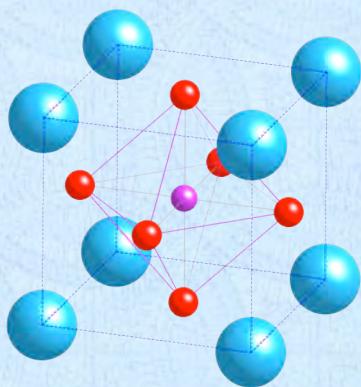
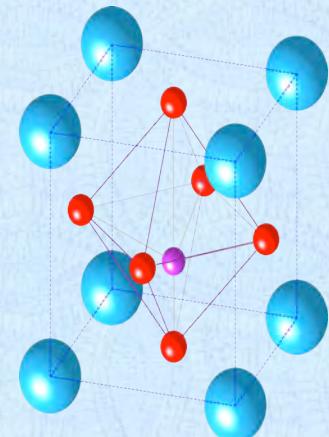


Polarization dynamics and atomic structure on in situ grown ferroelectric films



Arthur P. Baddorf

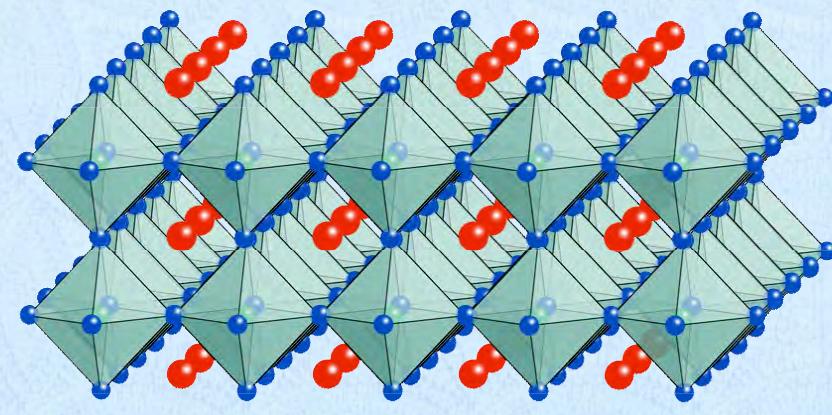


**Junsoo Shin
Von Braun Nascimento
Rob Moore
E.Ward Plummer**

**Ho-Nyung Lee
Hans Christen
Albina Y.Borisevich
Peter Maksymovych
Sergei V. Kalinin**

SrRuO_3

SrRuO_3 Thin films



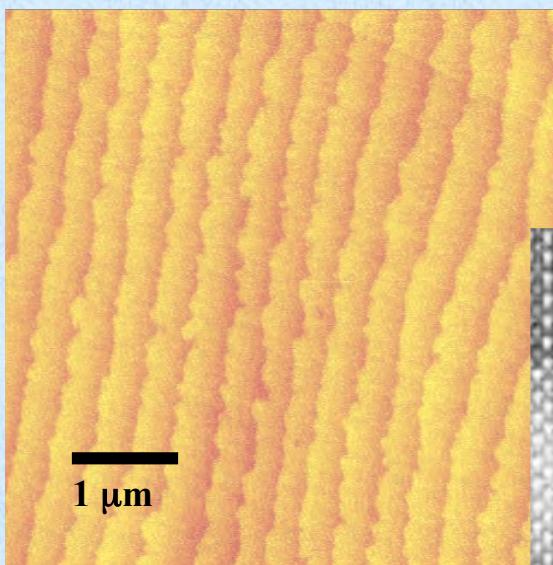
● Sr ● O ● Ru (center of octahedra)



- Ferromagnetic metal
- Perovskite oxide – with good transport properties
- Electrode for oxide based devices

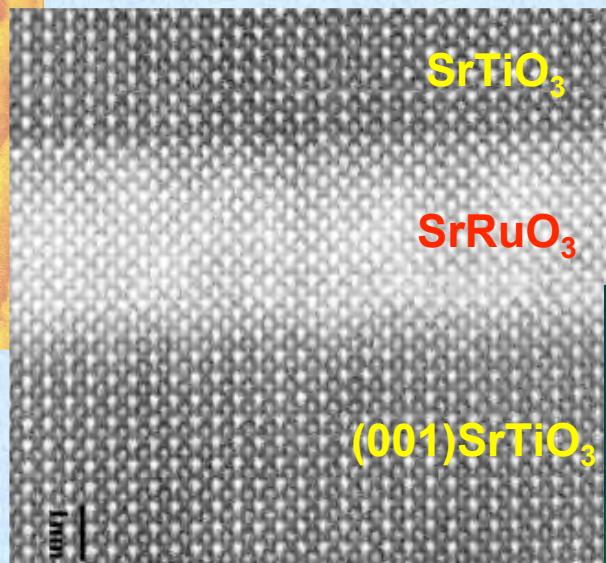
SrRuO₃: The Ideal Oxide Electrode

ambient AFM



4nm thick SrRuO_3 film

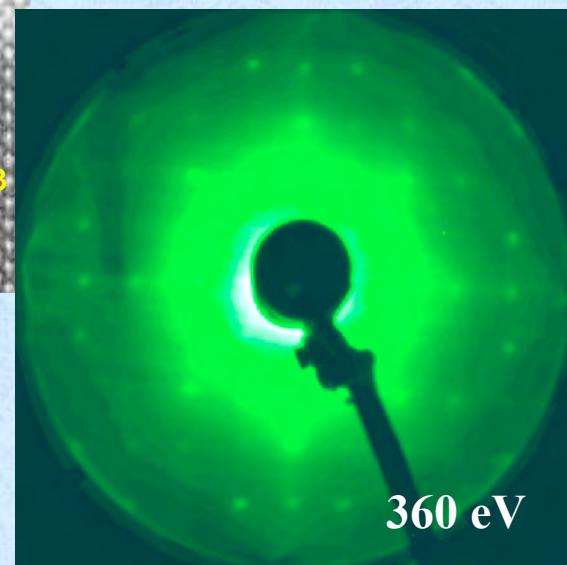
cross-sectional STEM



STEM by M. F. Chisholm (ORNL)

