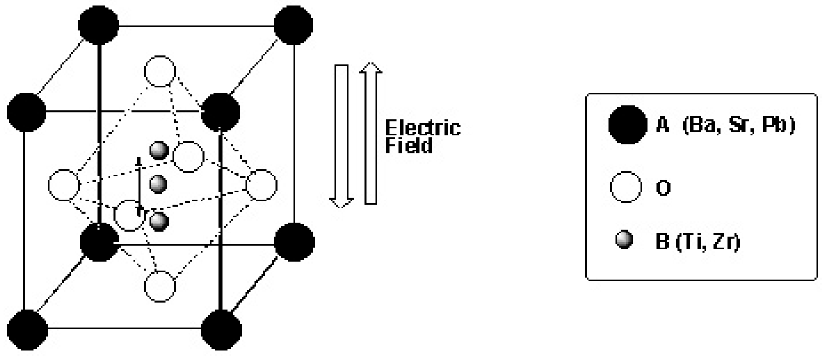


If depolarizing field is uncompensated, T_C suppression will be equal to the Curie constant *C* (for $PbTiO_3$, $C = 1.5 \times 10^5$ K)

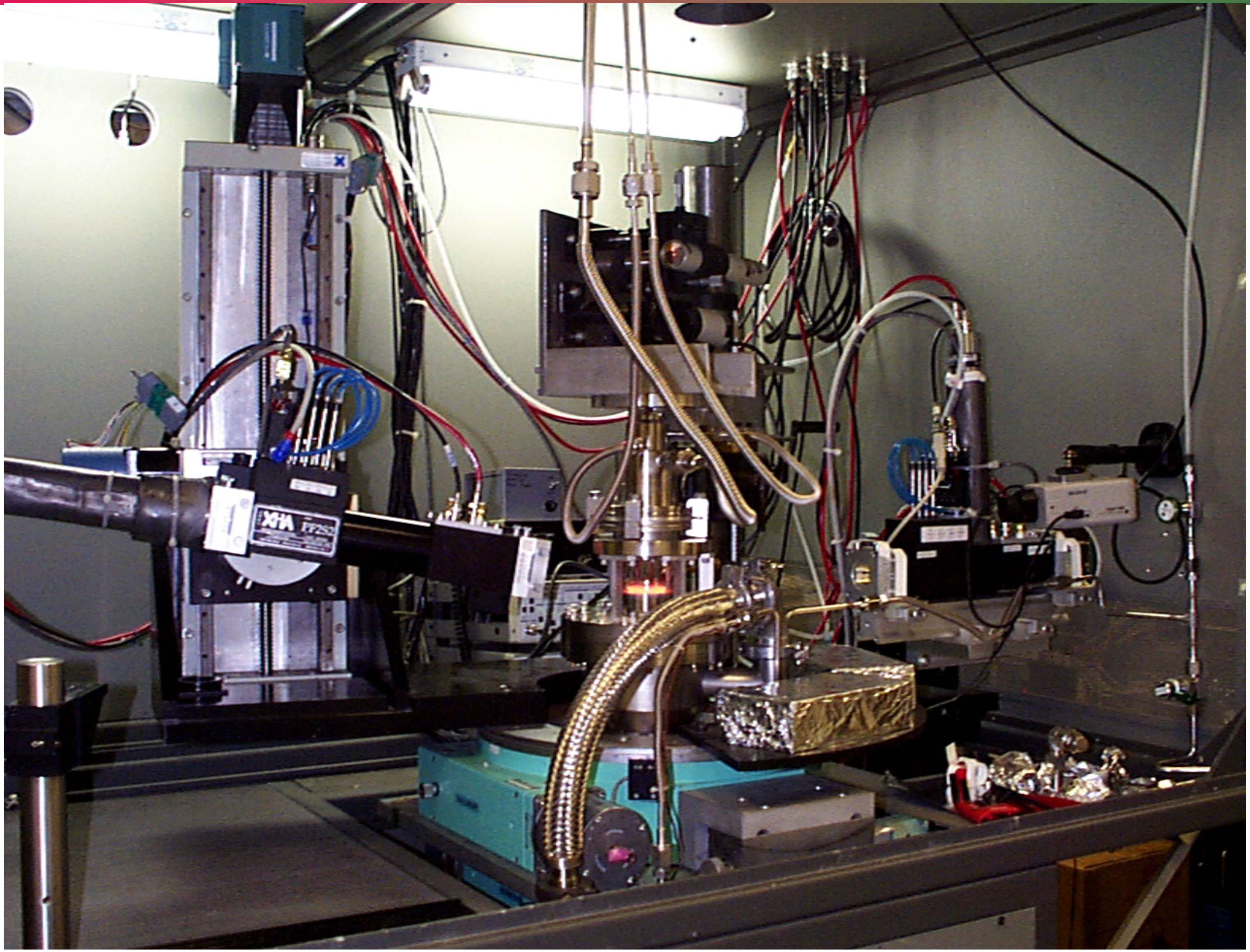
Approach

- Use x-ray scattering to study ultrathin films during growth and in-situ as a function of temperature and thickness
- $PbTiO_3$ is an ideal system -- prototypical perovskite ferroelectric, materials properties known
- Control strain state by studying coherently-strained epitaxial films on $SrTiO_3$





