Sandia National Laboratories

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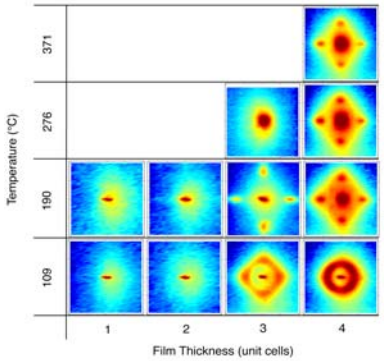
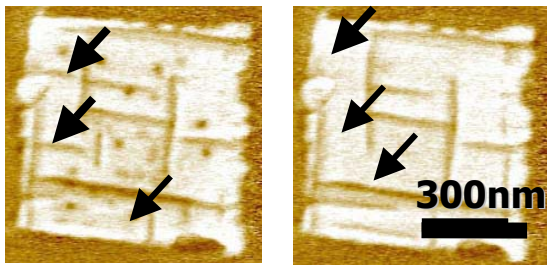
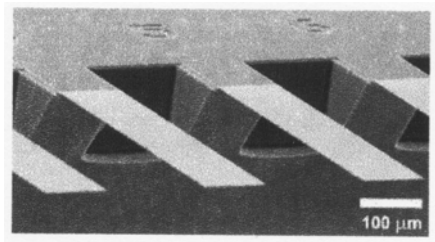


X-ray synchrotron studies reveal limit of ferroelectricity in ultra-thin $Pb_xZr_{1-x}TiO_3$ films

NANOSCALE PHENOMENA IN PEROVSKITE THIN FILMS



Piezo-image of PZT/LSCO nanocapacitor reveals 90˚ domain switching for the first time



PZT cantilevers with high molecular sensitivities

NORTHERN ILLINOIS UNIVERSITY

Northwestern

UNC-CH

Maryland

UNIVERSITY OF FLORIDA

Participating Institutions and Researchers

O. Auciello, J. A. Eastman, P. Fuoss, G. B. Stephenson, S. R. Phillpot, S. K. Streiffer

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INDUSTRIAL ASSOCIATES

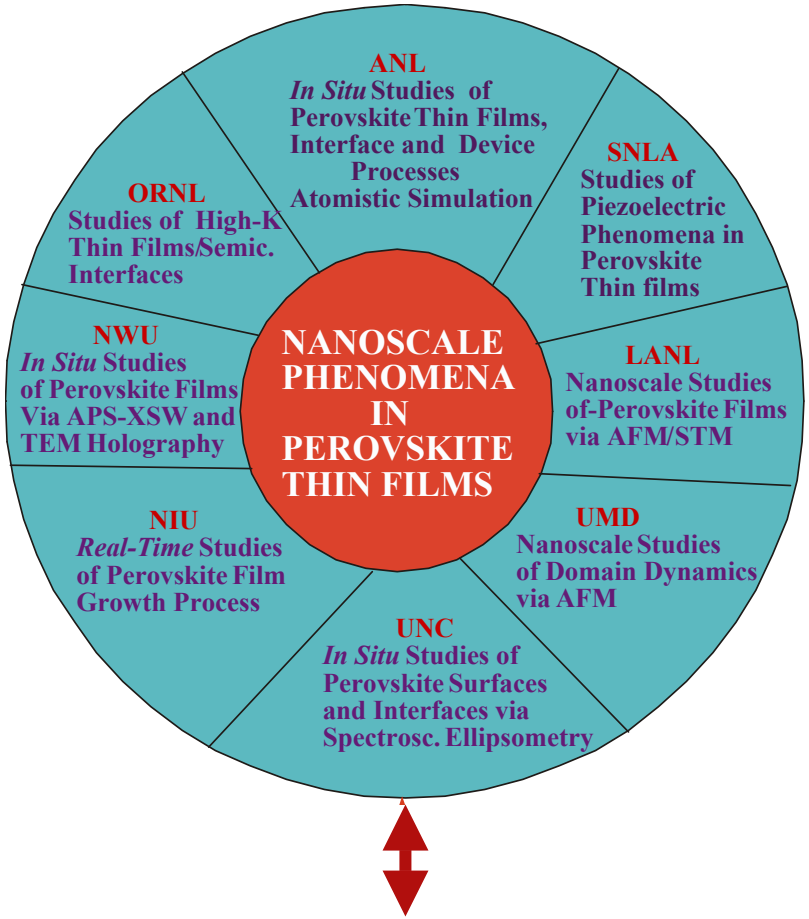
AGILENT **ATMI** **IONWERKS** **SYMETRIX**

Scope

- **Basic science**
  - Basic science of perovskite and high-k dielectric film/semiconductor interfaces
  - Basic science of established and novel piezoelectric thin films
  - Nanoscale science and technology of perovskite thin films

- **Enabling science for nanotechnologies**
  - Revolutionary gate oxides for next generation IC's
  - Novel energy storage capacitors, ferroelectric memories and dielectric tunable microwave devices
  - Novel MEMS and NEMS technology

CSP Perovskite Project Team and Research Themes



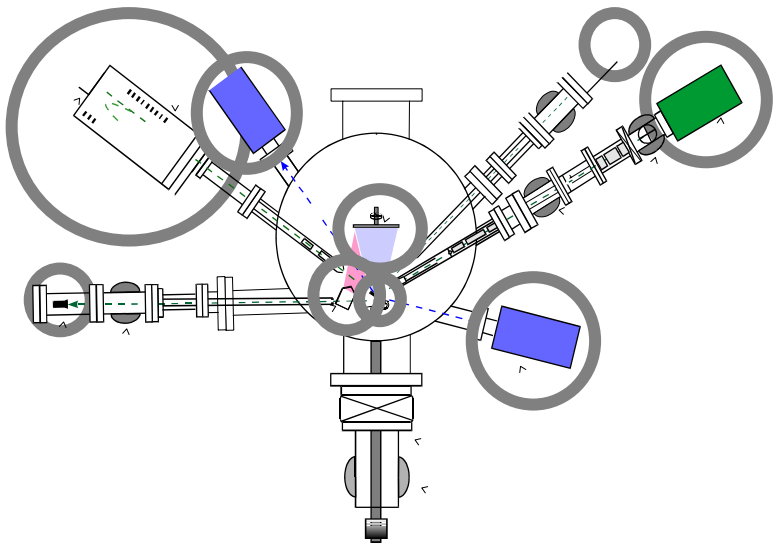
INDUSTRIES

Agilent Techn. (FERAM/High-K) ATMI (MOCVD-Perovskites)

Ionwerks (TOF-ISARS) Symetrix (FERAM/High-K)

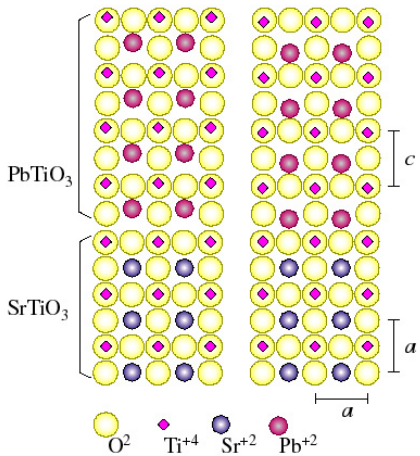
MOCVD-oxide film growth system at the BESSRC ANL-APS line for studies of perovskite film growth processes

Task 1 - Studies of Perovskite and Complex Oxide Film Growth and Interface Processes

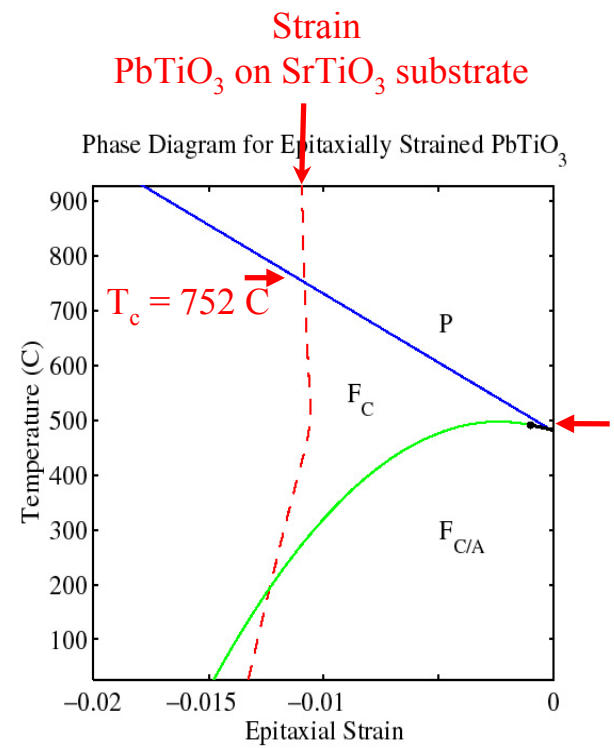


TOF-ISARS/Spectroscopic Ellipsometry system at UNC-CH for film growth and interface studies

Motivation for studies of $PbTiO_3$ Films



- **$PbTiO_3$ is a model ferroelectric material.**
- **High quality $PbTiO_3$ epitaxial thin films are produced by metal-organic chemical vapor deposition (MOCVD).**
  - **closely lattice matched to $SrTiO_3$ substrate**
  - **tetragonal axis normal to film on $SrTiO_3$thin films can be grown**
  - **that are fully lattice matched (unrelaxed)**
- **Paraelectric-to-ferroelectric phase transition T_c predicted to depend on epitaxial strain.**
  - **260°C enhancement predicted in T_c for $PbTiO_3$ on $SrTiO_3$**



after N. A. Pertsev and V. G. Koukhar *PRL* **84**, 3722 (2000).

G. B. Stephenson, J. A. Eastman,
S. K. Streiffer, O. Auciello, P. Fuoss

C. Thompson

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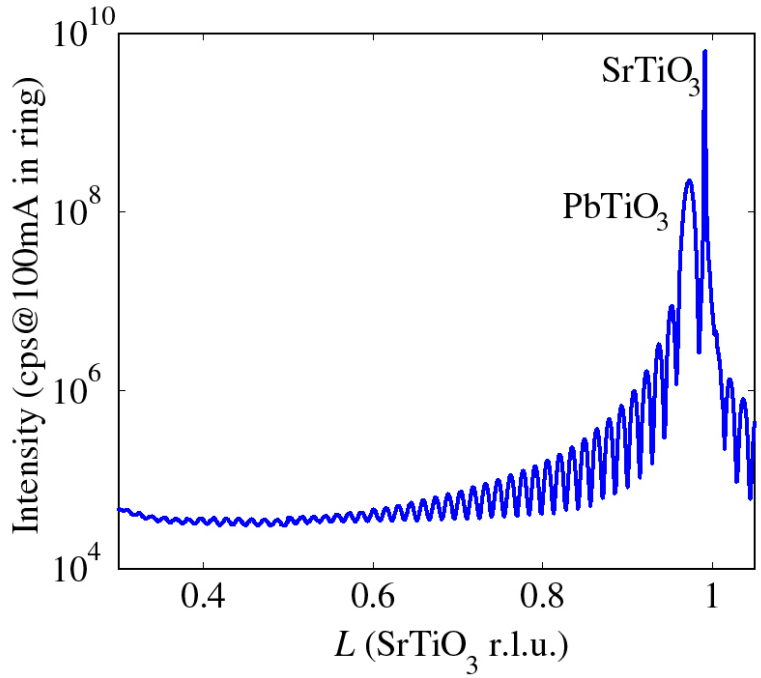
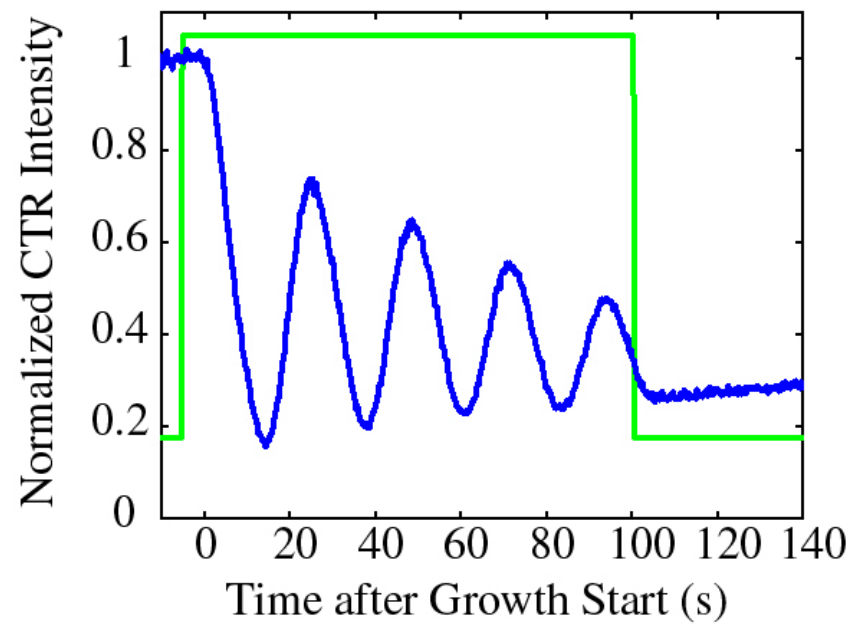
Thickness Control to Sub-Unit-Cell Accuracy