J. Shin, S. V. Kalinin, H. N. Lee, H. M. Christen, R. G. Moore, E. W. Plummer, and A. P. Baddorf *J. Mater. Res.* (2004)

electron diffraction

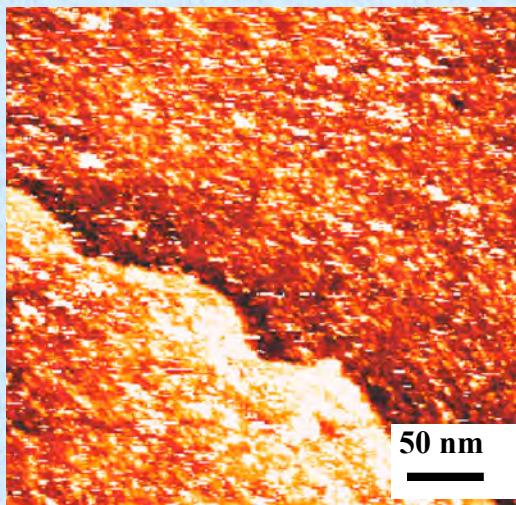


360 eV

SrRuO₃: An Abysmal Failure

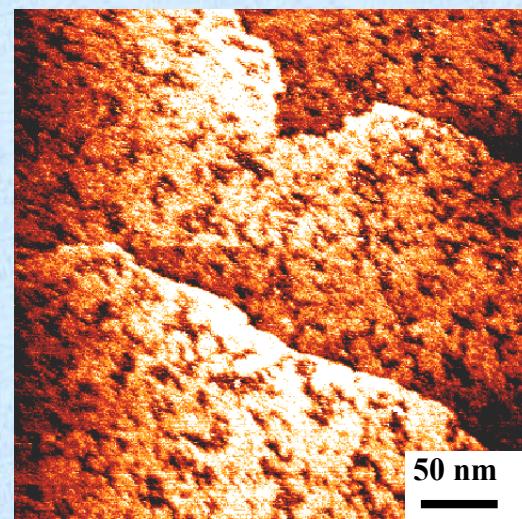
STM images at RT

annealing temperature
RT

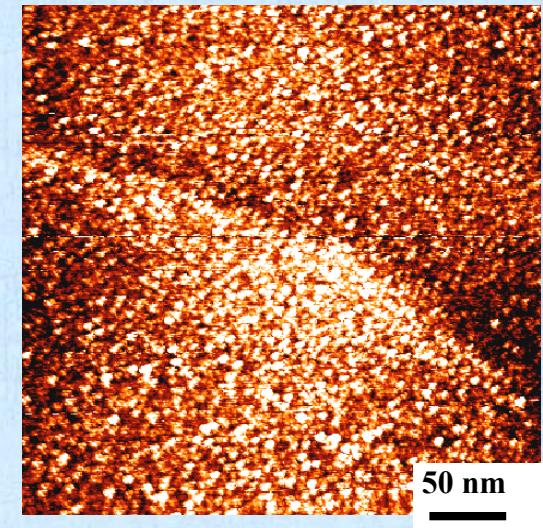


Exposed to air then annealed in vacuum

300°C



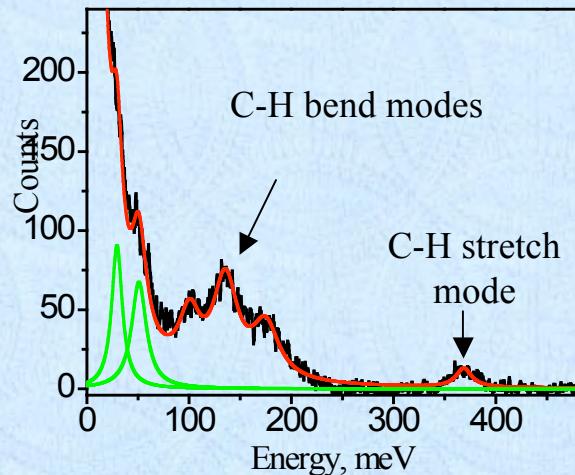
800°C



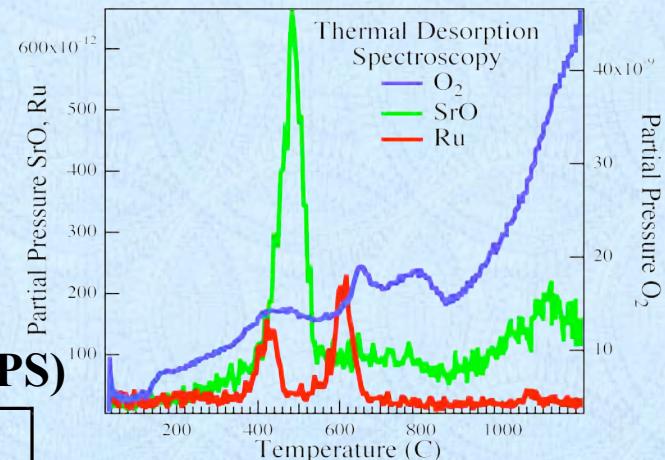
- Surface falls apart after gentle anneal

The Culprit: Air Exposure

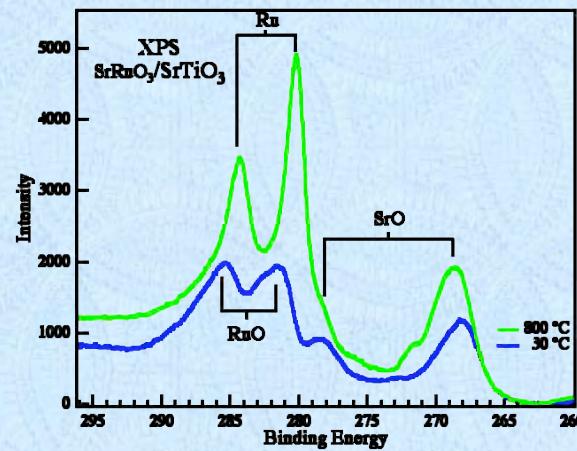
vibrational spectroscopy (HREELS)



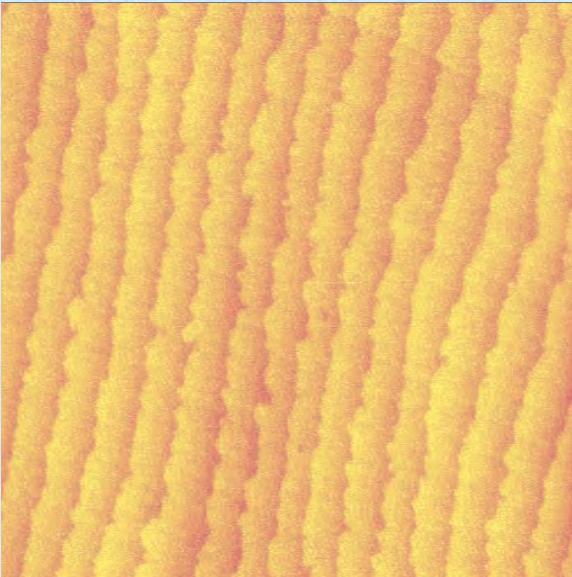
thermal desorption (TDS)



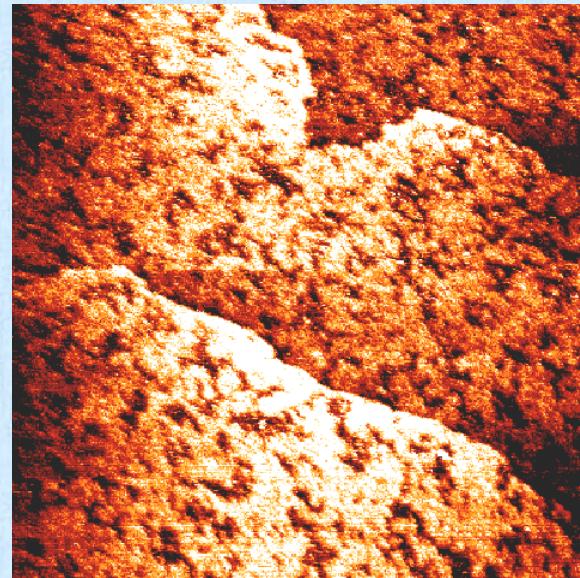
electron spectroscopy (XPS)

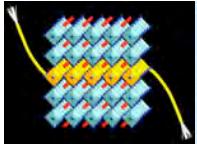


- Adsorbed hydrocarbons react with the surface
- Metallic Ru and oxide Sr remain



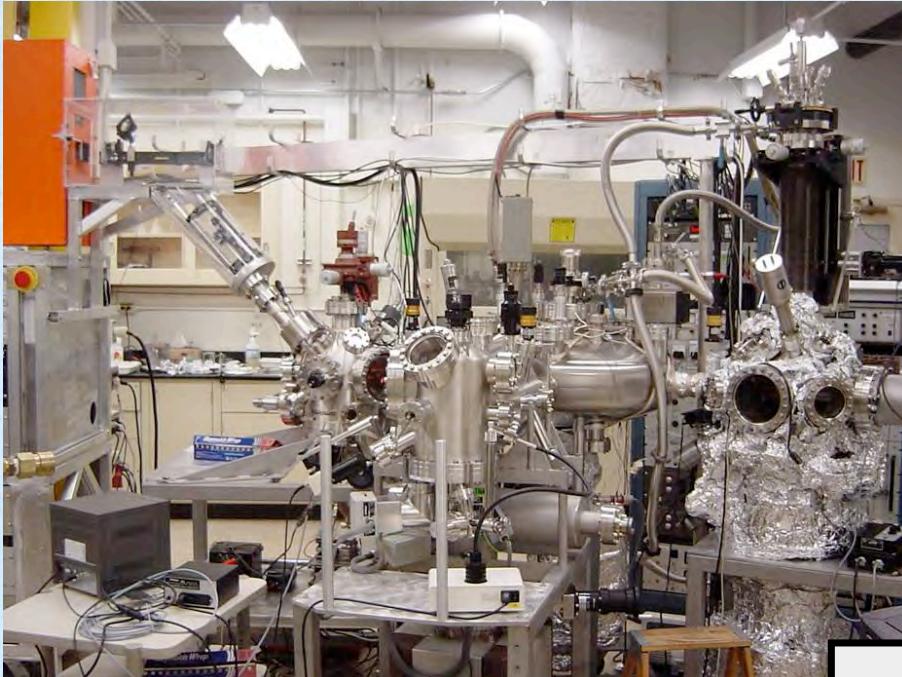
Even “inert” oxides react in air





NanoTransport System

In-situ Growth and Characterization of Oxide Films



PLD growth
Electron Diffraction
Electron Spectroscopy
LEED-IV structure
VT STM/AFM

Advantages for ultrathin ferroelectrics:

- ❖ high degree of control
- ❖ avoids contamination
- ❖ no top layer metal interface
- ❖ no pin hole/defect complications