In Situ X-ray / Chemical Vapor Deposition Chamber at 12ID



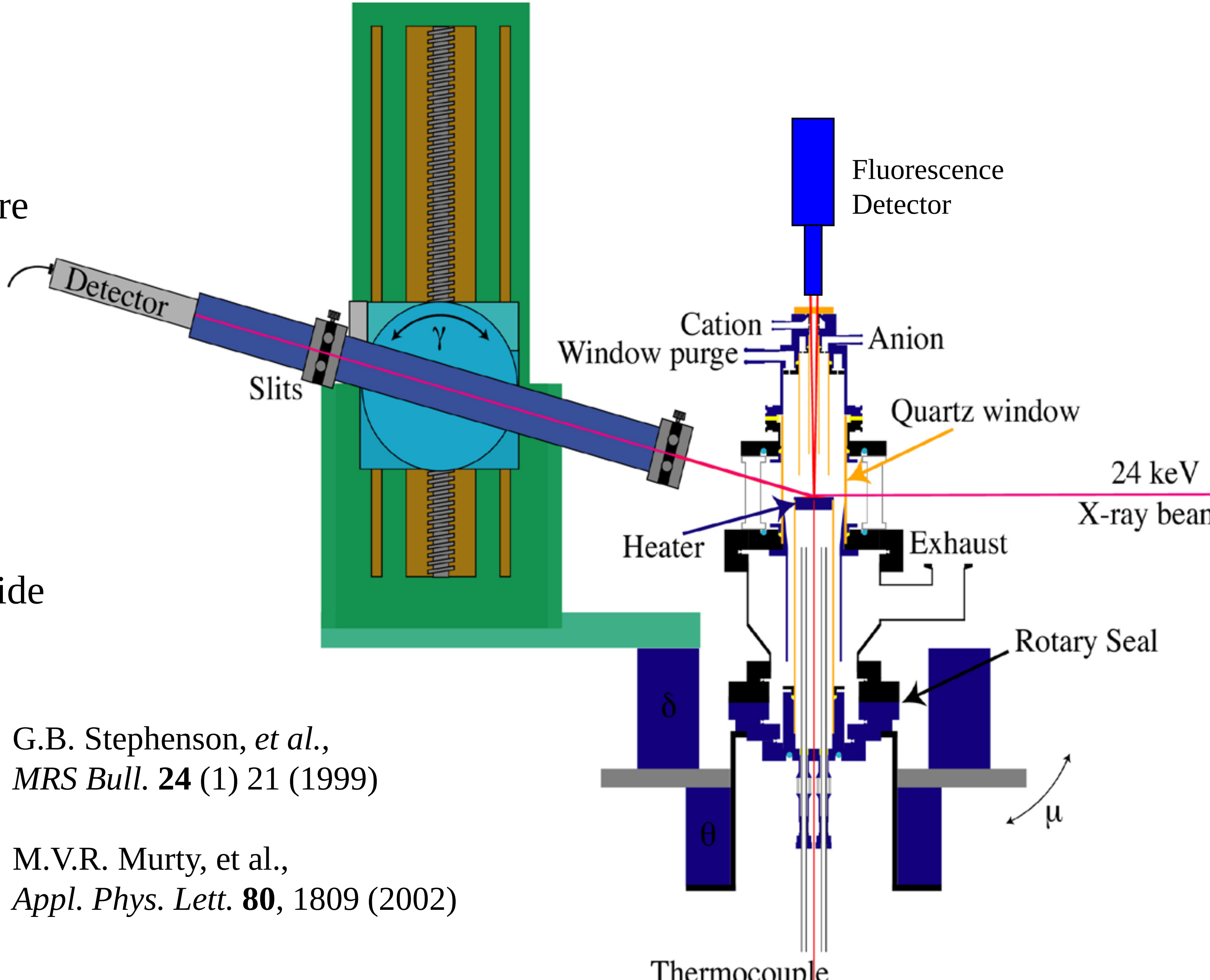
In Situ X-ray Studies of Chemical Vapor Deposition

Typical $PbTiO_3$
Growth Conditions:

Substrate temperature
600-850°C

Reactor pressure
10 Torr

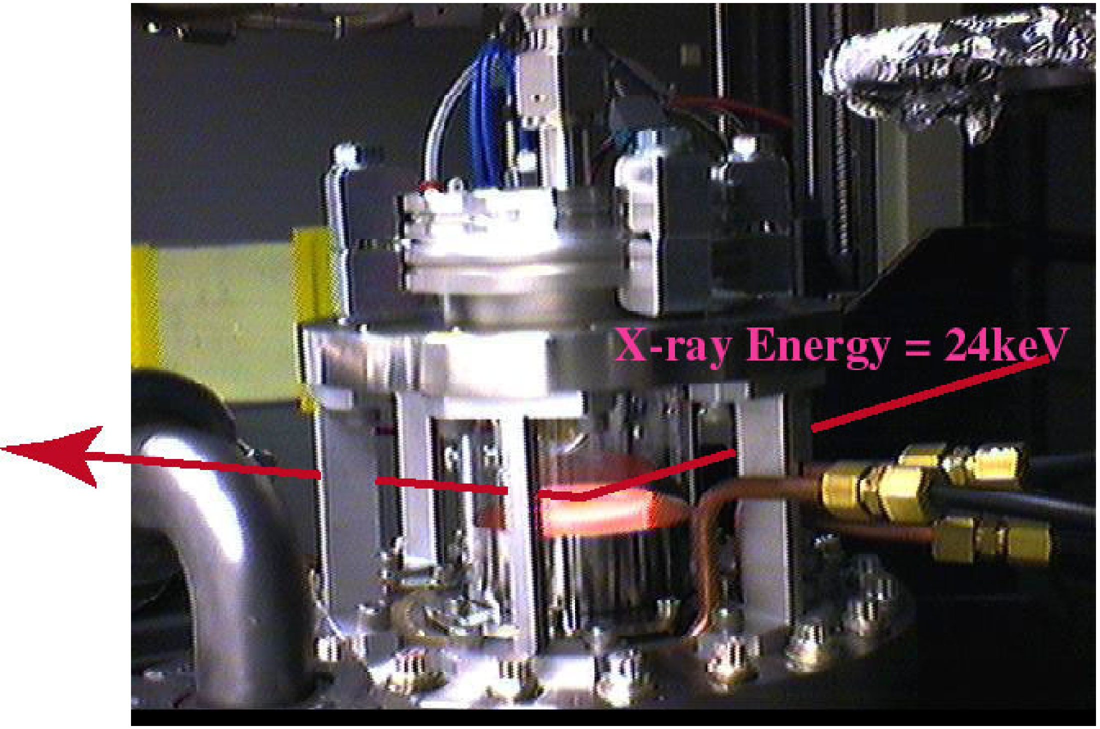
Precursors:
Tetraethyl Lead
Titanium Isopropoxide



G.B. Stephenson, *et al.*,
MRS Bull. **24** (1) 21 (1999)

M.V.R. Murty, et al.,
Appl. Phys. Lett. **80**, 1809 (2002)

In-situ X-ray Characterization of Films Grown by Metal-Organic Chemical Vapor Deposition (MOCVD)