Thickness Oscillations during Growth of 9-Unit-Cell-Thick Film



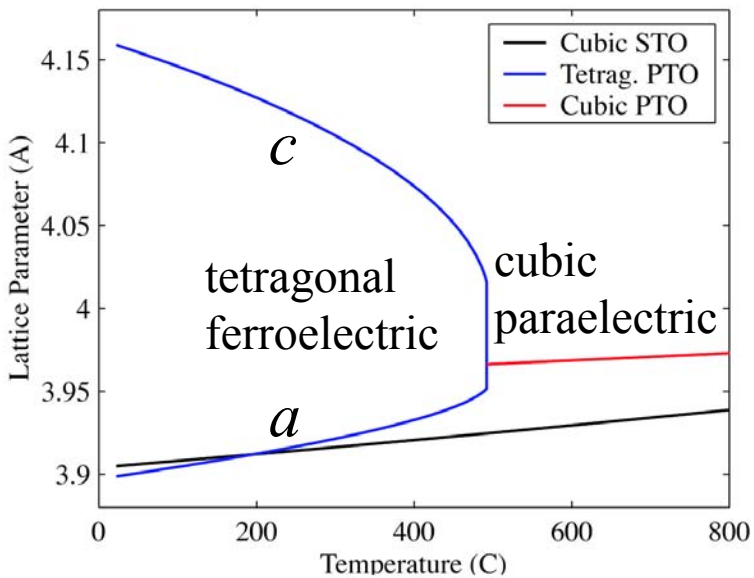
- Thickness fringes indicate atomically-smooth interfaces
- Monitor initial growth by observing formation of thickness fringes

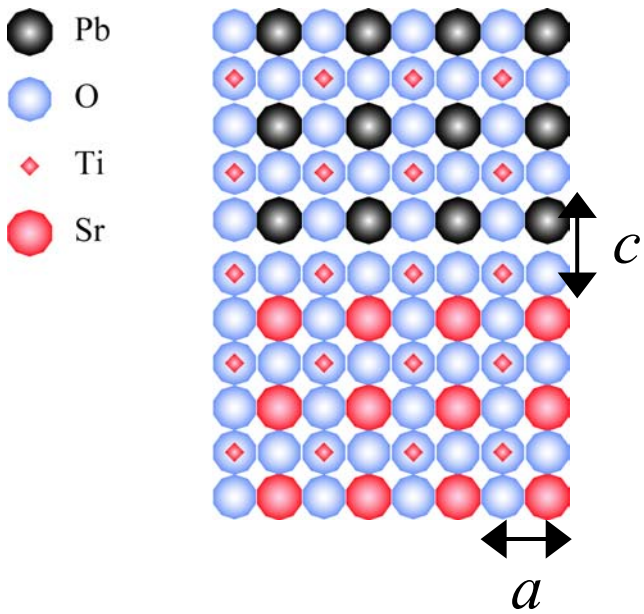
- Period of oscillations depends on L; at $L = 0.5$, period corresponds to 2 unit cells

Lattice Parameter of $PbTiO_3$ and Ferroelectricity

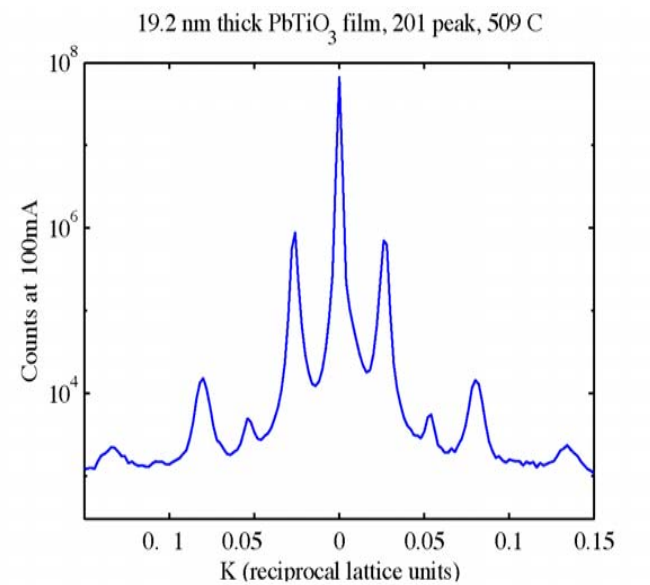
- $PbTiO_3$-on-$SrTiO_3$ misfit strain ≈ -1% at growth temperature
- Films remain coherently strained up to thicknesses of 40 nm

- Lattice parameter *a* of the ferroelectric $PbTiO_3$phase is lattice matched to the $SrTiO_3$ substrate
- This favors polarization axis (*c*) normal to the film surface

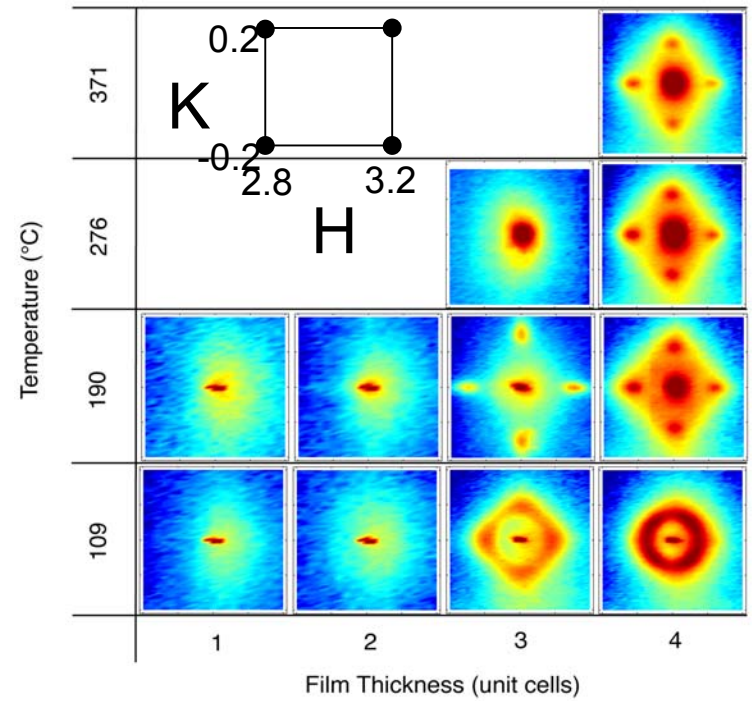




Limit of Ferroelectricity in Ultra-thin $PbTiO_3$ Films Revealed by Synchrotron X-ray Scattering



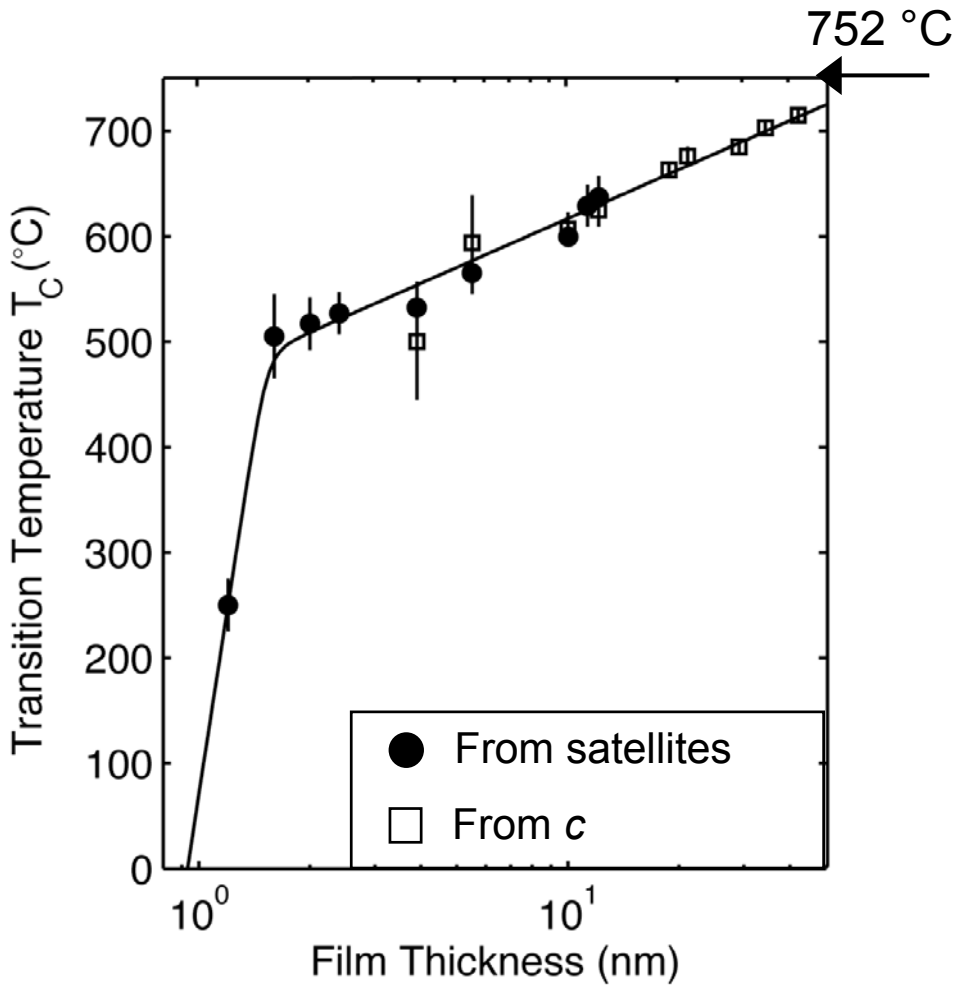
Nanoscale 180˚ ferroelectric strip domain revealed by satellite peaks around main diffraction Bragg peak in synchrotron X-ray scattering studies