Growth

AFM/STM

Characterization

RHEED

Transfer

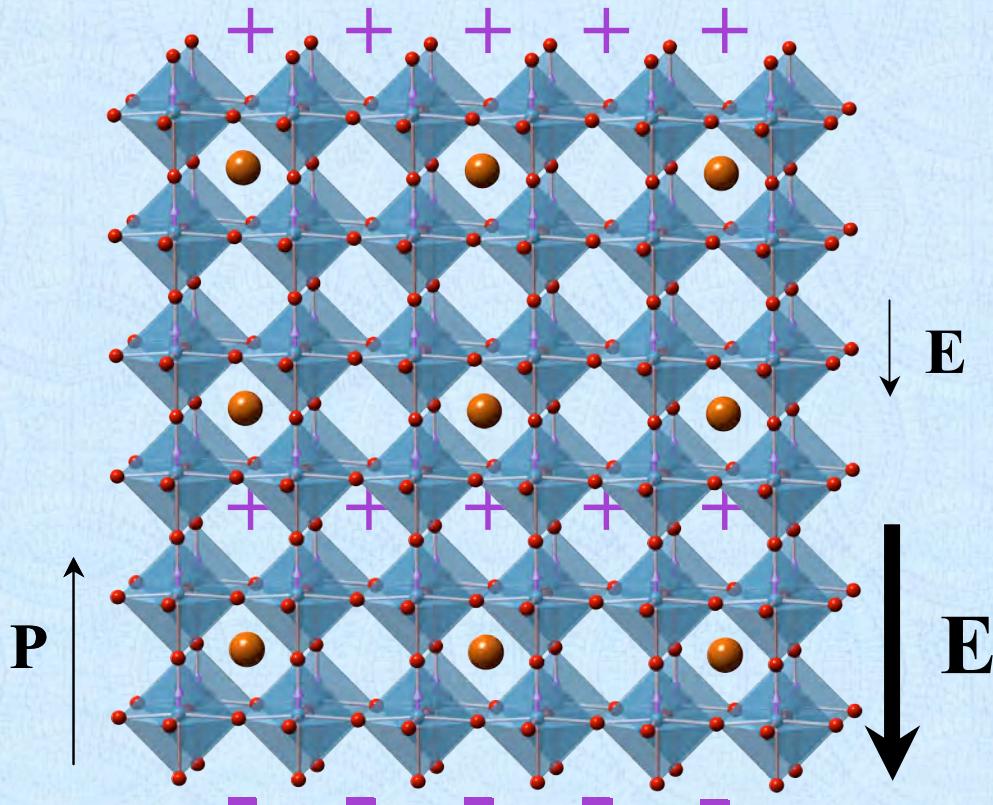
Load Lock

LEED

AES
XPS

Ultrathin Ferroelectric films

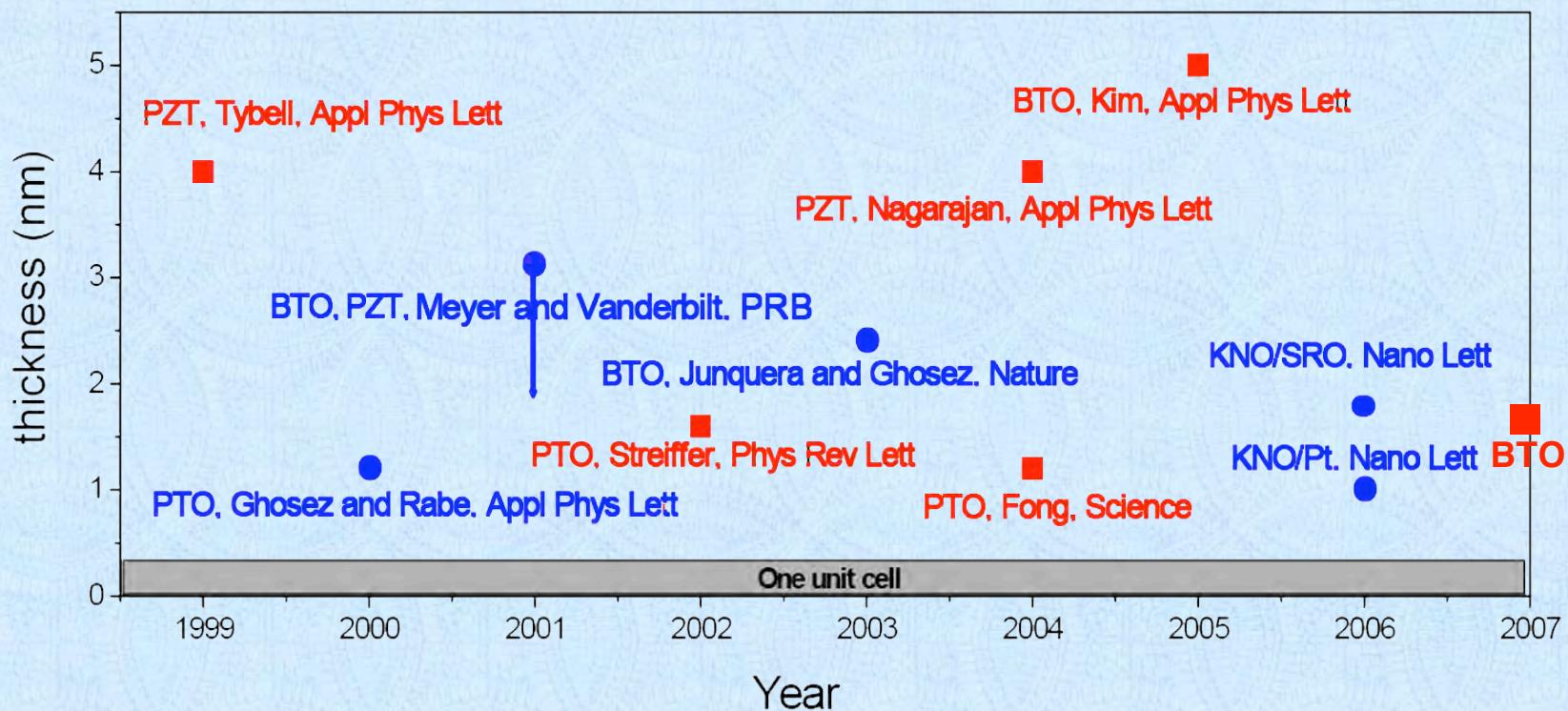
Ferroelectrics couple structure and electrical field



- ❖ spontaneous polarization
- ❖ voltage controlled motion
- ❖ high dielectric response
- ❖ nonvolatile memory

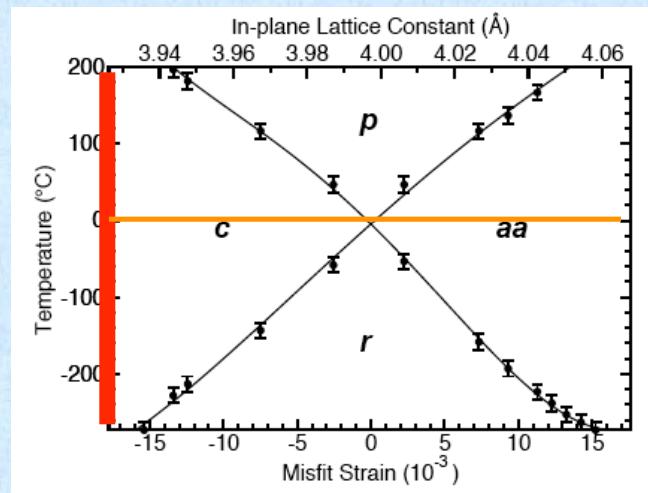
Depolarizing field may limit thinness

Minimum Ferroelectric film Thickness



BaTiO₃

BaTiO₃/SrRuO₃/SrTiO₃



- p** none
- aa** in-plane
- r** diagonal
- c** Z

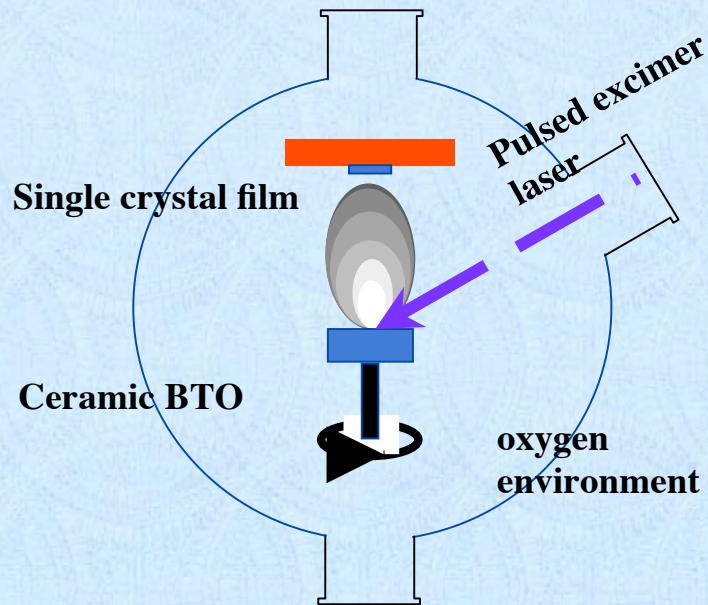
Diéguez, ... Rabe, Vanderbilt PRL04

Strain favors vertical polarization over wide range
of temperature

growth

film Growth

Film growth by pulsed laser deposition



- ❖ high pressure O₂ (10-100 mTorr)
- ❖ high temperature (650-825 °C)
- ❖ UHV compatible