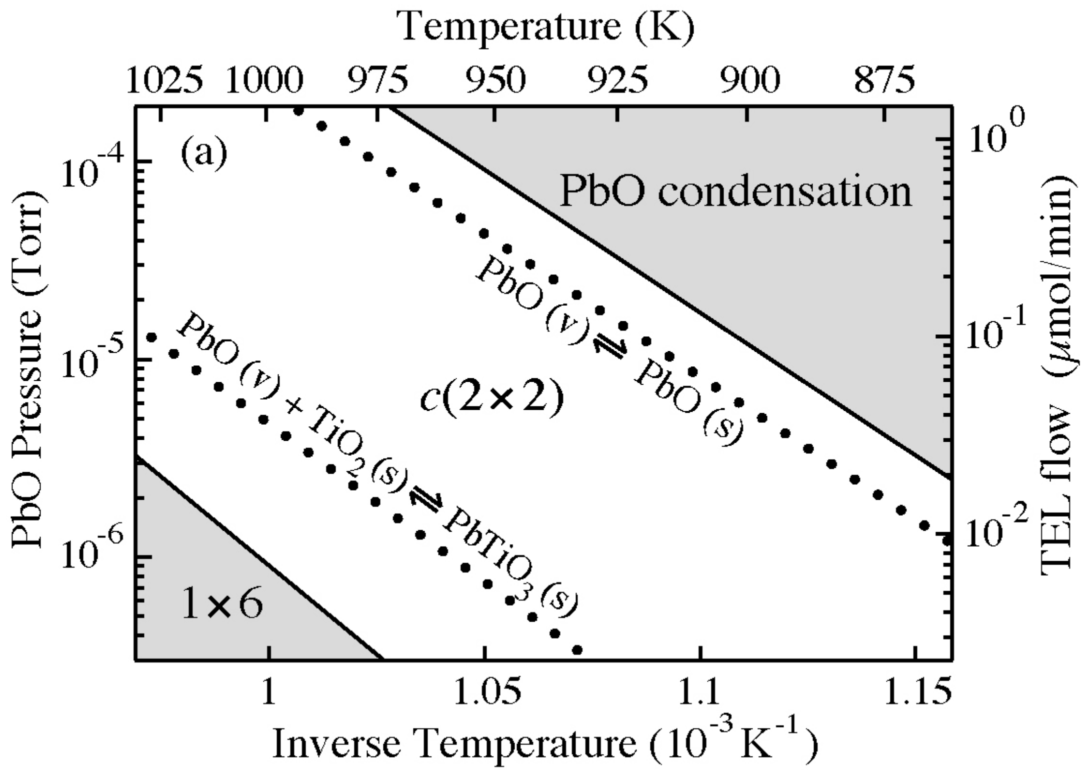


Advanced Photon Source,
BESSRC beamline 12ID-D,
Argonne National Laboratory

- Films observed in growth chamber
  - Precise control of film thickness to sub-monolayer accuracy
  - Equilibrium vapor pressure controlled over film
    - maintains stoichiometry
    - crucial for studies at high temperature
  - Can study films at high T after growth, avoiding any irreversible relaxation that may occur upon cooling to room T

$PbTiO_3$ Surface Phase Diagram

- A c(2×2) reconstruction is the equilibrium surface structure across the entire $PbTiO_3$ single-phase field.
- A poorly ordered (1×6) reconstruction is observed at PbO pressures below the $PbTiO_3$ stability line, and is believed to be a nonequilibrium Ti-rich structure.



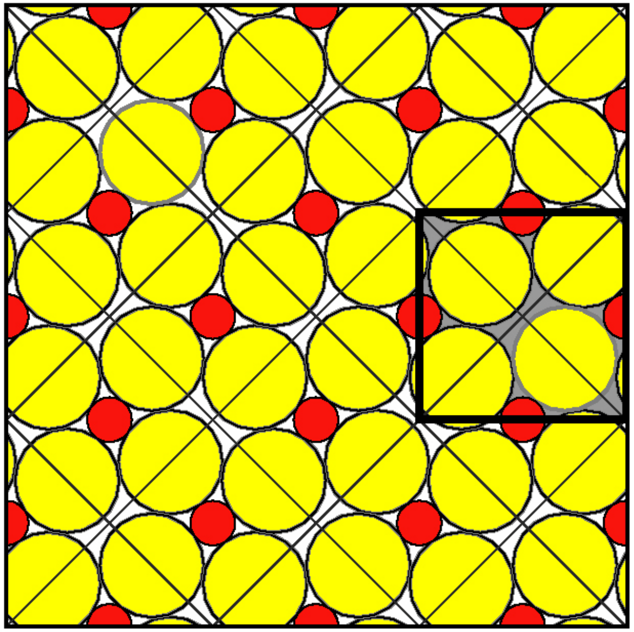
A. Munkholm *et al.*, *Phys. Rev. Lett.* **88**, 016101 (2002).

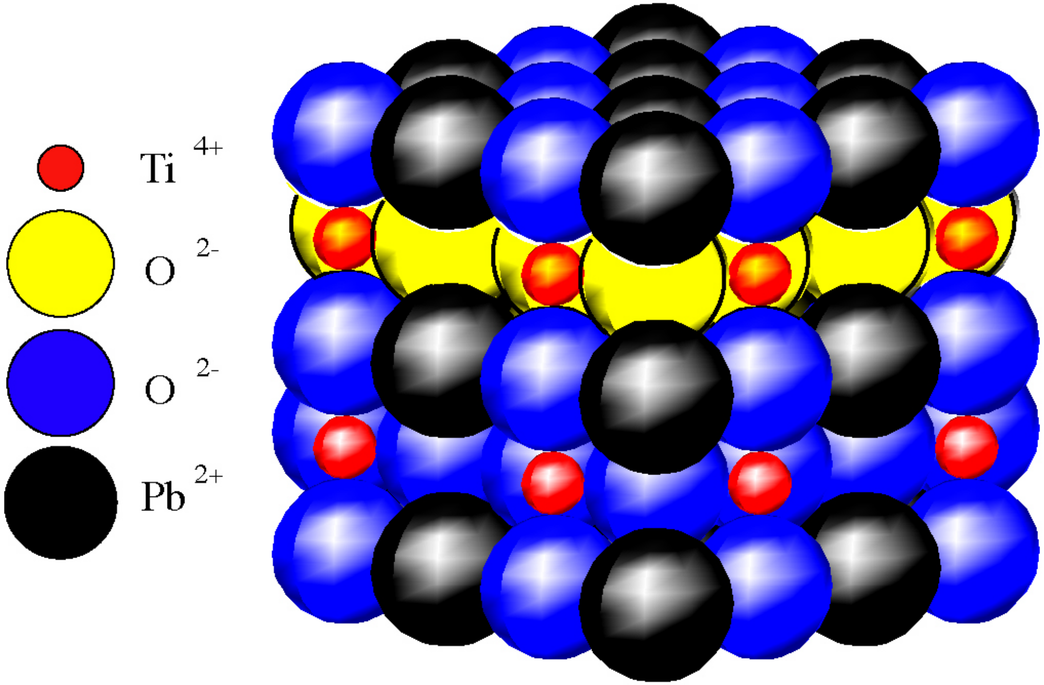
Equilibrium Surface Structure of $PbTiO_3$