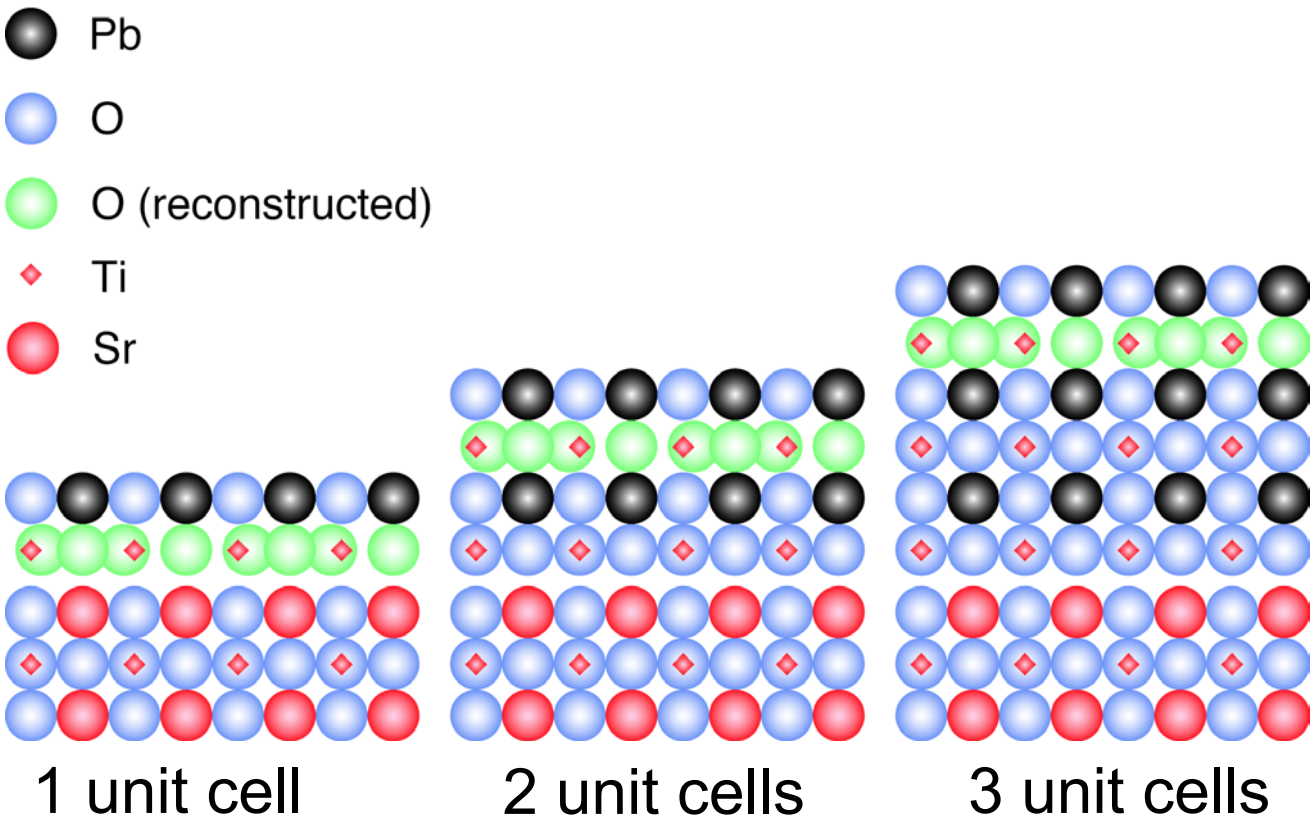
Diffuse x-ray scattering spectra reveal ferroelectric phase stable down to three-unit-cell-thick $PbTiO_3$ film (1.2 nm) with T_C ~250 °C

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
- Questions:
  - What causes dependence of T_C on film thickness?
  - Why is critical thickness 3 unit cells?

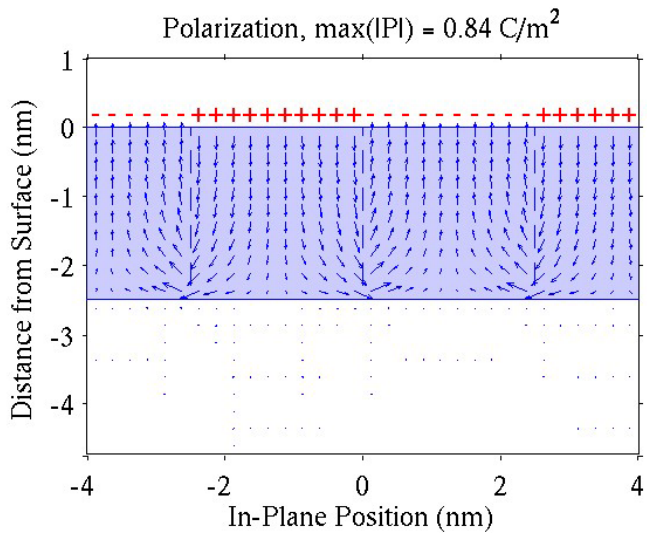


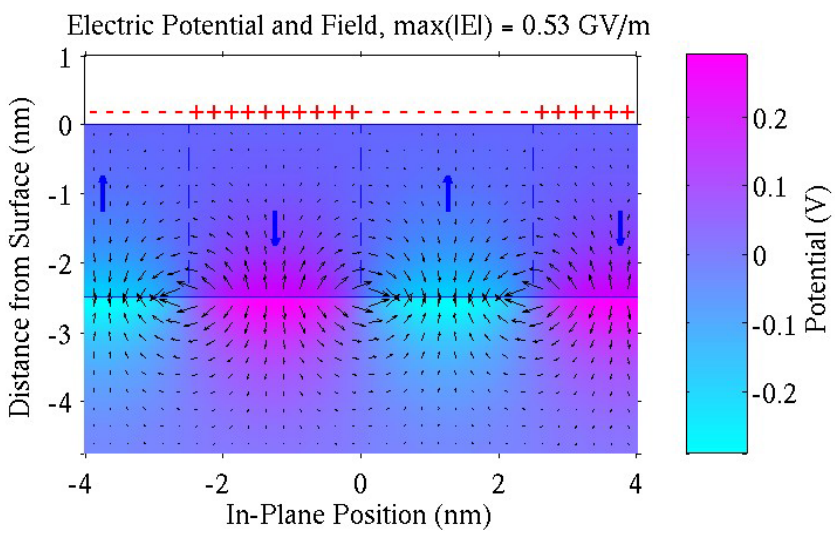
Why is Critical Thickness 3 Unit Cells?



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

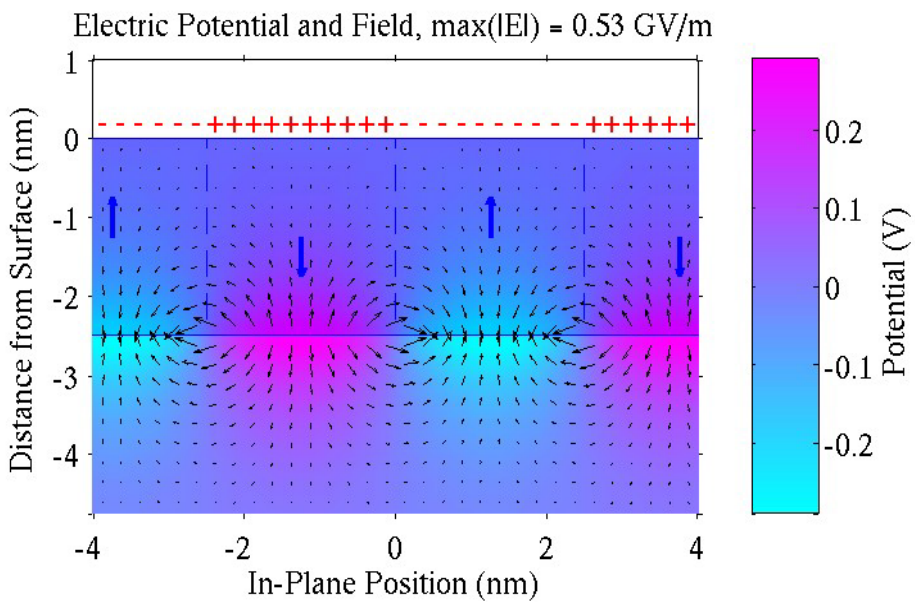
Polarization and Field Distributions





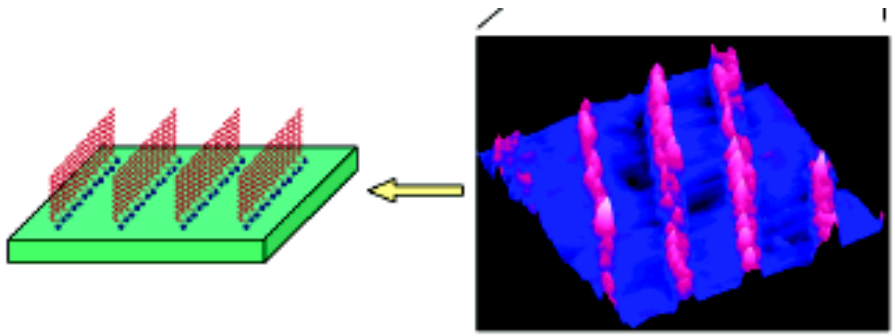
- Observed stripe period agrees with theory
- In our case, assume upper surface is compensated by free charge, $\rho_S = \pm 3.5\times10^{14}\ e/\mathrm{cm}^2$, so that electric fields are localized at interface with substrate
- Suppression of T_C from theory is smaller than observed

Using Ferroelectric Domains as Templates



- Charges compensating the surface can be exchanged with species of interest.
- This could provide self-assembled patterning on the nanometer scale.

- Groups are beginning to use this idea to template materials on the micron scale.
- **Our domains are on nanometer scale.**

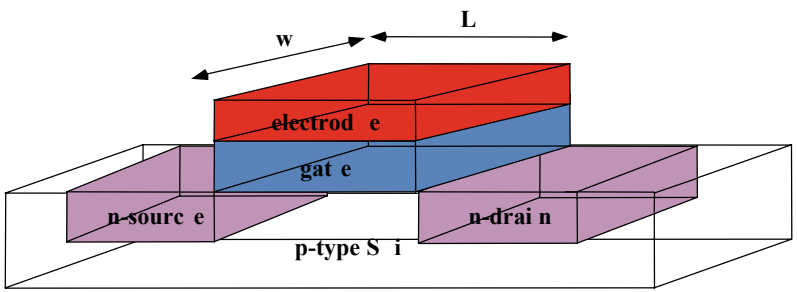


Kalinin et al. Nanoletters 2 (2002) 589

New High-k Gate Dielectric Needed in Next Generation Nanoelectronics due to Limitation of SiO_2

MOSFET

$C = \varepsilon_{sio_2} L.w / t_{sio_2}$ $\varepsilon_{sio_2} = 3.9$

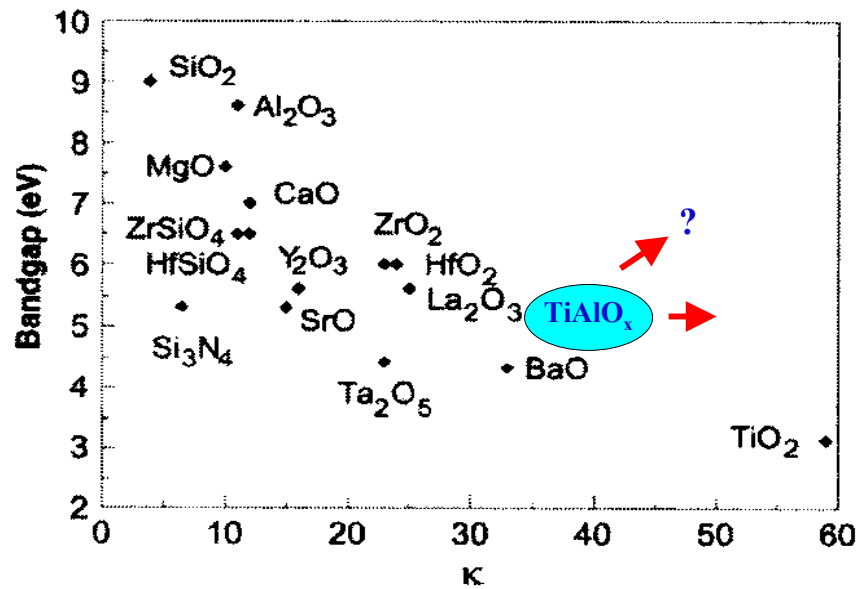


$L \downarrow \rightarrow$ $t_{sio_2} \downarrow \rightarrow$ C = constant

at $t_{sio_2} = 10$ Å scaling breaks down due to either pinholes in SiO_2 layer and/or e^- tunneling through gate into electrode layer