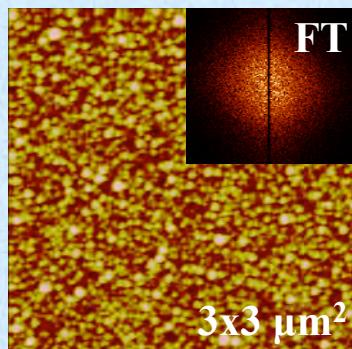
kinetically limited growth

Growth of BaTiO₃/SrTiO₃ using kinetic limitations

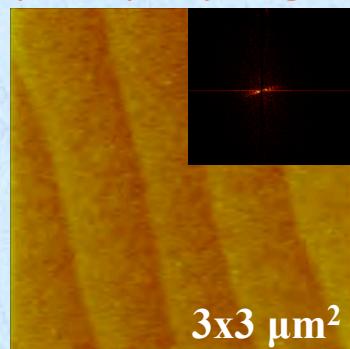
AFM

Junsoo Shin, A.Y. Borisevich, S.V. Kalinin, E.W. Plummer, and A.P. Baddorf, APL 2007 in print

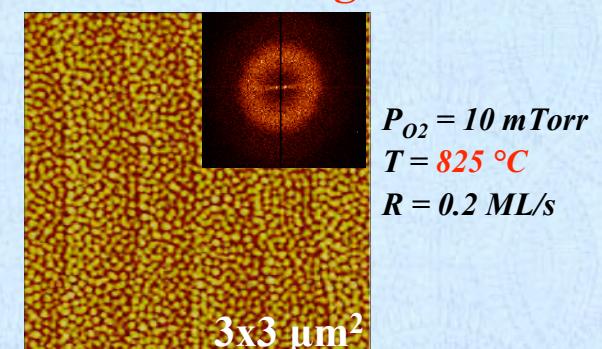
3D island growth



Layer-by-layer growth

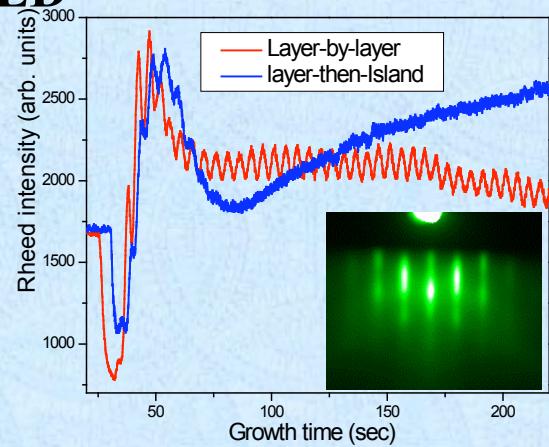


Pseudo 2D island growth

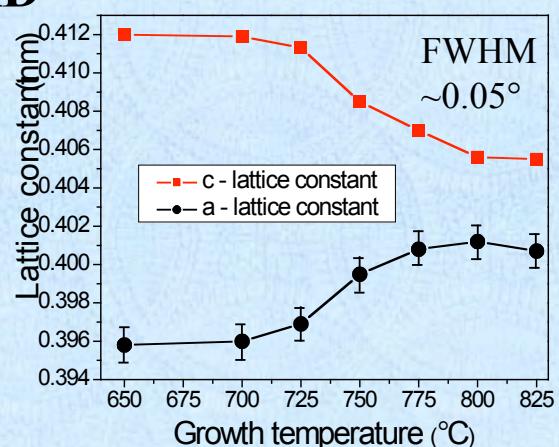


new growth mode

RHEED

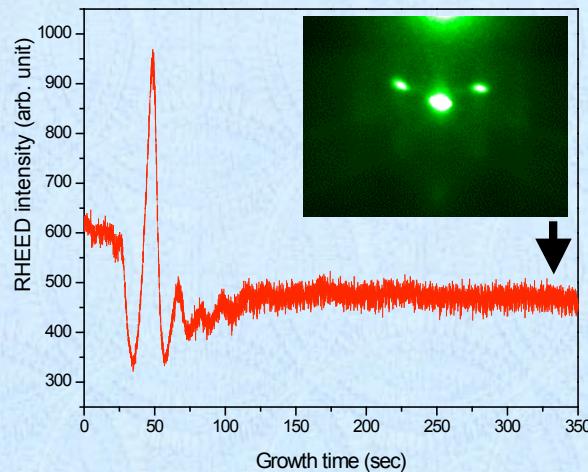


XRD



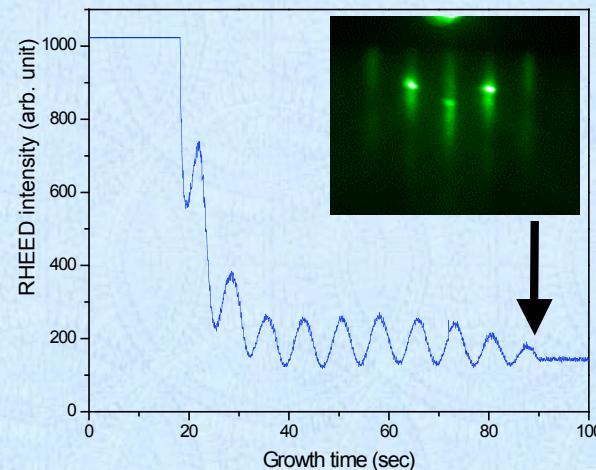
Ultra-thin BaTiO_3 with metallic electrode ($\text{BaTiO}_3/\text{SrRuO}_3/\text{SrTiO}_3$)