c(2 × 2) Reconstruction

A. Munkholm *et al.*, *PRL* **88**, 016101 (2002).

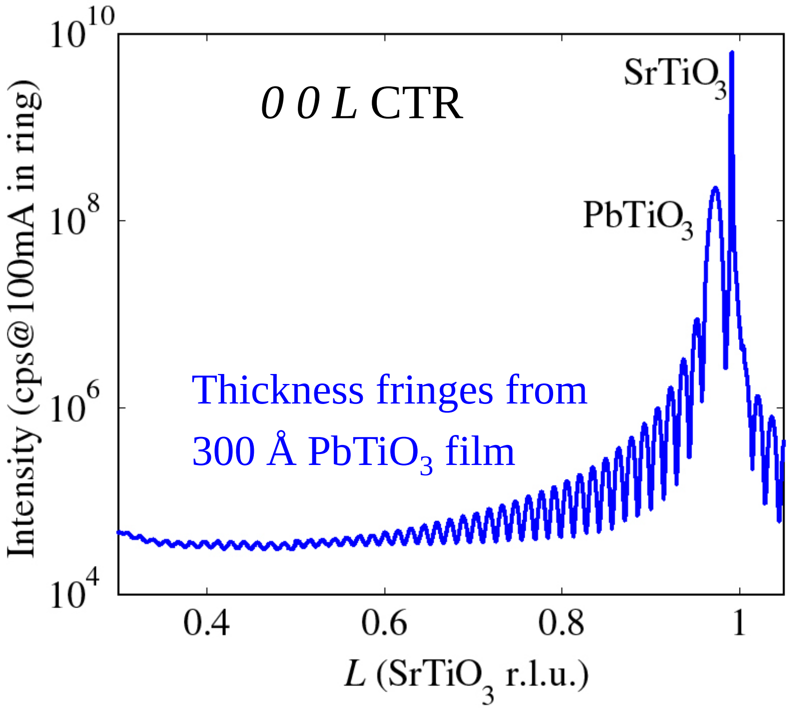
The equilibrium surface is a PbO-terminated, single-unit-cell layer with an antiferrodistortive structure, obtained by 10º oxygen octahedral rotations. *This reconstruction occurs on films of all thicknesses down to a single unit cell.*

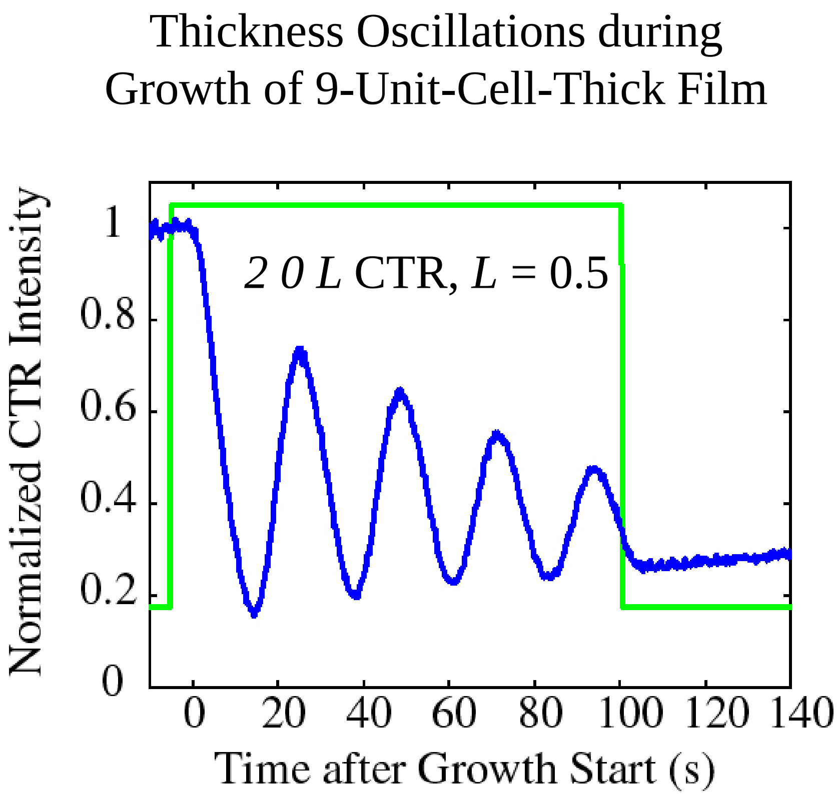




This reconstruction now found in *ab intio* calculations by C. Bungaro *et al.*, cond-mat/0410375 (2004)

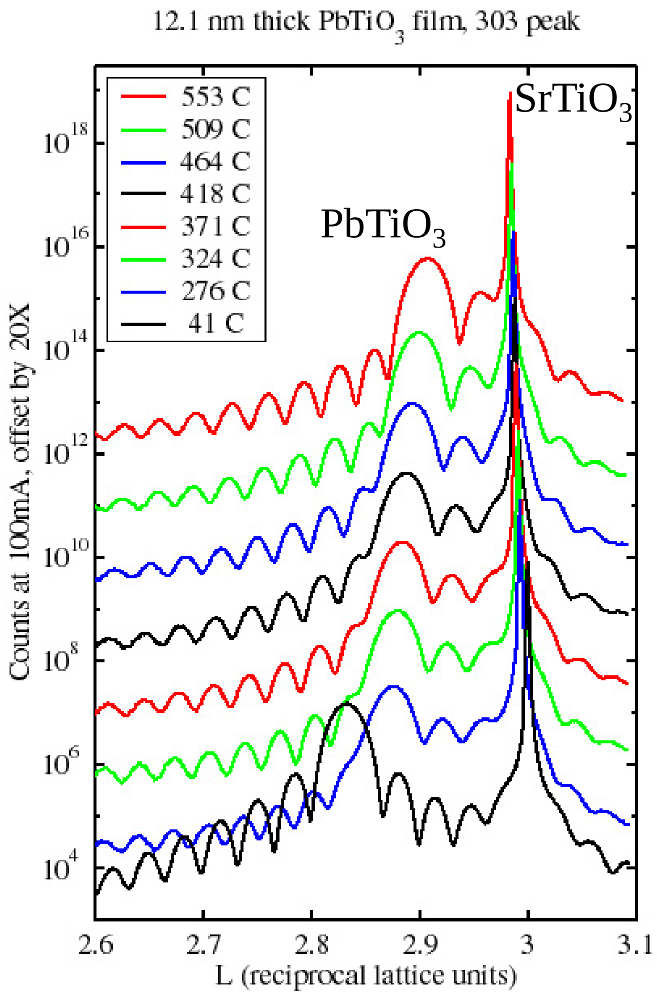
Thickness Control to Sub-Unit-Cell Accuracy