NEED HIGH-K LAYER

$t_{high\text{-}k} = \varepsilon_{high\text{-}k}\, t_{eq}/3.9$

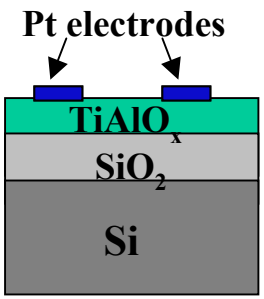


Next generation of nanoscale microchips requires a new paradigm in materials for CMOS(high-k dielectrics). $TiAlO_x$ alloy may be the material

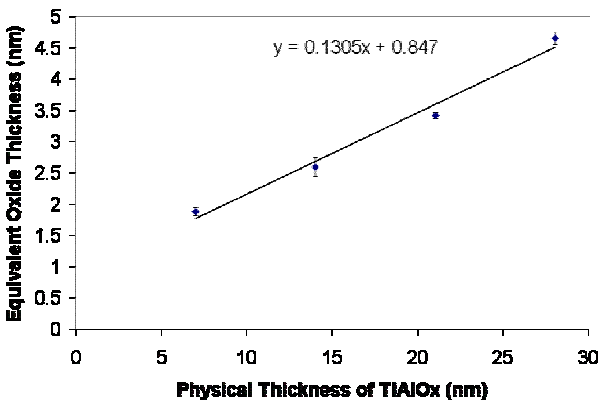
$TiAlO_x$ combined bandgap and dielectric constant goes beyond the limits of current high-k layers proposed as alternative gates for next generation of microcircuits

W. Fan, S. Saha, B. Kabius
O. Auciello, J.A. Carlisle,
C.M. Lopez, N.A. Suvarova
E.A. Irene
R.P.H. Chang

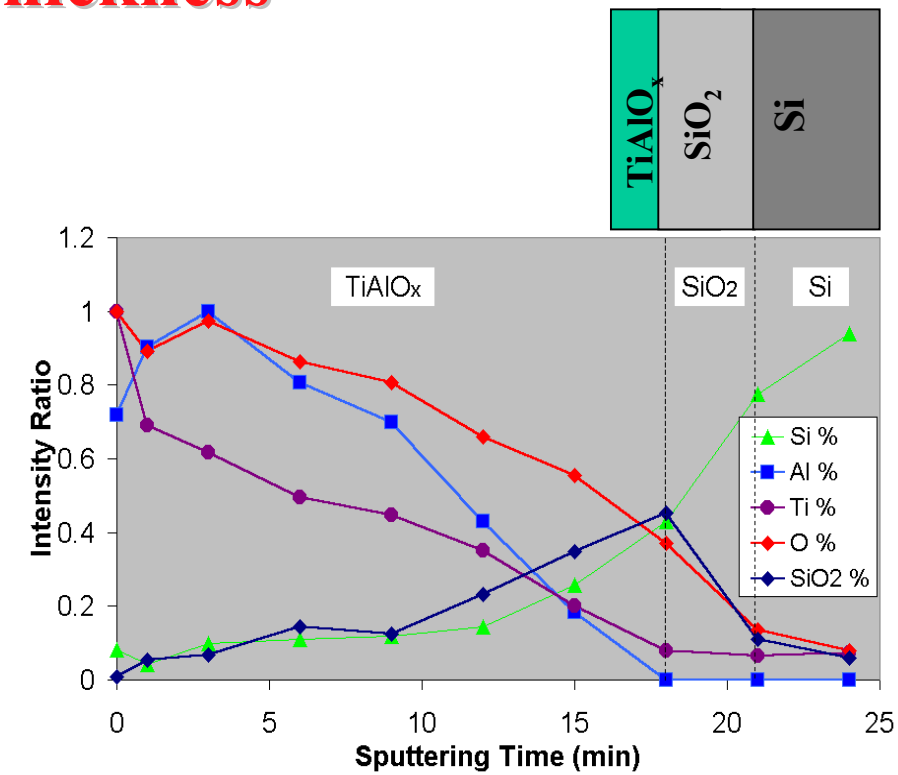
Analysis of $TiAlO_x$ / Si and SiO_2 Equivalent Oxide Thickness



$$C = \varepsilon_o \, k \, A / t$$



SiO_2 EOT vs $TiAlO_x$ physical thickness shows that the SiO_2 IL is ~ .9 nm



$TiAlO_x$ (7 nm) / Si oxidized with atomic oxygen at 500°C reveals ~ 1nm thick SiO_2 interfacial layer

Consideration of thermodynamics and kinetics of Ti and Al preferential oxidation with respect to Si and dielectric characteristics of TiO_2 and Al_2O_3 provided the insightful idea of investigating TiAl alloys as high-k dielectric layer

O. Auciello
(patent pending)

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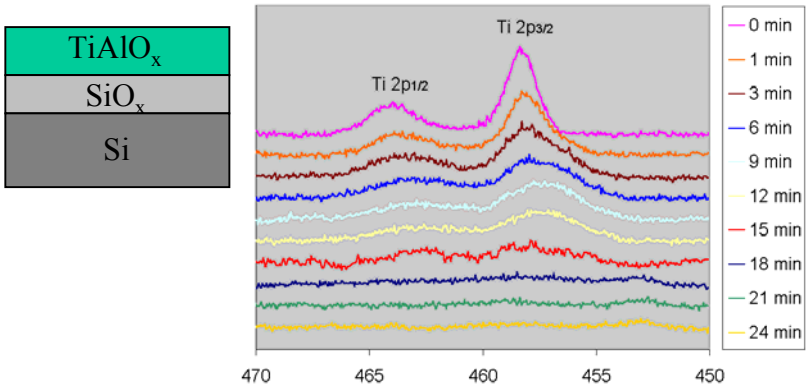
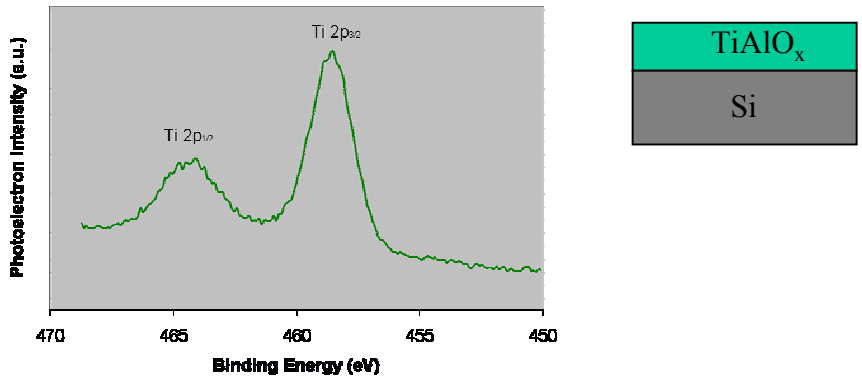
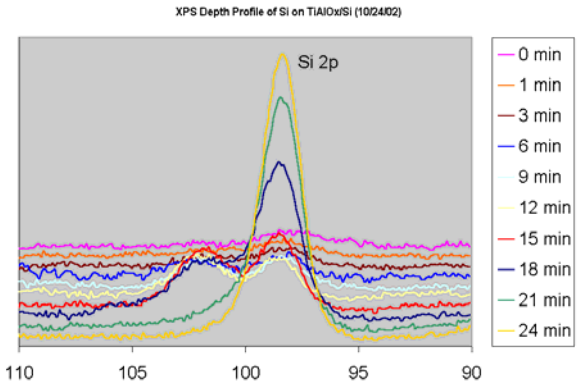
XPS Depth Profile Analysis of $TiAlO_x$/Si (500° vs RT)



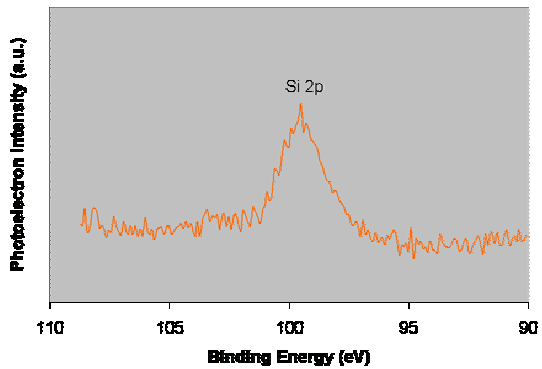
XPS depth profile of $TiAlO_x$ (7 nm) / Si oxidized w/ atomic oxygen at 500 °C shows TiOx peaks down to the TiAlOx/Si interface



XPS depth profile of $TiAlO_x$ (7 nm) / Si oxidized w/ atomic oxygen at RT shows TiO_x peaks down to the TiAlOx/Si interface



XPS shows both Si and SiO_2 peaks at the $TiAlO_x$/Si interface indicating the presence of a SiO_2 interfacial layer



XPS shows only a Si peak at the $TiAlO_x$/Si interface indicating that oxidation at RT practically eliminates SiO_2 interfacial layer formation

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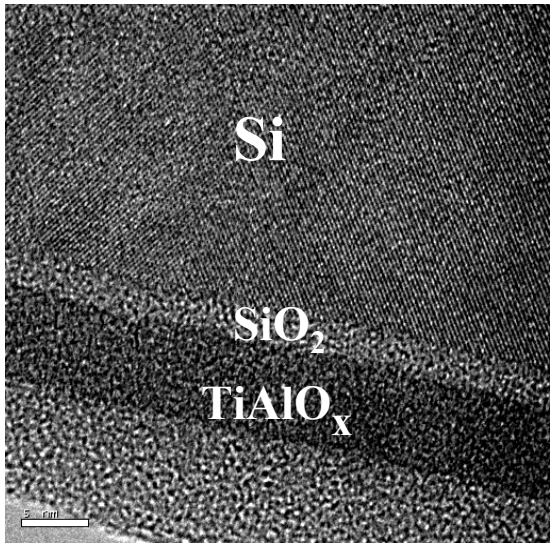
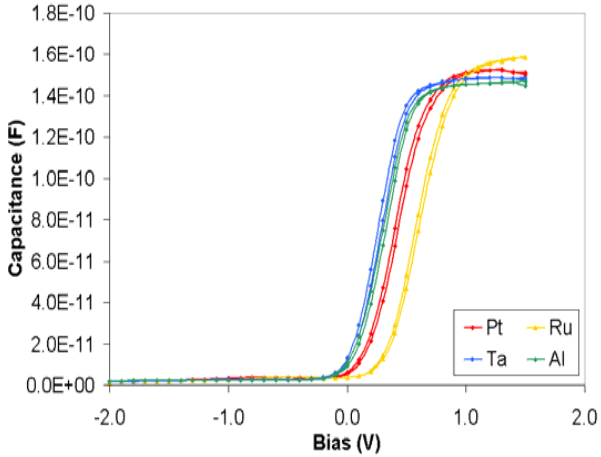
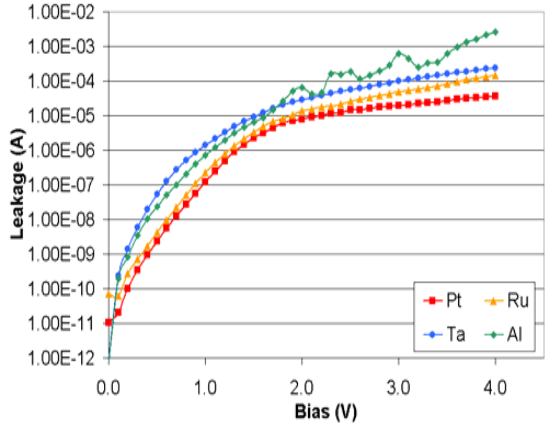
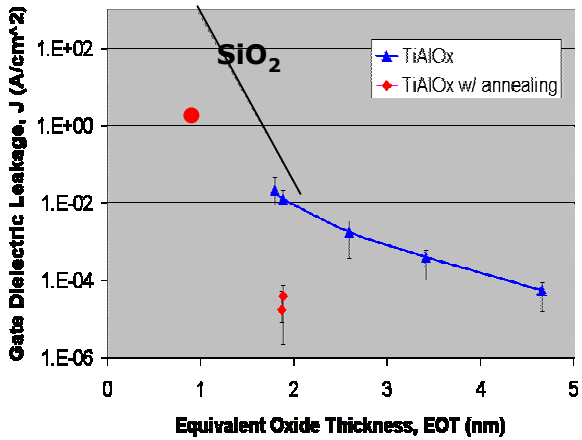
HRTEM and Electrical Properties of $TiAlO_x$ Agree in Composition, Microstructure & Properties