SrRuO_3
step flow growth

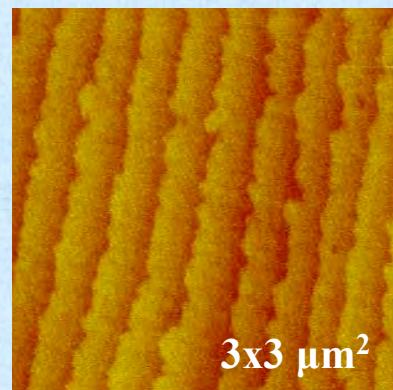


RHEED

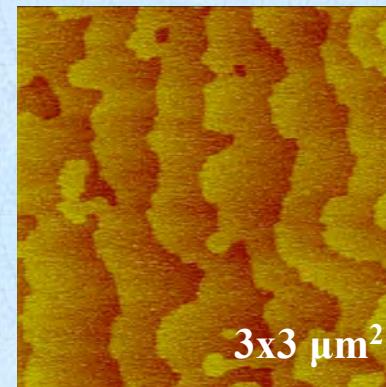
BaTiO_3
layer by layer growth



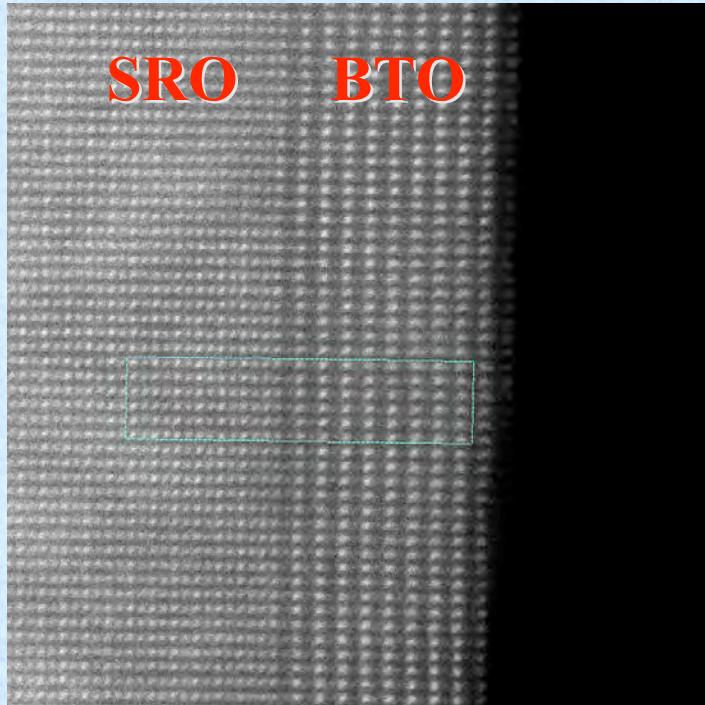
AFM
ex-situ



15 nm thick



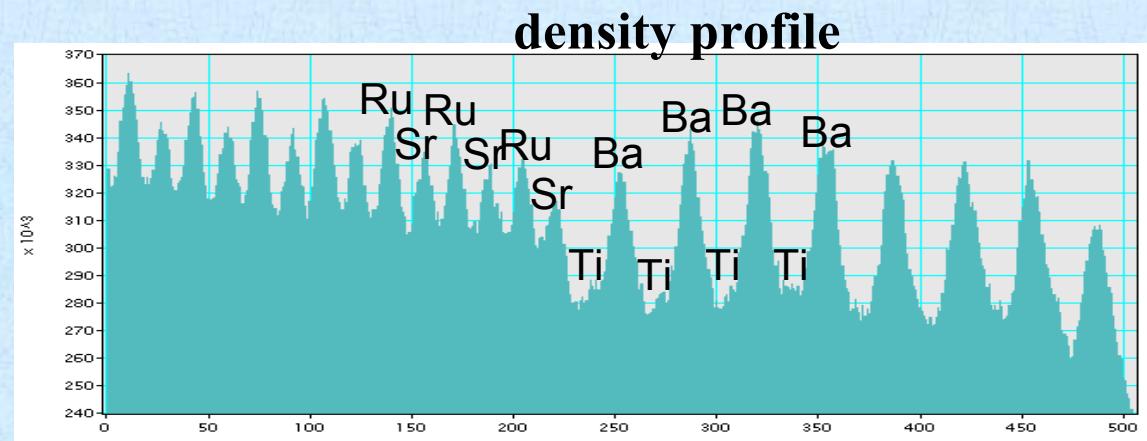
10 ML = 4.2 nm



BaTiO₃ - SrRuO₃ Interface

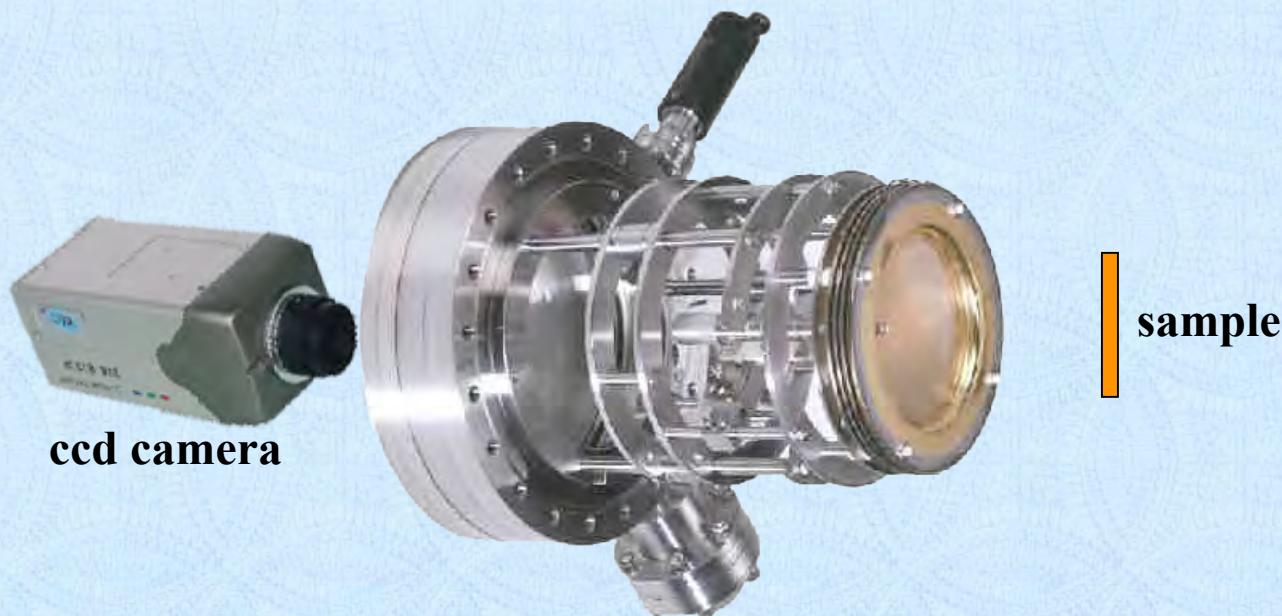
STEM

- ❖ crystalline
- ❖ clean interface
- ❖ possible mixing in one layer



structure

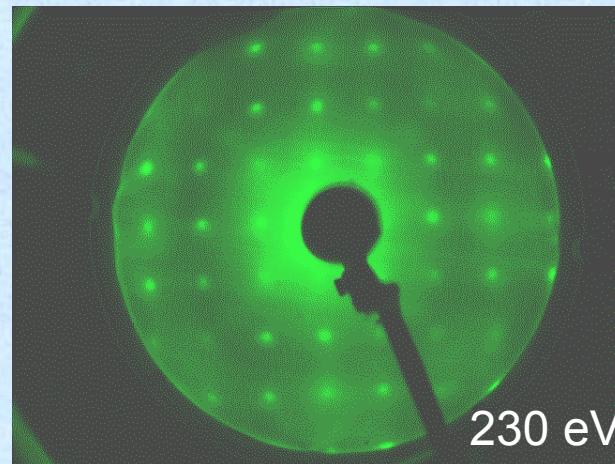
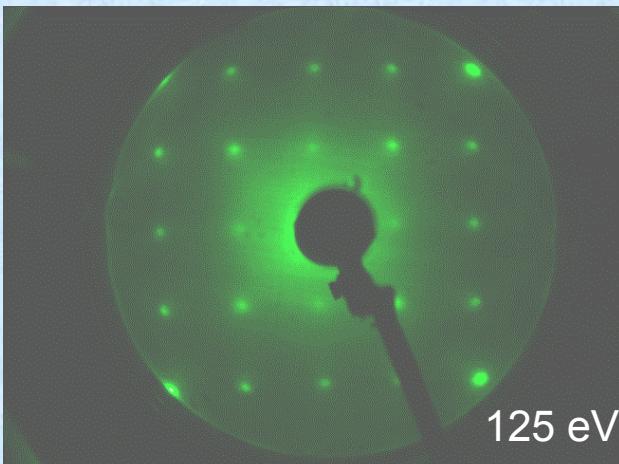
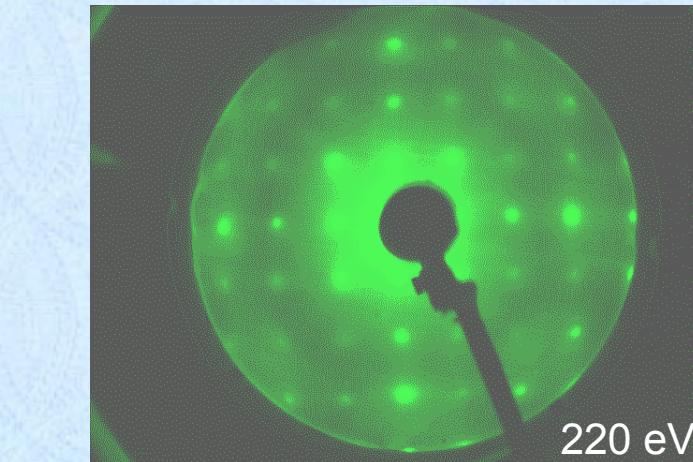
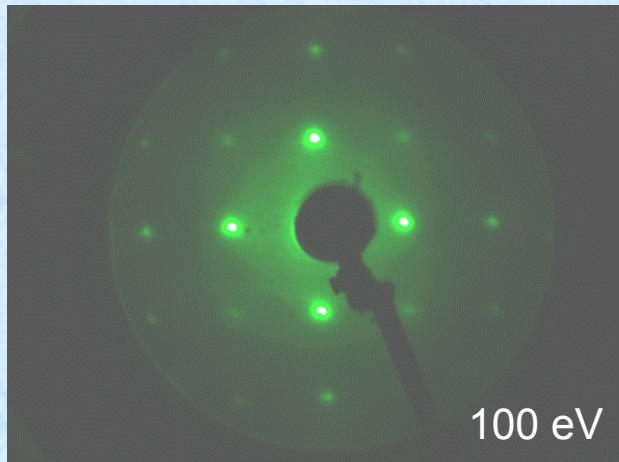
low Energy Electron Diffraction LEED



Low Energy Electron Diffraction

10 ML BTO/SRO/STO

Junsoo Shin, V.B. Nascimento, A.Y. Borisevich, E.W. Plummer, S.V. Kalinin, and A.P. Baddorf
submitted to PRL