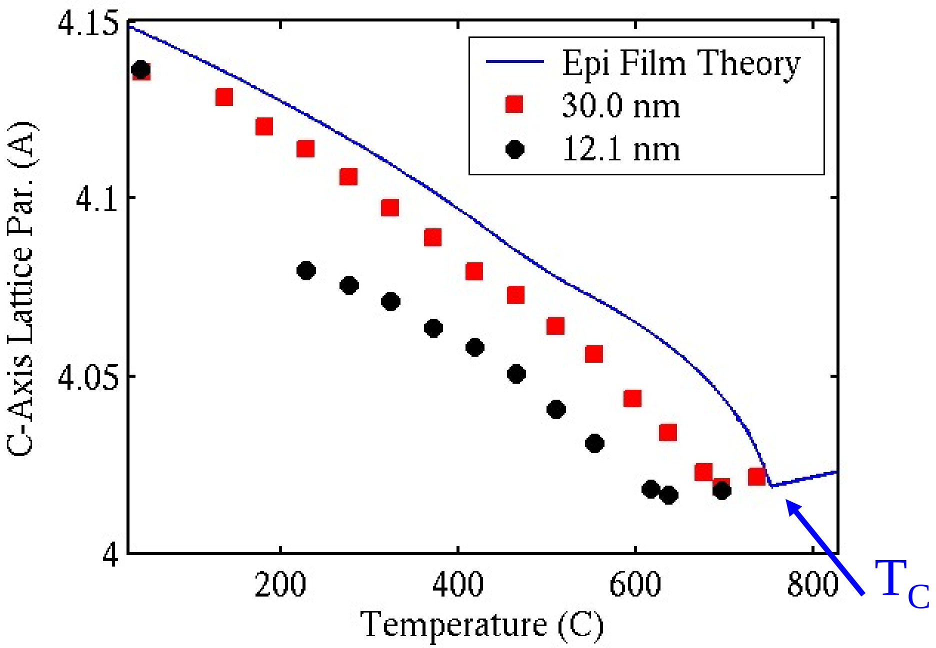


- Thickness fringes indicate atomically-smooth intefaces
- Can monitor initial growth by observing formation of thickness fringes
- Period of oscillations depends on *L*; at *L* = 0.5, period corresponds to 2 unit cells

Determination of T_C from *c*-Axis Lattice Parameter



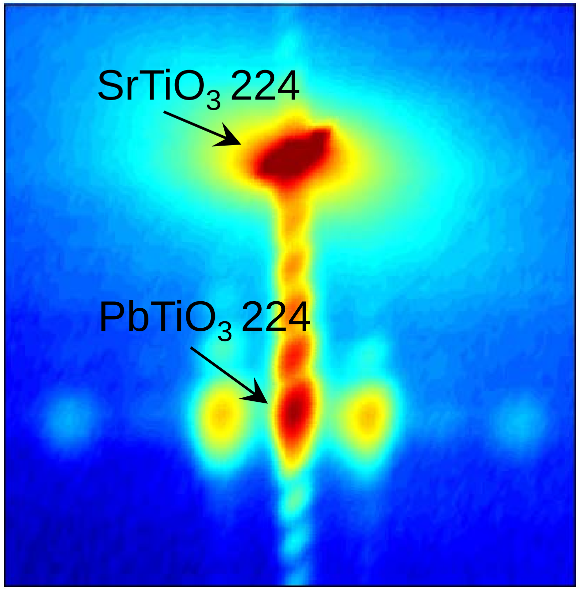
- Ferroelectric phase transition identified by measuring lattice parameter of $PbTiO_3$ as function of temperature
- Phase transition is continuous, as predicted by theory for epitaxial film
- T_C is elevated less than thick-film prediction, and depends on thickness



In-Plane Satellite Peaks Observed ➔ 180° Stripe Domains

- Satellites with equal spacings in Δ*Q* are observed at $PbTiO_3$ reflections with $L\neq0$
- No satellites observed around $L=0$ peaks (displacements are in c-axis direction)
- Wavevector of modulation is in-plane

L



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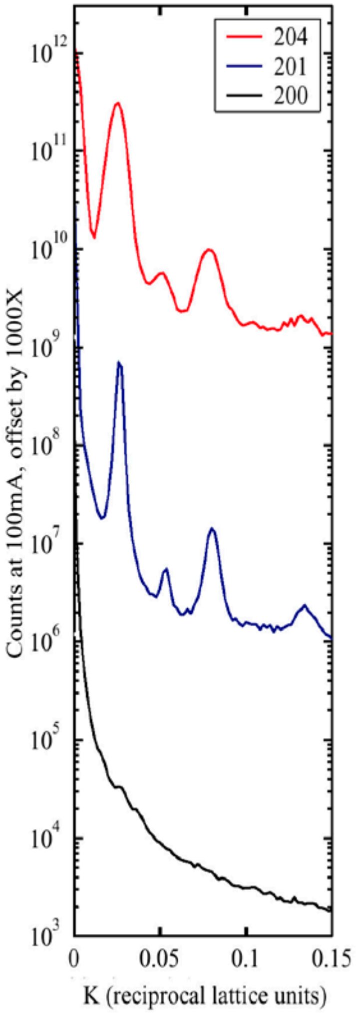
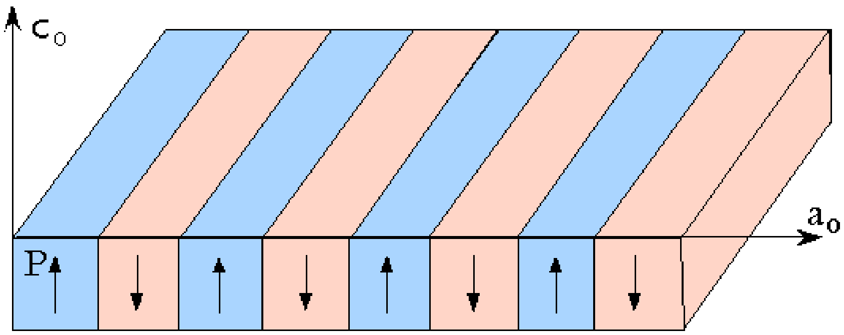
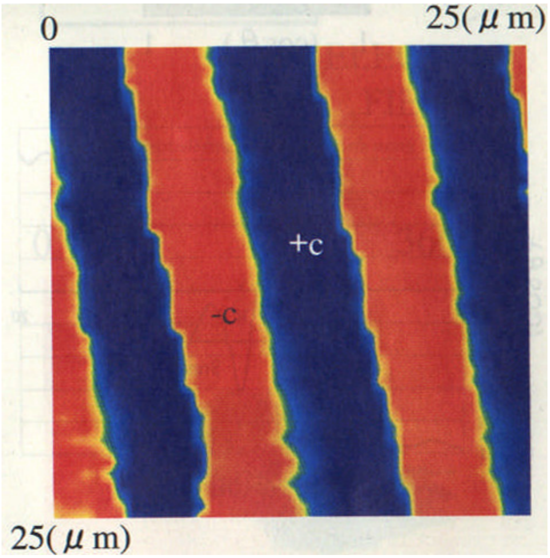


S.K. Streiffer et al., *PRL* **89**, 067601 (2002)

180° Stripe Domains in Ferroelectrics

- 180-degree stripe domains: lamella with alternating polarity
- Experimentally observed in bulk ferroelectrics (e.g., $BaTiO_3$), but no previous reports of their detection in thin films
- Associated with minimization of the electric field energy ("depolarizing field")
- Often assumed that film conductivity is high enough to suppress stripe domain formation