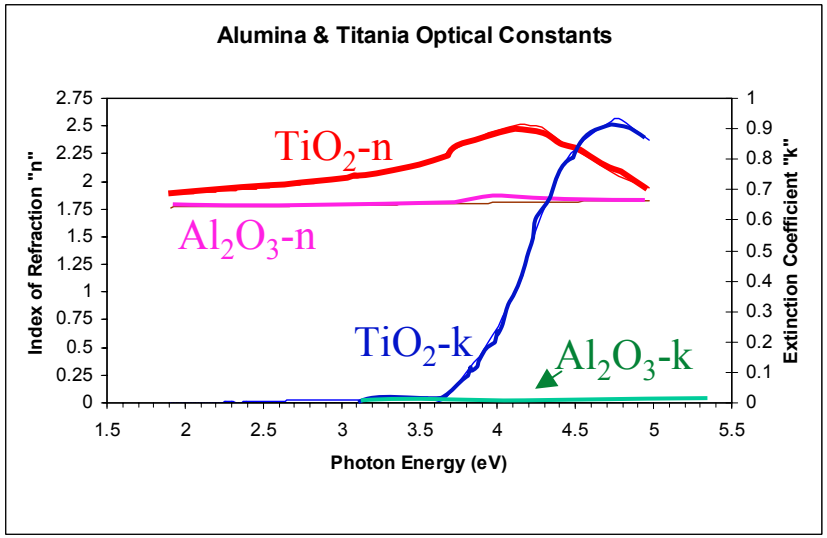


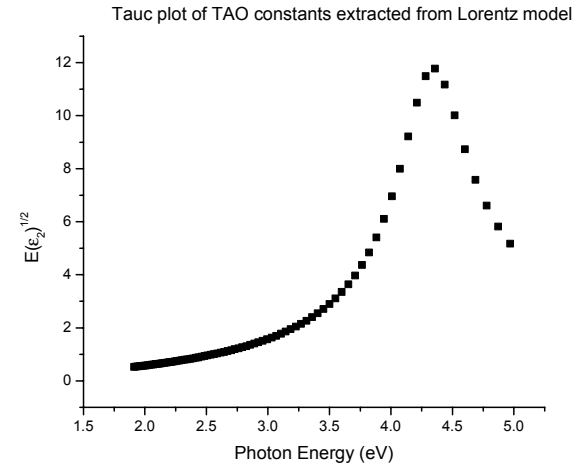
HRTEM of TiAlOx/Si heterostructure after oxidation of TiAl layer at 500 ˚C reveals a ~ .9 nm thick SiO_2 interfacial layer and a clear amorphous microstructure in the $TiAlO_x$ layer

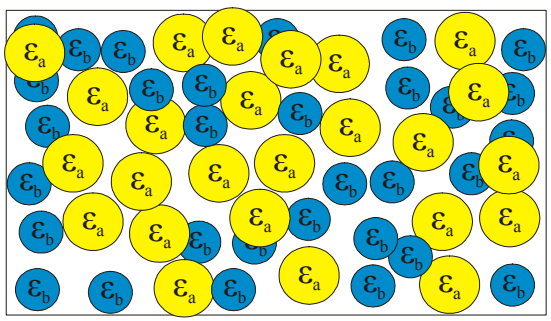


$TiAlO_x$ alloy layers exhibit excellent electrical properties although they have not been optimized yet

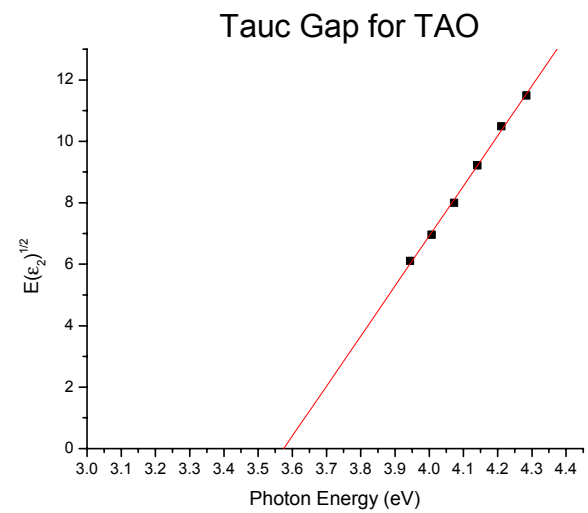
Bandgap and Optical Properties of $TiAlO_x$ Layers Measured via Spectroscopic Ellipsometry







- Al_2O_3
- TiO_2



- **Bruggeman Effective Medium Approximation (BEMA)**

  Mixed Composition, Inhomogeneous

Silicide/Oxide Interfaces Heteroepitaxy and Electrostatic Boundary Conditions for the Study of Domain Dynamics

- **Knowledge of path-dependent process and structure series for growing crystalline oxides on semiconductors (COS)**

- **Submonolayer silicides play a critical role in COS**

- **Studies of structure specific interface electrostatics:**
  - Studies to understand how the silicide phases develop and how the transition from the silicide to the oxide occurs.

R. McKee

M.J. Bedzyk

O. Auciello

Summary of Accomplishments

In Situ Synchrotron X-Ray Scattering Studies of Perovskite Films

- **Observed predicted increase of T_c due to film strain thick films**
- **180° stripe domains appear upon cooling through T_c =» *depolarizing field significant***
- **Films as thin as 3 unit cells are ferroelectric at room T =» *stripe domains are effective at neutralizing depolarizing field***

Nanoscale Studies of $TiAlO_x$ Alloy as a High-k Dielectric Layer

- **A $TiAlO_x$ alloy layer provides a novel amorphous oxide hybrid candidate with high permittivity and low leakage to replace SiO_2 for the next generation of gate dielectrics**

- **Initial studies of oxidation processes and composition-microstructure-property relationships of $TiAlO_x$ alloy provided insights into fundamental physical, chemical and structural processes critical to the optimization of the properties of $TiAlO_x$ thin films**

Future Work

In Situ Synchrotron X-Ray Scattering Studies of Perovskite Films

- Vary epitaxial constraint: $Pb(Zr_xTi_{1-x})O_3$ on $SrTiO_3$, and other substrates (e.g., conductive $SrRuO_3$); vary electrical boundary conditions
- Use of stripe domains as templates
- Study effects of lateral patterning on domain structures

Nanoscale Studies of $TiAlO_x$ Alloy as High-k Amorphous Dielectric Layer

- Study synthesis of $TiAlO_x$ alloy layer via MBE and ALD to investigate whether deposition methods with atomic layer resolution provide better control of composition and microstructure and yield better properties
- Add Prof. Darrell Schlom (PennState University) to the team working on high-k dielectrics with ANL

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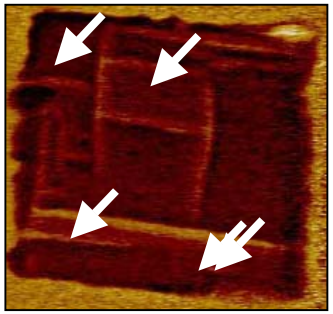
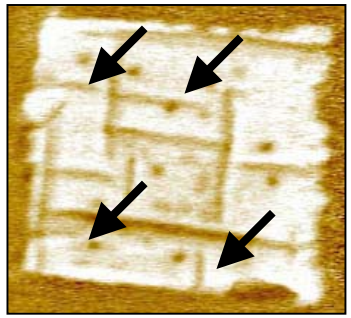
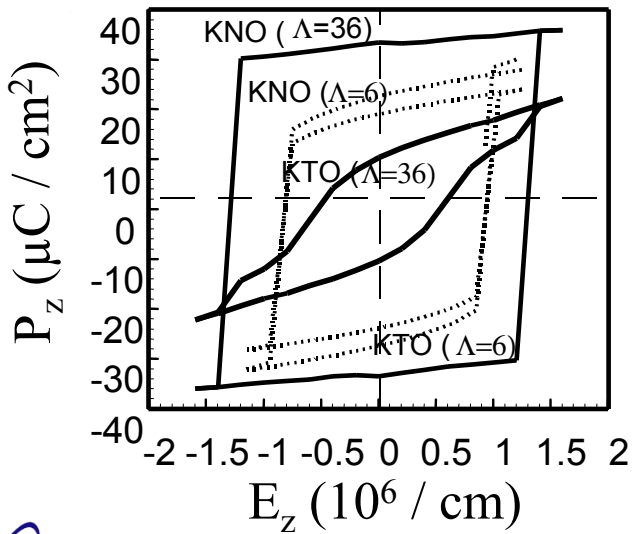




90° Ferroelectric domain motion observed for the first time in nanostructured capacitors

Task 2 - Nanoscale Structure- Property Relationships in Perovskite Systems

Computer simulations provide insights into perovskite superlattices



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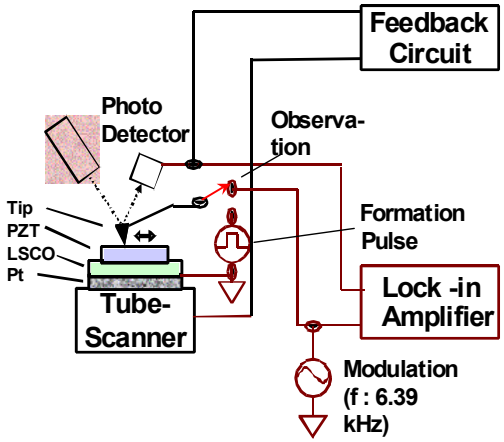
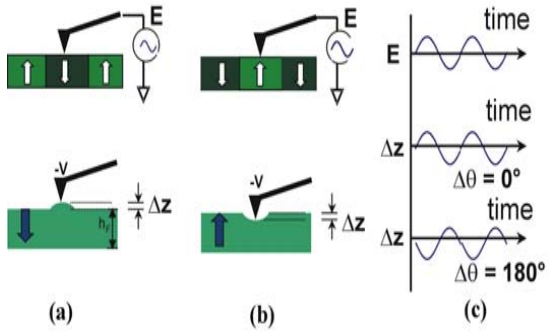
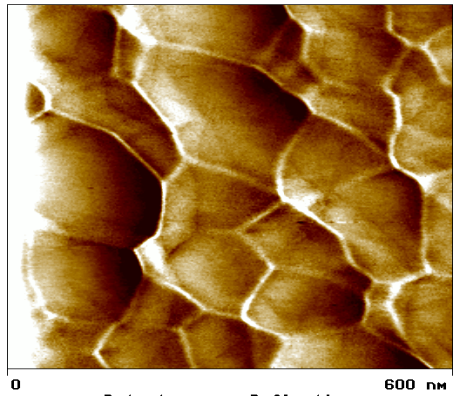
AFM Piezoresponse Imaging for Studying Domains



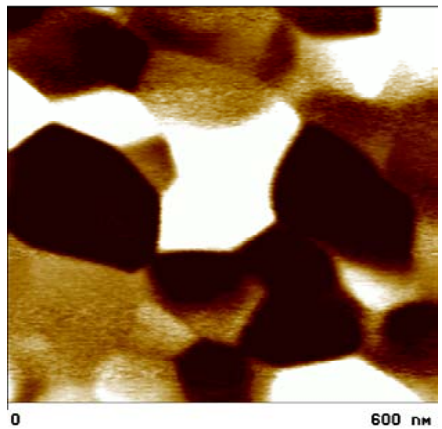
Schematic of AFM piezoresponse imaging system for nanoscale studies of ferroelectric domains



Polarization domains created in a ferroelectric film by application of electric fields between the top electrode (AFM tip) and the bottom electrode layer of a capacitor