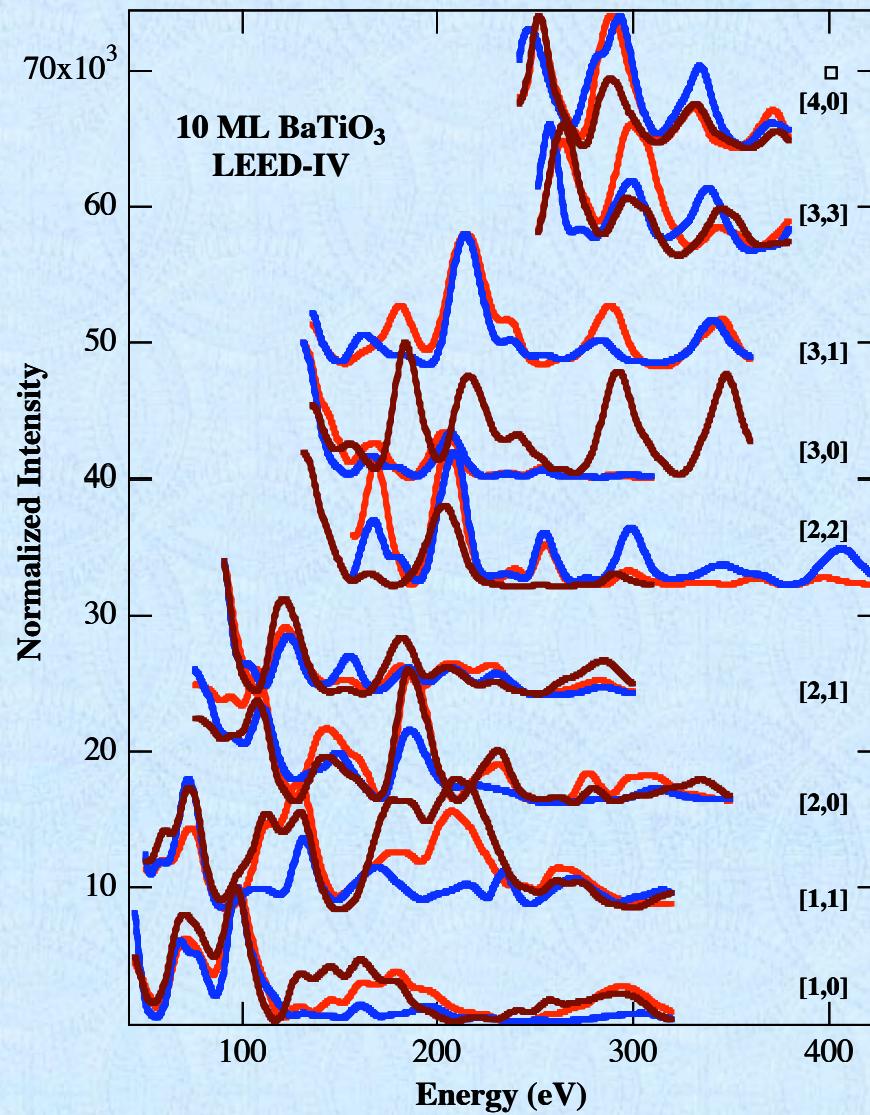
- ❖ crystalline
- ❖ tetragonal

LEED-IV 10 ML BaTiO₃ film

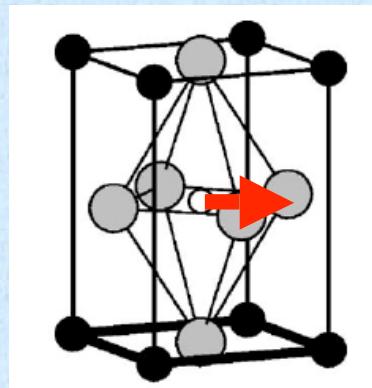
unpolarized
 $R_p = 0.44$

experiment

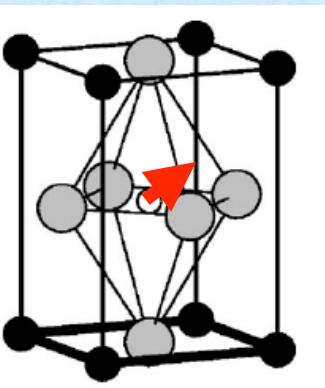
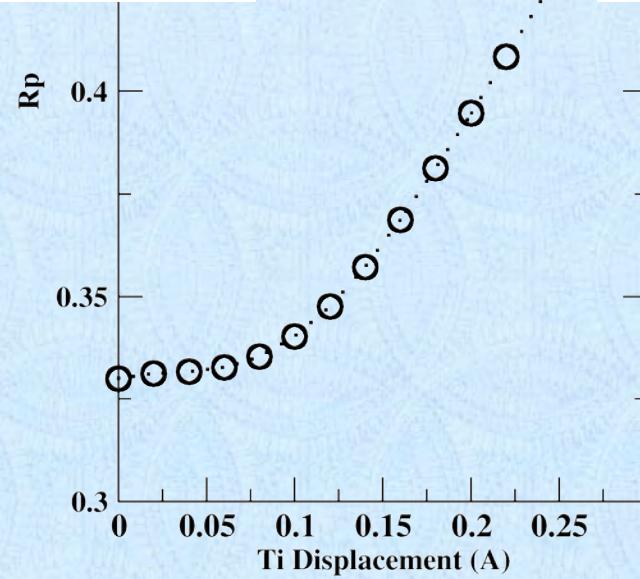
best model
 $R_p = 0.32$



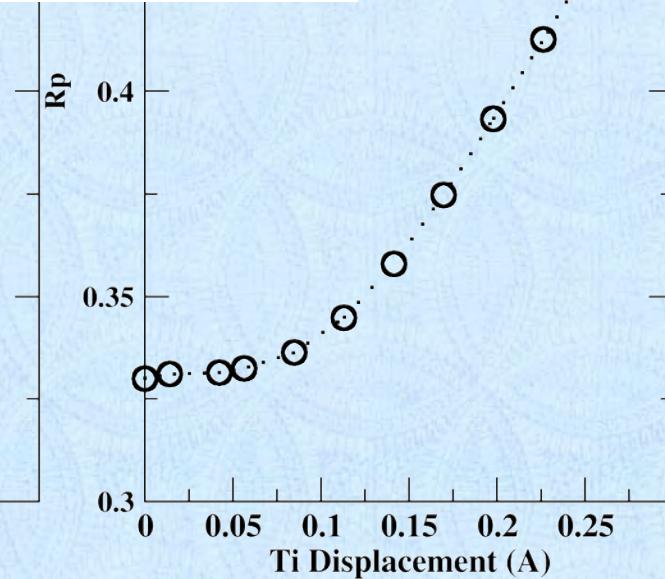
In-Plane Ti Displacement



(100)

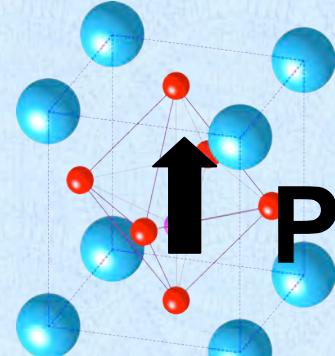
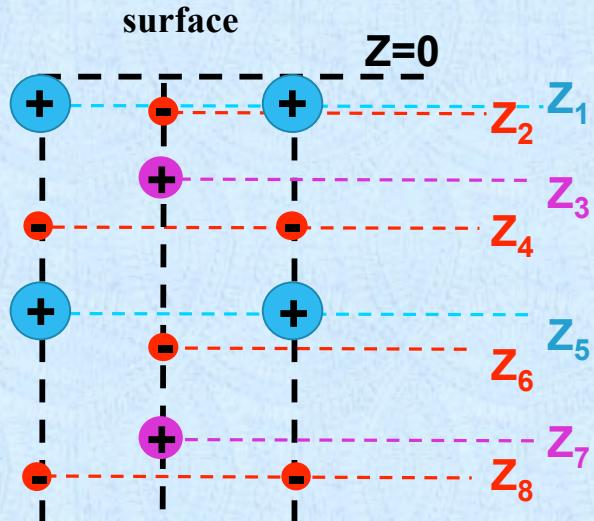


(110)



- ❖ best fit with no in-plane Ti displacement
- ❖ possibly large in-plane RMS

10 ML BaTiO₃ Structure



Structure

Z ₁	0.0964 ± 0.04 Å
Z ₂	0.1185 ± 0.04 Å
Z ₃	1.9595 ± 0.03 Å
Z ₄	2.1169 ± 0.05 Å
Z ₅	4.1854 ± 0.04 Å
Z ₆	4.3029 ± 0.07 Å
Z ₇	6.1838 ± 0.05 Å
Z ₈	6.3039 ± 0.09 Å

Polarization

$$\eta(\text{BaO}, \text{TiO}_2) = [\Delta Z(\text{Ba, Ti}) - \Delta Z(\text{O})]/\text{lattice constant } c$$