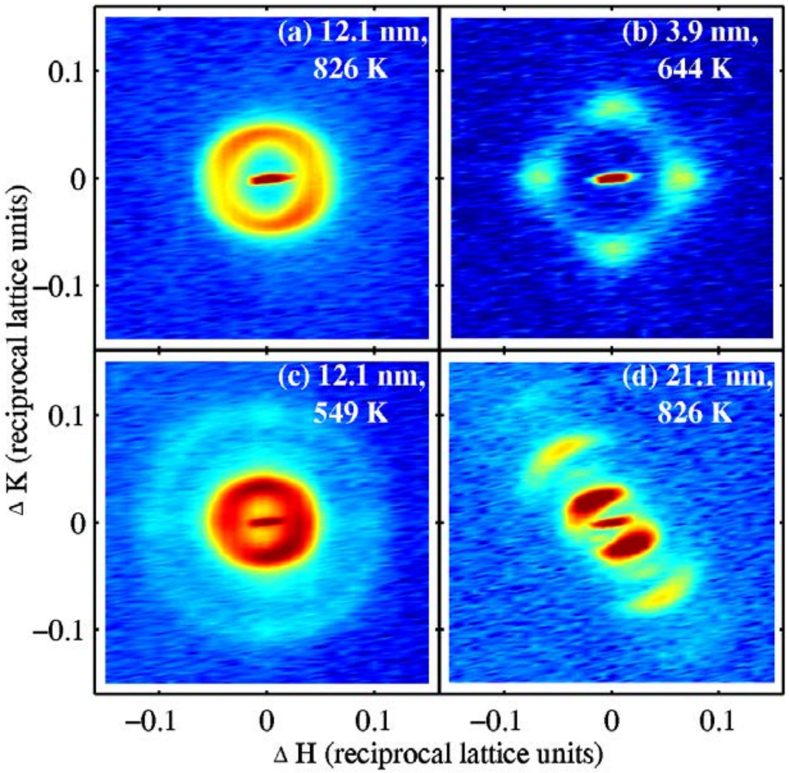


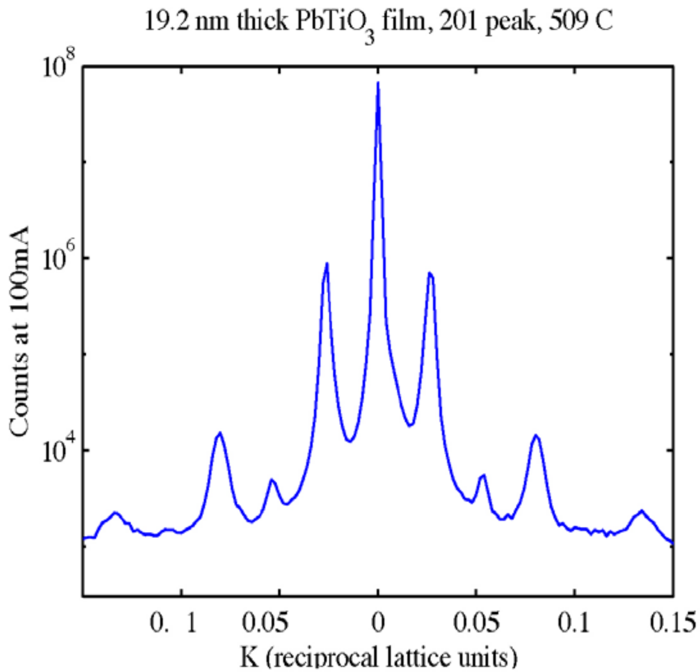


$BaTiO_3$

Y. Cho *et al.*, Jpn. J. Appl. Phys., **38**, 5689 (1999)

Nanoscale 180° Stripe Domains





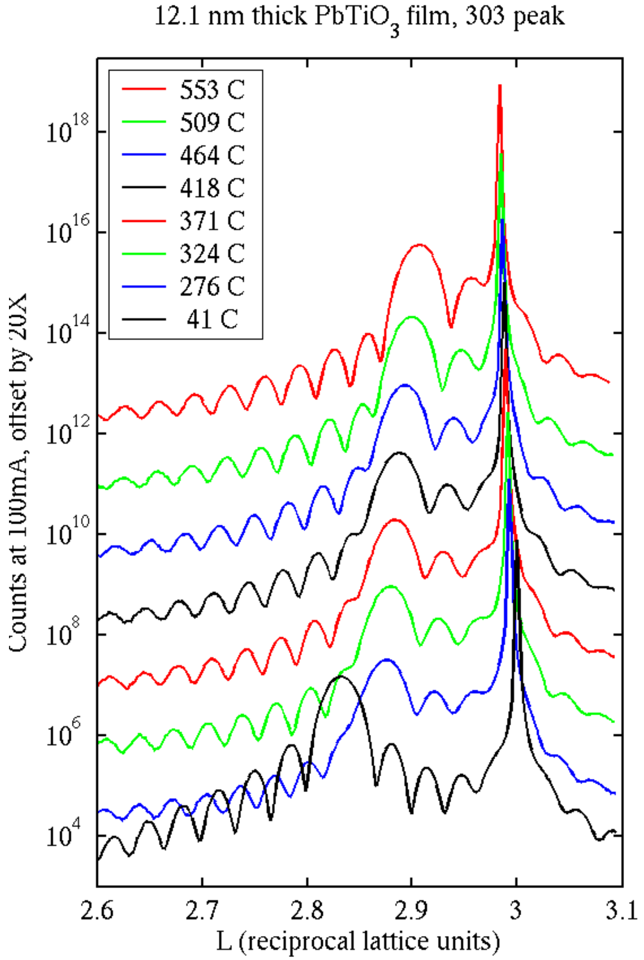
- See various alignments of stripes from in-plane diffraction
- When non-crystallographically aligned, stripes are parallel to miscut steps

- Under some conditions, see high-order harmonics
- Odd orders strongest ⇒ 50:50 ratio of up/down

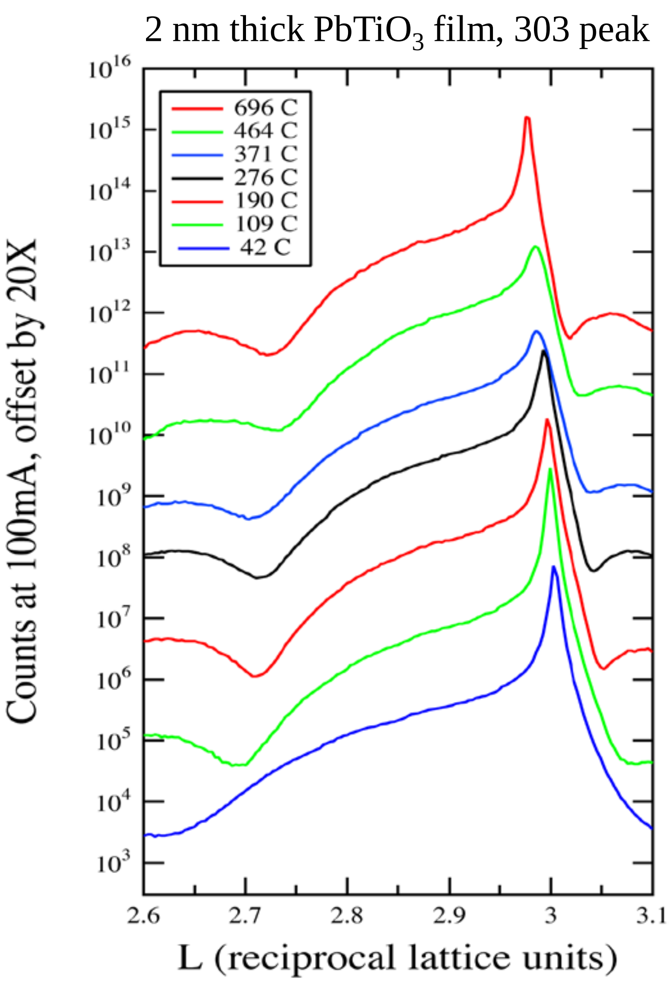
S.K. Streiffer et al., *PRL* **89**, 067601 (2002)