Topography Image



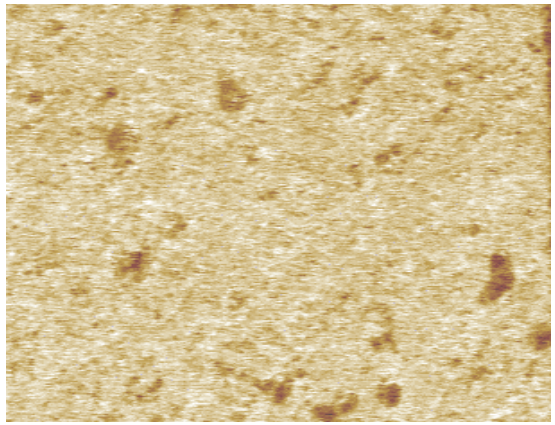
Piezoresponse Domain Image

D.J. Kim, O. Auciello

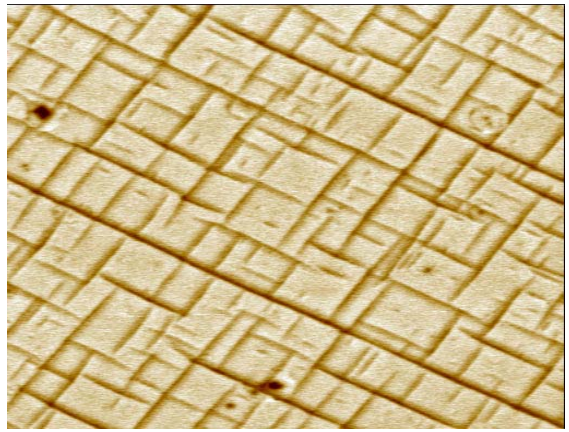
ARGONNE NATIONAL LABORATORY

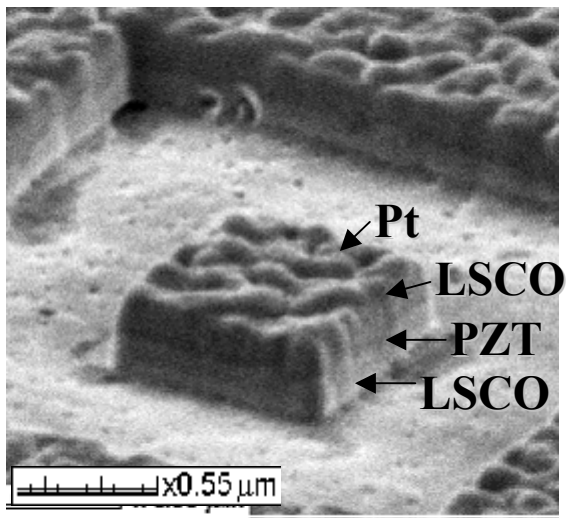
N. Valanoor
R. Ramesh

AFM Piezoresponse Imaging of 90° Ferroelectric Domains in Micro- and Nanostructured Capacitors

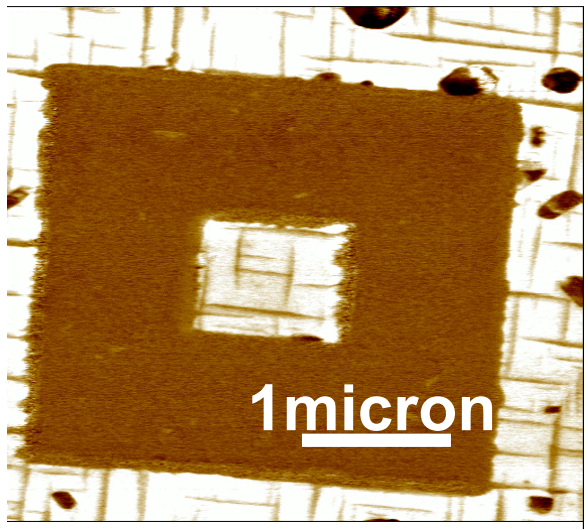


Micro





Nano



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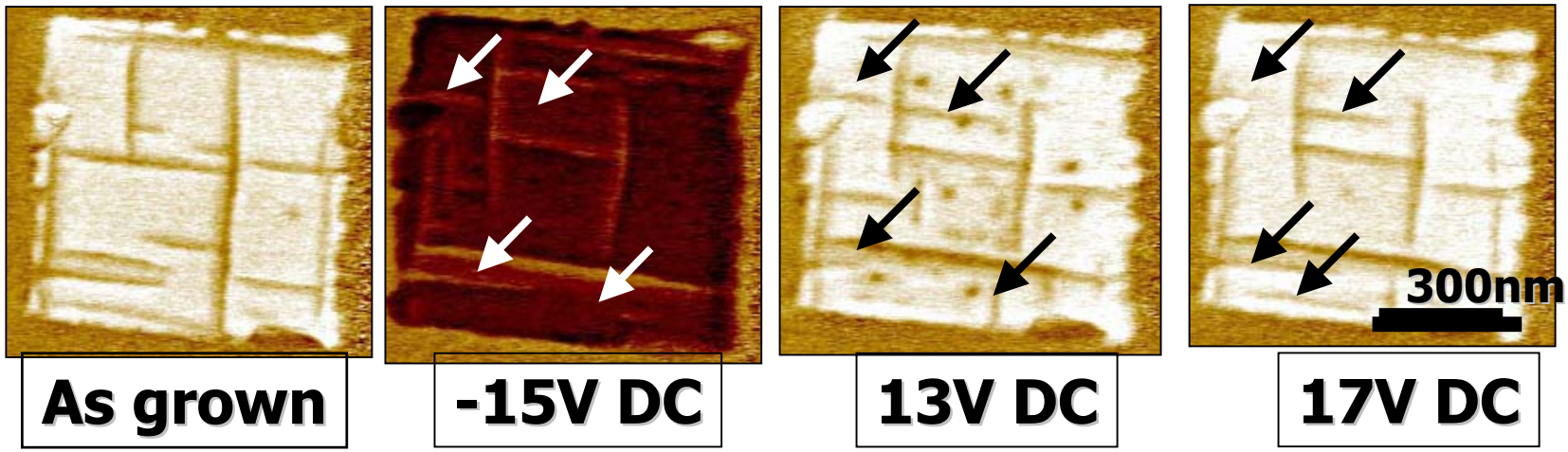
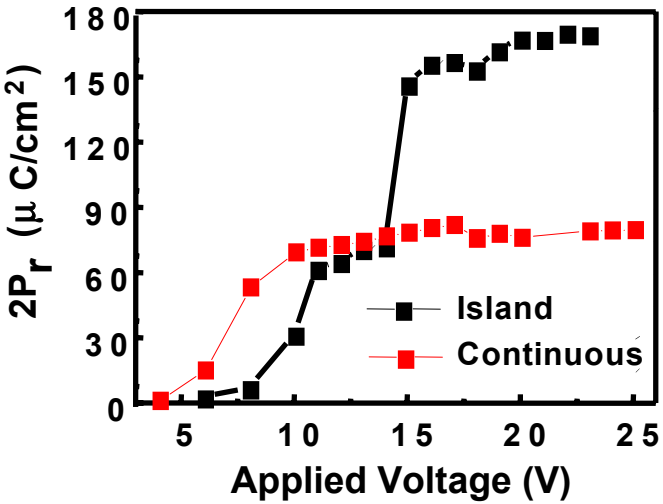
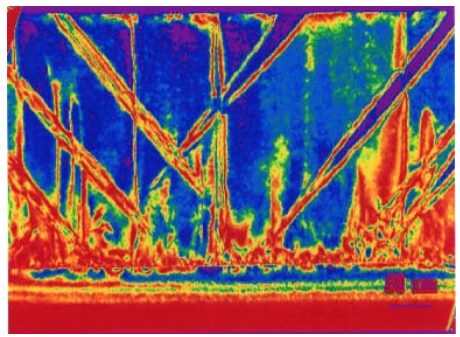
Motion of 90° Domain Walls (Switching) Seen for the First Time in Nanostructured Capacitors





90°domain wall motion switching in PZT nanocapacitor results in higher polarization



Cross-section TEM shows 90° ferroelectric domains in PZT

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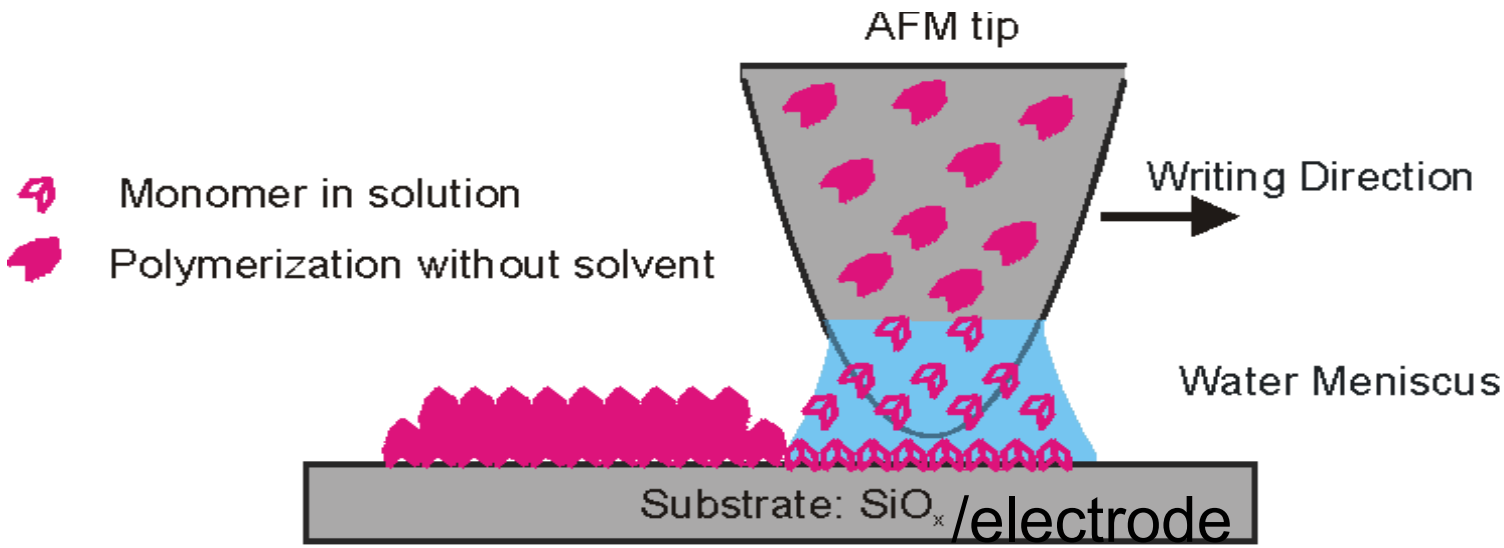
Direct Sol-Derived Dip-Pen Nanopatterning