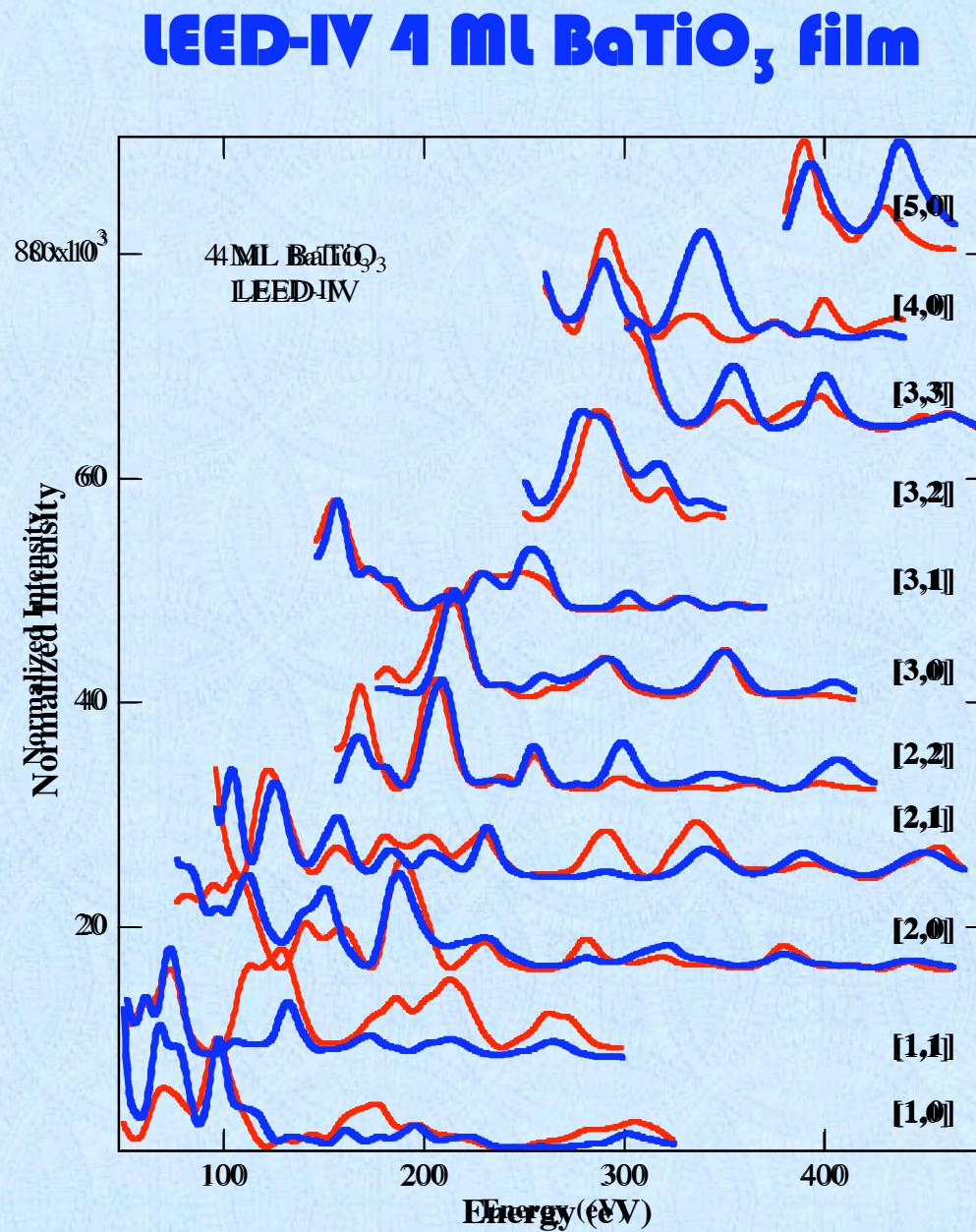
layer	Surface of films	Surface of bulk*		Bulk**
	LEED-IV exp.	DFT theory applied E _{ext}	DFT theory without E _{ext}	Neutron and XRD
1 st , η(BaO)	- 0.0053	- 0.038	+ 0.0151	±0.0240
2 nd , η(TiO ₂)	- 0.0376	- 0.025	- 0.0046	±0.0285
3 rd , η(BaO)	- 0.0281	- 0.022	+ 0.0039	±0.0240
4 th , η(TiO ₂)	- 0.0287			±0.0285

*Meyer and Vanderbilt PRB63, 205426 (2001)

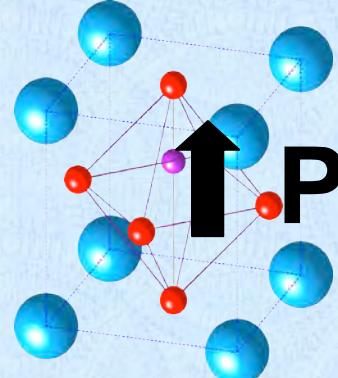
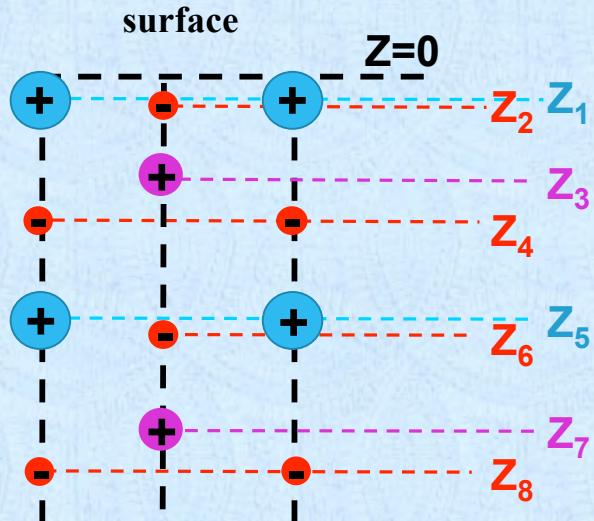
** Harada Acta Cryst. A26, 336 (1970)

- ❖ upward polarization
- ❖ BaO termination, surface relaxation
- ❖ top dead layer, inside similar to bulk

experiment
model
 $R_p = 0.30$



4 ML BaTiO₃ Structure



Structure

Z_1	$0.0738 \pm 0.03 \text{ \AA}$
Z_2	$0.1078 \pm 0.04 \text{ \AA}$
Z_3	$1.9243 \pm 0.02 \text{ \AA}$
Z_4	$2.0648 \pm 0.05 \text{ \AA}$
Z_5	$4.1308 \pm 0.04 \text{ \AA}$
Z_6	$4.1863 \pm 0.07 \text{ \AA}$
Z_7	$6.0643 \pm 0.04 \text{ \AA}$
Z_8	$6.2046 \pm 0.10 \text{ \AA}$

Polarization

$$\eta(\text{BaO}, \text{TiO}_2) = [\Delta Z(\text{Ba, Ti}) - \Delta Z(\text{O})]/\text{lattice constant } c$$

layer	Surface of films	Surface of bulk*		Bulk**
	LEED-IV exp.	DFT theory applied E_{ext}	DFT theory without E_{ext}	Neutron and XRD
1 st , $\eta(\text{BaO})$	- 0.0083	- 0.038	+ 0.0151	± 0.0240
2 nd , $\eta(\text{TiO}_2)$	- 0.0342	- 0.025	- 0.0046	± 0.0285
3 rd , $\eta(\text{BaO})$	- 0.0135	- 0.022	+ 0.0039	± 0.0240
4 th , $\eta(\text{TiO}_2)$	- 0.0341			± 0.0285

*Meyer and Vanderbilt PRB63, 205426 (2001)

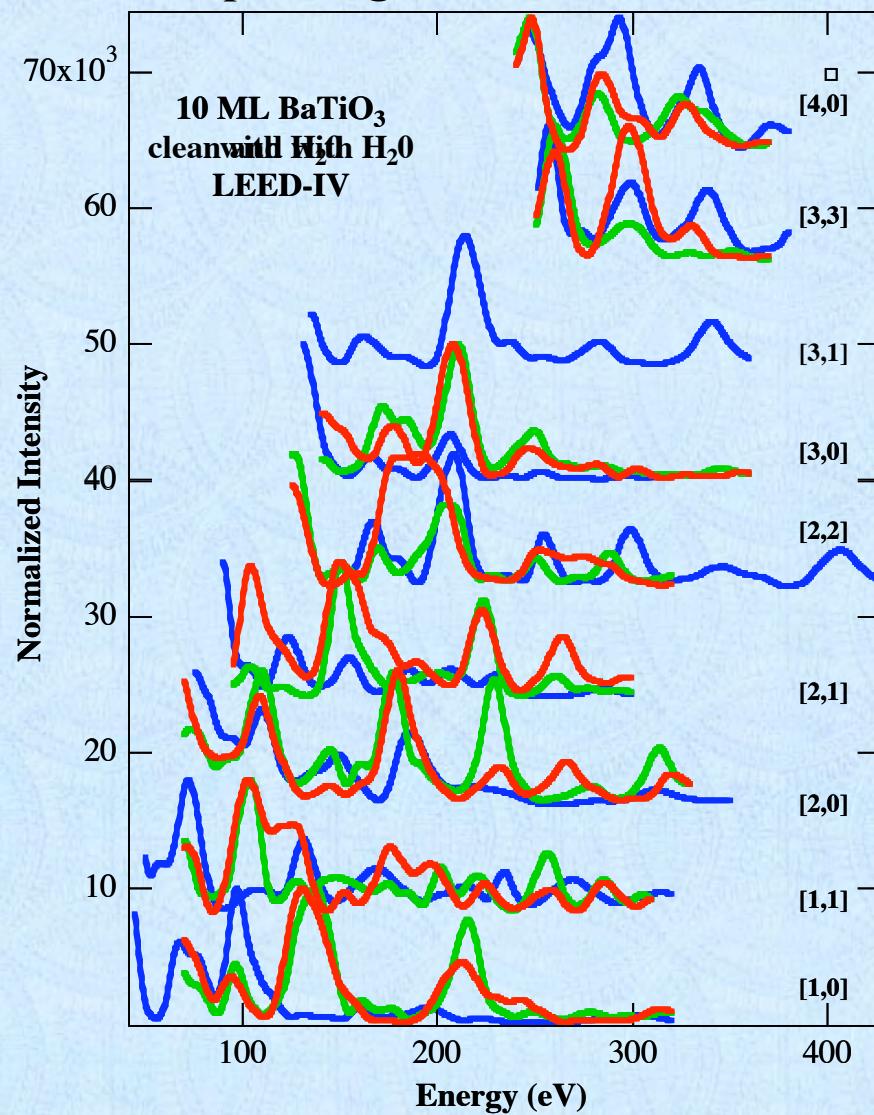
** Harada Acta Cryst. A26, 336 (1970)