Finding T_C in Ultrathin Films:
c-axis Lattice Parameter is Difficult to Extract

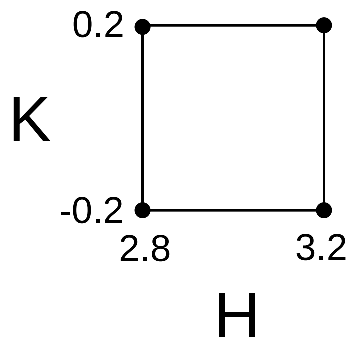
thin film



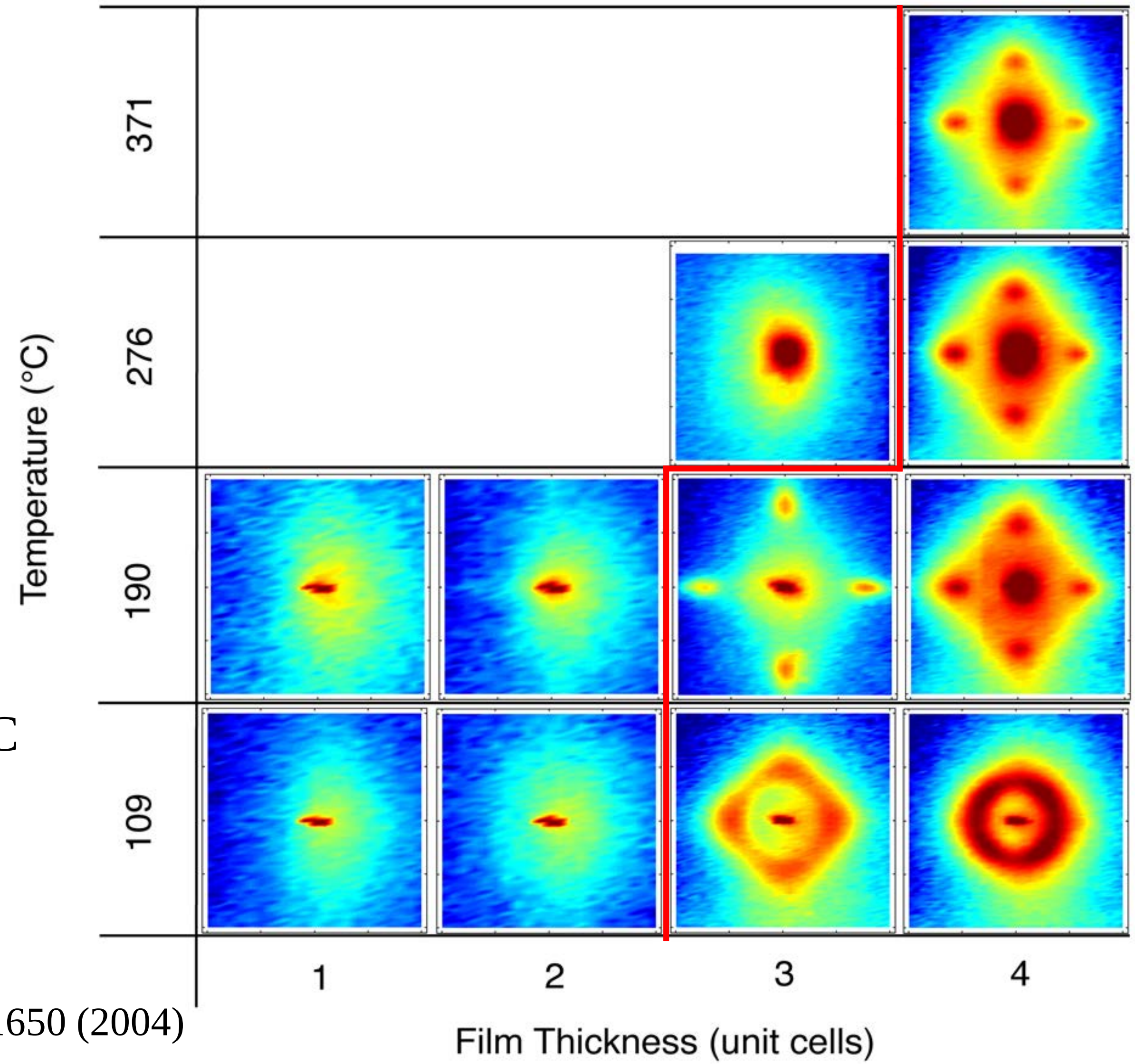
ultrathin film



Finding T_C in Ultrathin Films: Onset of Satellites



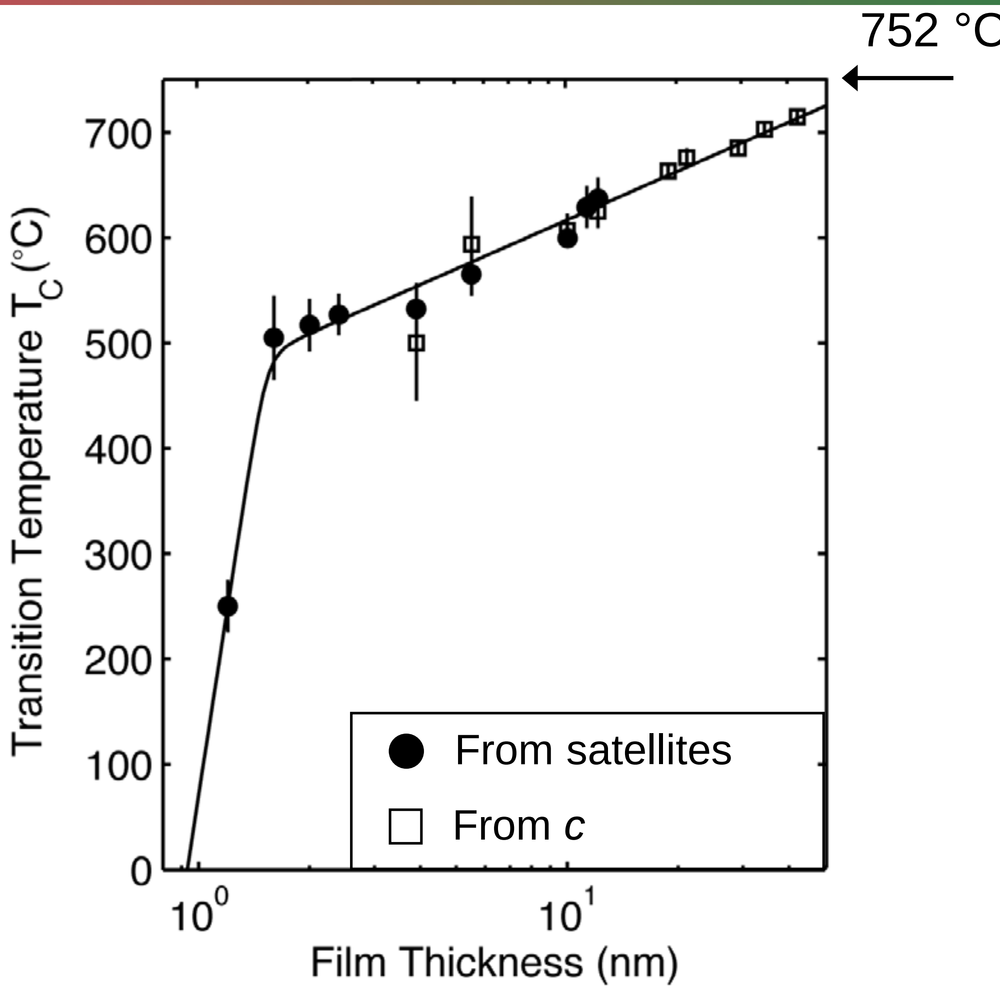
- Ferroelectric phase is stable in three-unit-cell-thick film (1.2 nm) with T_C ~250 °C
- *Ex situ* x-ray measurements at -153 °C found no ferroelectric transition in 2 unit cell sample



D.D. Fong et al., *Science* **304**, 1650 (2004)

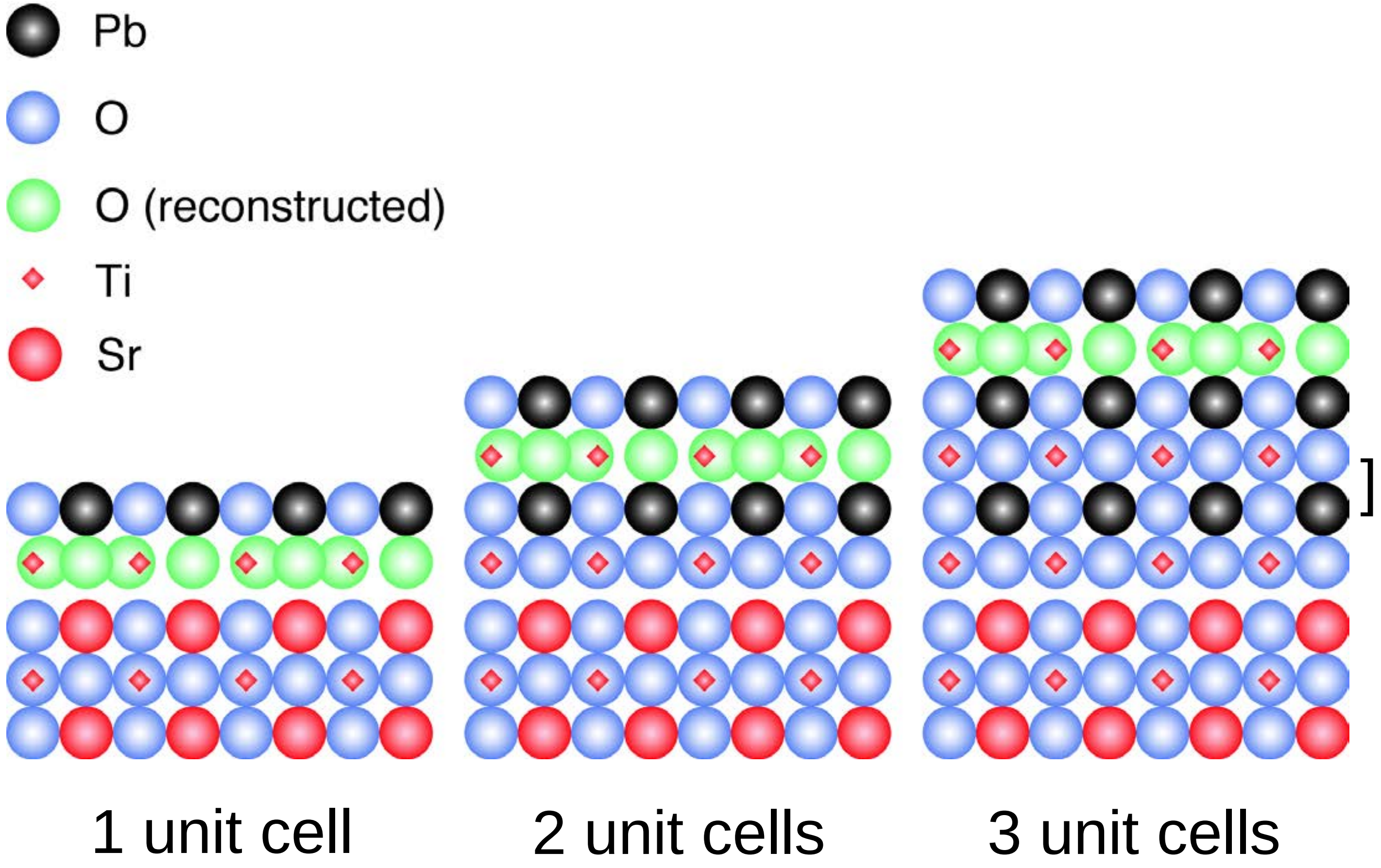
Dependence of T_C on Film Thickness

- T_C determined from onset of stripes agrees with that from lattice parameter
- See gradual decrease, then abrupt drop in T_C at 3 unit cells
- What causes dependence of T_C on film thickness?



D.D. Fong et al., *Science* **304**, 1650 (2004)

Why is 3-Unit-Cell Thickness Required for Ferroelectricity?



- 3 unit cells is minimum thickness for film to contain TiO_2 or PbO layers having the bulk $PbTiO_3$ nearest-neighbor environment

D.D. Fong et al., *Science* **304**, 1650 (2004)

Conclusions and Outlook

- *In situ* x-ray scattering studies provide understanding of synthesis and phase transitions in ultrathin ferroelectrics
  - Equilibrium surface structure of $PbTiO_3$
  - MOCVD growth mechanisms
  - Sub-monolayer thickness control
  - Nanoscale thickness effects on phase stability
  - 180˚ stripe domain formation
  - Effects of mechanical and electrical boundary conditions
- Competition between polarization, depolarizing field, epitaxial strain, domain formation, intrinsic surface effects, and interface compensation by charged species produce unexpectedly rich behavior in ultrathin ferroelectric films
- We have just begun to understand these phenomena to the point where we can predict and control them