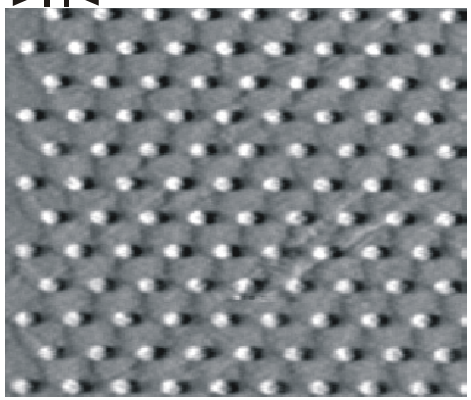


V.P. Dravid

O. Auciello

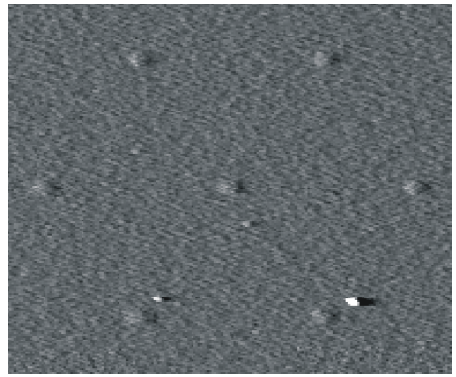
Nanodot Arrays of PZT on gold substrate

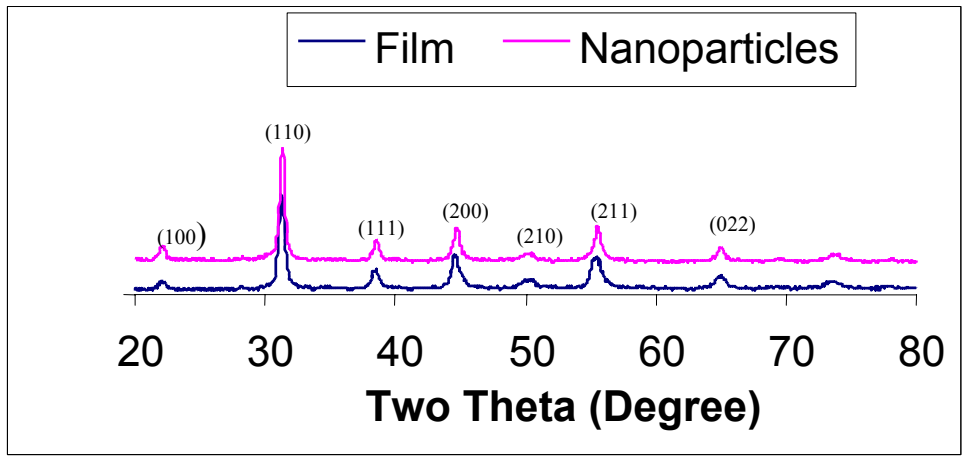
150 nm



Thermal Treatment
650° for ~ mins

70 nm





Summary and Future Work on Nanocapacitors and Piezoresponse Imaging of Domains

Current Results

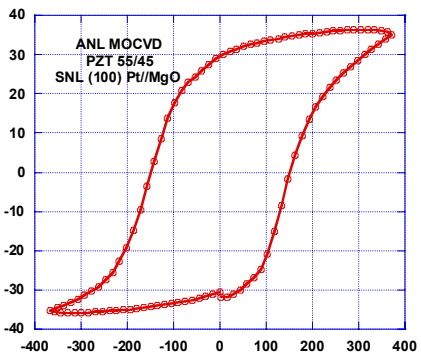
- Studies of polarization dynamics in nanostructured ferroelectric capacitors fabricated with FIB demonstrated for the first time switching of 90˚ domains
- Initial studies to develop DPN patterning of ferroelectric nanocapacitors

Future Work

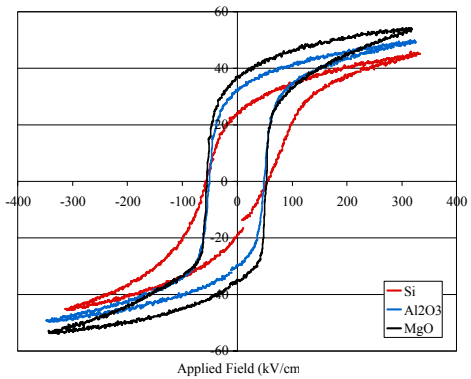
- Fabricate Nanocapacitors using e-beam lithography and self-assembly approaches
- Studies of polarization dynamics in nanostructured ferroelectric capacitors fabricated by e- beam lithography, DPN, and self-assembly approaches

Stress-Induced Orientation and Piezoelectric & Dielectric Properties of PZT Thin Films

- PZT films fabricated by MOCVD (ANL) and CSD (SNL) permits wide range of structural evolution
  - Single crystal to fine grain mono- 90° domain polycrystalline materials
  - 100% a-domain PZT films possible with UMD (100) $SrTiO_3$ on Si substrates
  - AFM (LANL and UMD) to characterize growth and piezoelectric response
  - FIB to determine size - domain effects on ferroelectricity



ANL-MOCVD PZT (55/45) film exhibit good dielectric hysteresis



SNL CSD PZT 40/60 Films exhibit increased polarization w/c-axis orientation (tested up to 1MV/cm)

	On Alumina	On MgO	On Silicon	ANL-MgO
P Max	34	40	30	35
Premanent	29	33	22	30
K	710	506	980	748
d31	42	57	37	36

Dielectric Constant @ 1 kHz/0.1 V ac

- ANL-MOCVD PZT 55/45 film (0.85 µm) on (100) Pt // MgO
- Other films: SNL CSD PZT 40/60 (0.75 µm)

B. Tuttle, P. Clem, J. Dawley, G. Brennecka, D. Williams, J. Wheeler, W. Olson

Sandia National Laboratories

G. Bai, S.K. Streiffer, O. Auciello

ARGONNE NATIONAL LABORATORY

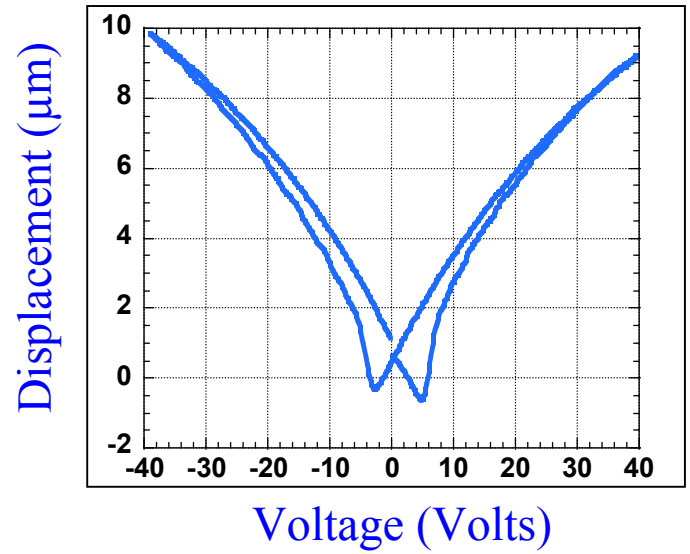
M. Hawley

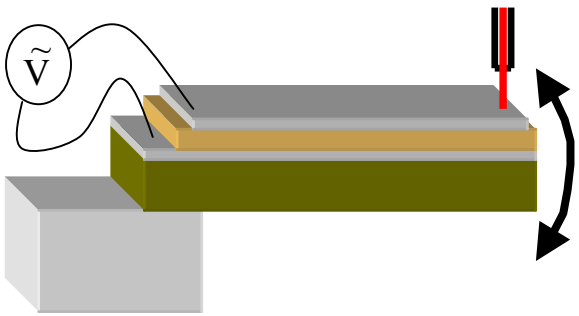
Los Alamos NATIONAL LABORATORY

R. Ramesh, N. Valanoor

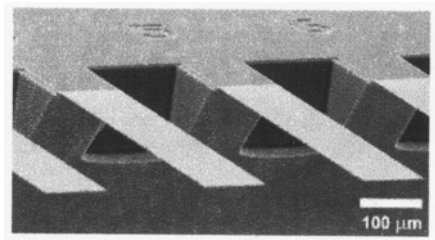
Impact of Nanoscale Genesis of Domains on Piezoelectric and Dielectric Response

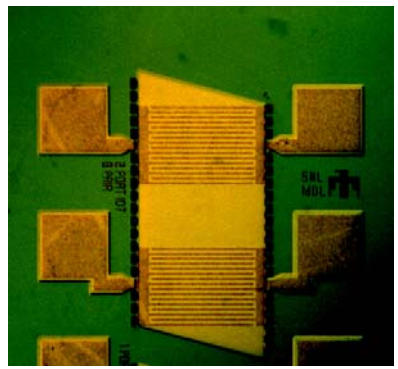
- Domain Orientation Influence on Piezoresponse
- Films: ANL MOCVD, SNL CSD, UMD MBE/PLD
- Crystallinity: Random Polycrystalline ensembles to Oriented Single Crystal
- SNL Supplied Thin Si and Highly 001 Oriented Pt /MgO Substrates to ANL
- SNL Characterized Piezo Response of CSD PZT on Pt coated MgO and Si Wafers





MEMS PZT Film Molecular Detection Devices





Cantilever Beams With Different Molecular Sensitivities

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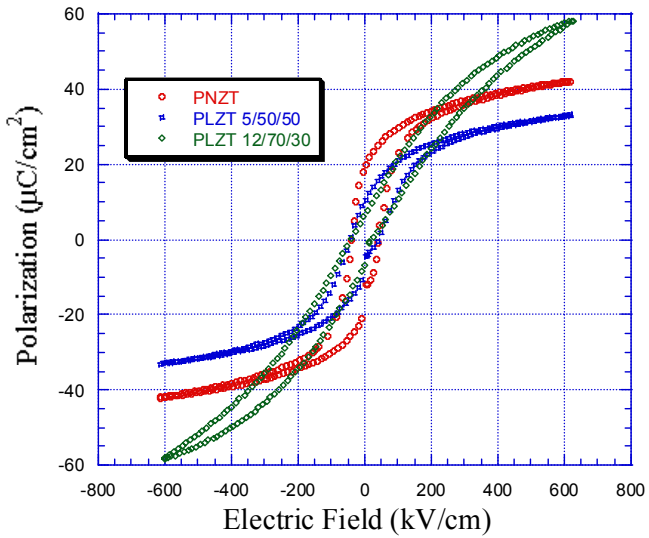
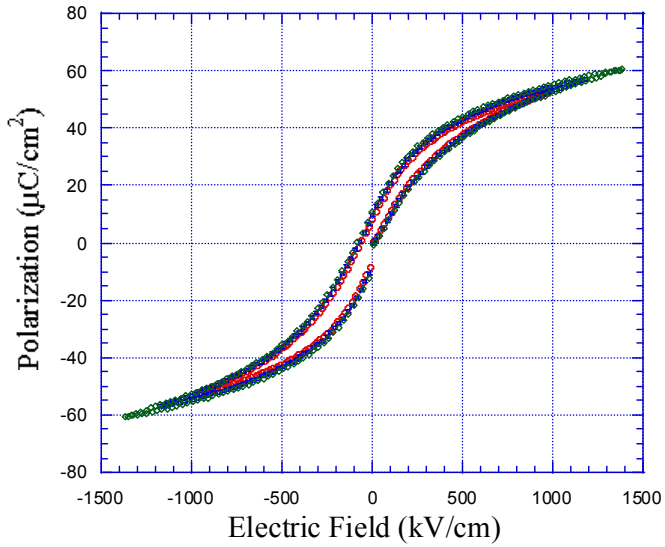
Properties of Volumetrically Efficient Thin Film Capacitors for Integrated Micro-Systems



PNZT and PLZT Films



PLZT 12/30/70

	K	*d.f.*
PLZT 5/50/50	775	0.018
PNZT 5/50/50	1069	0.024
PLZT 12/70/30	1205	0.025

Elect. Diameter: 700 μm

Film Thick.: 0.4 - 0.6 μm

Breakdown Strength:1.5 MV/cm (0.6 μm thick)

Linear Approximation:

E_D = 22 J/cm^3 Dielectric Only

E_D = 16.5 J/cm^3 with electrode

Sandia National Laboratories

Summary of Results on Control of Dielectric and Piezoelectric Properties of PZT Thin Films

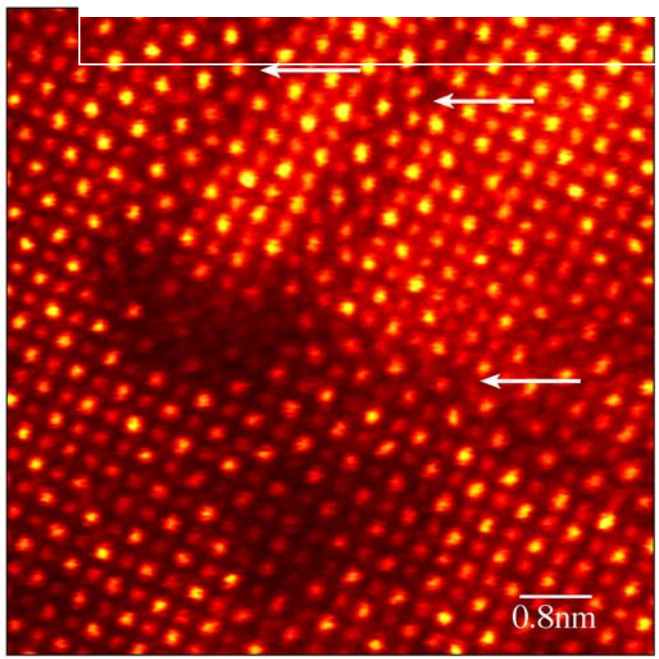
Present Work

- 90° domain structure can be tailored by controlling the stress state of the film during cooling through the Curie Temperature
- Properties of stress-oriented films follow trends predicted by single crystal calculations
- Work on Zr-rich PZT thin films reveal that control of composition leads to tailored properties such as high breakdown fields
- PZT-based cantilevers provide platform for molecular sensors