- ❖ upward polarization
- ❖ quite similar to 10 ML film

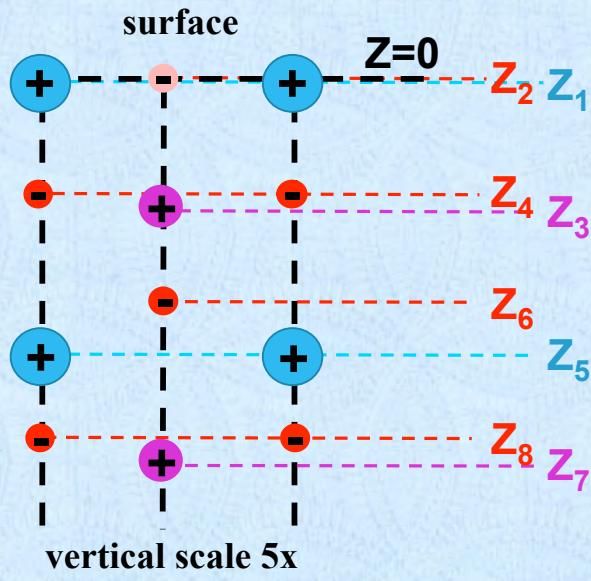
LEED-IV H_2O on 10 ML BaTiO_3 film

corresponding to ~ 60 msec in ambient

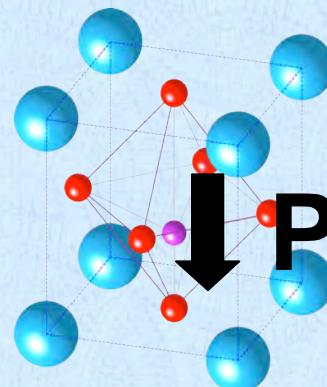
clean
with H_2O
model
 $R_p = 0.39$



H₂O exposed BaTiO₃ Structure



Ba Ti O



Structure

Z_1	$0.0155 \pm 0.03 \text{ \AA}$
Z_2	$-0.0053 \pm 0.08 \text{ \AA}$
Z_3	$2.1136 \pm 0.03 \text{ \AA}$
Z_4	$2.0527 \pm 0.06 \text{ \AA}$
Z_5	$4.1100 \pm 0.08 \text{ \AA}$
Z_6	$3.9299 \pm 0.09 \text{ \AA}$
Z_7	$6.3236 \pm 0.05 \text{ \AA}$
Z_8	$6.2327 \pm 0.12 \text{ \AA}$

Polarization

$$\eta(\text{BaO}, \text{TiO}_2) = [\Delta Z(\text{Ba, Ti}) - \Delta Z(\text{O})]/\text{lattice constant c}$$

layer	Surface of films	Bulk**
	LEED- IV exp.	Neutron and XRD
1 st , $\eta(\text{BaO})$	+ 0.0050	± 0.0240
2 nd , $\eta(\text{TiO}_2)$	+ 0.0145	± 0.0285
3 rd , $\eta(\text{BaO})$	+ 0.0430	± 0.0240
4 th , $\eta(\text{TiO}_2)$	+ 0.0217	± 0.0285

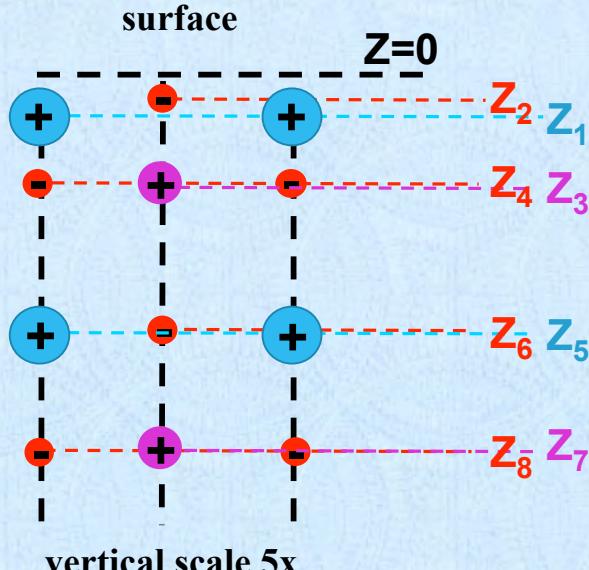
** Harada Acta Cryst. A26, 336 (1970)

- ❖ reversed polarization
- ❖ oxygen vacancies
- ❖ polarization: reduced

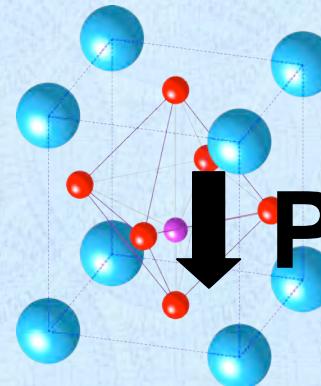
relaxation

The Dead layer

First Principles BaTiO₃ Structure



Meyer and Vanderbilt PRB63, 205426 (2001)
Meyer, Padilla, and Vanderbilt arXiv:Cond-Mat (1999)

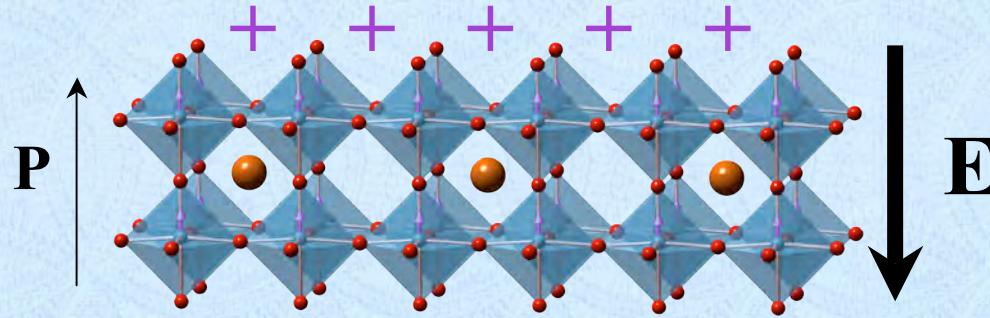


- ❖ relaxation
- ❖ surface of unpolarized bulk is polarized inward
- ❖ for BaO termination, 20% bulk corrugation
- ❖ $\downarrow_{\text{relaxation}} + \uparrow_{\text{spontaneous}} = \text{flat surface}$

depolarization

The Depolarizing Field

Depolarizing field didn't limit thinness



- ❖ dead layer?
- ❖ compensation?
 - chemisorption: H_2O , H
 - electron beam: 0.1 electron/unit cell/sec
- ❖ imprint (polarized by not switchable)?

We need UHV PFM!



Center for Nanophase Materials Sciences

www.cnms.ornl.gov

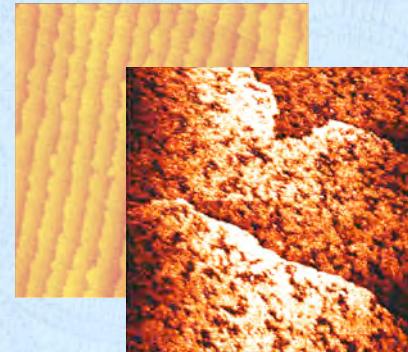
User Center

Summary

Even oxides react in air



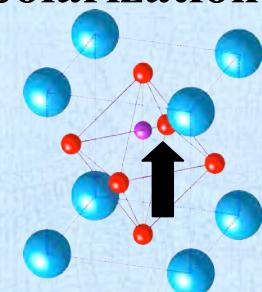
- ❖ highly oxidized
- ❖ fully strained
- ❖ well-ordered
- ❖ uniform and flat



New lower limit (4 and 10 ML) for BaTiO₃ polarization



- ❖ LEED-IV single domain, upward polarization
- ❖ H₂O exposure transforms; downward polarization
- ❖ $\downarrow_{\text{relaxation}} + \uparrow_{\text{spontaneous}} = \text{flat surface}$



For ultrathin films, the future is UHV PFM