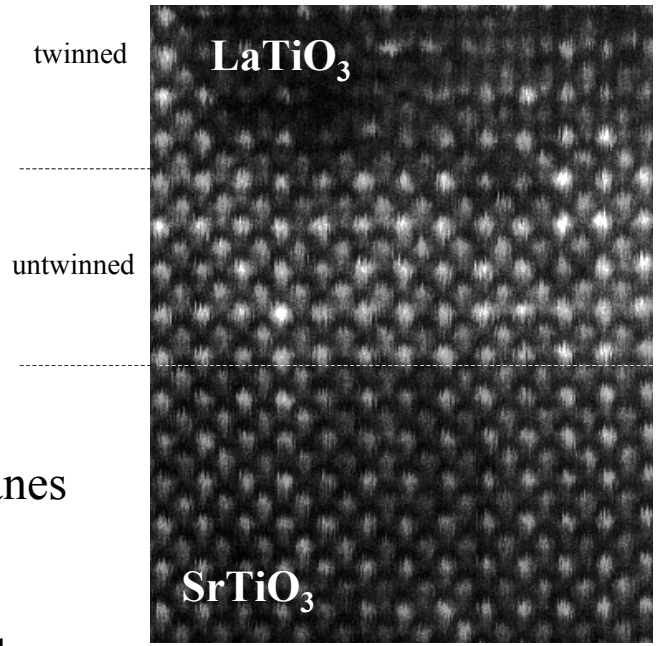
Future Work

- Focus on properties of PZT-based cantilevers for molecular sensors

Planar Defects in Epitaxial $LaTiO_{3+x}$ Films on $SrTiO_3$



- Twinned structure indicates insertion of oxygen planes
- First few unit cells do not undergo phase transition
  - transport properties of strained layers?

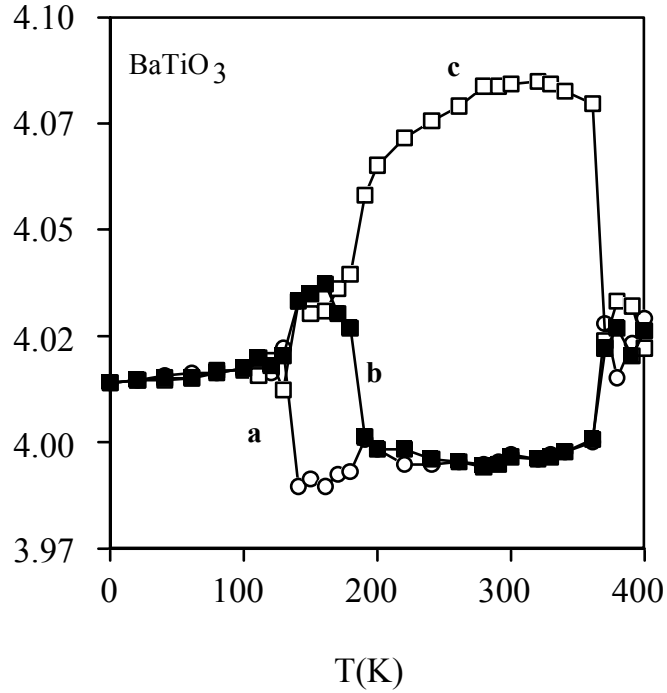


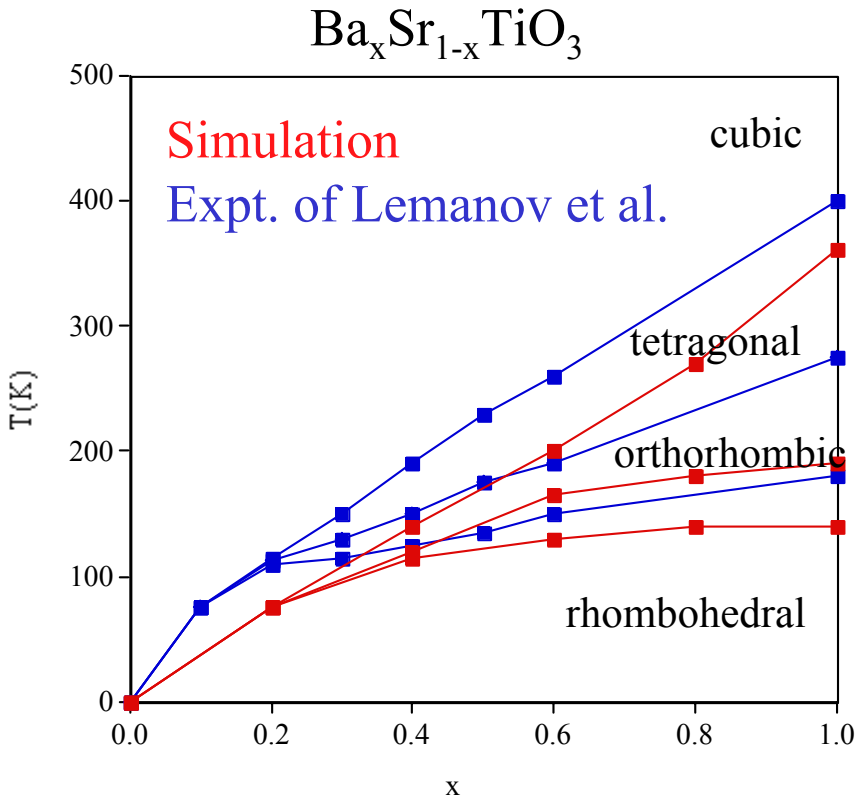
- Distortion of the $LaTiO_{3-x}$ cubic unit cell at (110 faults)
- Fault is created by the intercalation of O along {110} planes
- The $La_5Ti_5O_{17}$ phase is present between the two faults arrowed at the top of the image
- Arrowed {110} faluts distort the $LaTiO_{3+x}$ cubic unit cell and locally raise the valence of Ti

D.P. Norton
UNIVERSITY OF FLORIDA

L. Boatner
M. Chisholm

Phase diagram of $BaTiO_3$ & $Ba_xSr_{1-x}TiO_3$ by Simulation





	Expt.	Simn.
Transition temperatures	400K	350K
	280K	180K
	180K	130K

- Reproduce phase diagrams
- Elucidate relationship between local structure and local ferroelectric properties

Tinte, Stachiotti, Phillpot, Sepliarsky, Wolf and Migoni (submitted to J. Phys. Cond. Matt.)

S. Phillpot

ARGONNE NATIONAL LABORATORY

Summary from Work on Oxides with Highly Correlated Electrons and Perovskite Superlattices

Present Work

- Understanding of para to ferromagnetic transitions and electronic stripe phases
- Understanding of planar defects in epitaxial $LaTiO_{3+x}$ films on $SrTiO_3$

Future Work

- Focus on continuous studies of perovskite super-lattices both experimentally and via computer simulations

Summary of Results from Work on Oxides with Highly Correlated Electrons and Perovskite Superlattices

Present Work

- Understanding of para to ferromagnetic transitions and electronic stripe phases
- Understanding of planar defects in epitaxial $LaTiO_{3+x}$ films on $SrTiO_3$

Future Work

- Focus on continuous studies of perovskite super-lattices both experimentally and via computer simulations

Summary of Results from Computer Simulations

Present Work

- **Achieved new insights into behavior of multilayer perovskite thin films**

Future Work

- **Will investigate new perovskite multilayers**

Scientific and Technological Payoff

- New understanding in how to precisely control fabrication of perovskite films (important class of complex oxides)
- Improved understanding of the relationship between processing, structure and properties - critical for advancing perovskite-based technologies
- New understanding of ferroelectric properties (domain dynamics) at the nanoscale
- Potential for opening new avenues in nanoscience and nanotechnology

Management Plan

- **Center coordinators**
  - Orlando Auciello - ANL
  - Duane Dimos - SNL

- **Funding - $300K / Year**
  - Three post docs and six students
    - Post docs/Students to work on collaborative projects
  - $20K - annual workshop

- **Conference calls - Videoconferencing - Website**

- **Annual workshop to recalibrate priorities/budget**

  - **2003 CSP Workshop held at Sandia National Laboratory on March 17**

Summary of Publications and Presentations

Publications:	**30**
Patent Applications:	**5**
Invited Presentations:	**40**
Contributed Presentations:	**9**

Publications

G. B. Stephenson, D. D. Fong, M. V. Ramana Murty, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, A. Munkholm, M. E. M. Aanerud, and Carol Thompson, *In situ x-ray studies of vapor phase epitaxy of $PbTiO_3$*, (in press **Physica B** (2003)).

S. K. Streiffer, J. A. Eastman, D. D. Fong, Carol Thompson, A. Munkholm, M. V. Ramana Murty, O. Auciello, G. R. Bai, and G. B. Stephenson, *Observation of Nanoscale 180° stripe domains in ferroelectric $PbTiO_3$ thin films*, **Phys. Rev. Lett. 89** (2002) 067601.

M. V. Ramana Murty, S. K. Streiffer, G. B. Stephenson, J. A. Eastman, Carol Thompson, G. -R. Bai, A. Munkholm, O. Auciello, *In situ x-ray scattering study of $PbTiO_3$ chemical vapor deposition*, **Appl. Phys. Lett. 18** (2002) 108.

A. Munkholm, S. K. Streiffer, M. V. Ramana Murty, J. A. Eastmen, Carol Thompson, O. Auciello, L. Thompson, J. F. Moore, and G. B. Stephenson, *Antiferrodistortive reconstruction of the $PbTiO_3$ surface*, **Phys. Rev. Lett. 88** (2002) 016101.

M. V. Ramana Murty, S. K. Streiffer, C. Thompson, O. Auciello, A. Munkholm, G. B. Stephenson, J. A. Eastman, G.–R. Bai, *In situ X-ray Scattering Study of $PbTiO_3$ Homoepitaxy by Metal-Organic Chemical Vapor Deposition*, Advanced Photon Source User Activity Report ANL-02/6 (January 2002).

Publications (continuation)

Y.G. Wang and V.P. Dravid. "Determination of electrostatic characteristics at a 24 degrees, [001] tilt grain boundary in a SrTiO3 bicrystal by electron holography", Philosophical Magazine Letters **82**(8): 425-432 (2002).

S.Y., Chung, S.J.L. Kang, et al., "Effect of sintering atmosphere on grain boundary segregation and grain growth in niobium-doped SrTiO3", Journal of the American Ceramic Society **85**(11): 2805-2810 (2002).

M. Su, X.G. Liu, S.Y. Li, V.P. Dravid, C.A. Mirkin, "Moving beyond molecules: Patterning solid-state features via dip-pen nanolithography with sol-based inks,"J. of the American Chemical Society **124** (8): 1560-1561 (2002).

Xiwei Lin,V.P. Dravid, O. Auciello, C. Bjormander and C.M. Foster, "Dynamics of Ferroelectric Domains in PZT Thin Films", **to be submitted**, Journal of Applied Physics, June 2003.

Publications

B. T. Liu, K. Maki, S. Aggarwal, B. Nagaraj, V. Nagarajan, L. Salamanca-Riba, R. Ramesh, A. M. Dhote, O. Auciello, "Low-Temperature Integration of Lead-Based Ferroelectric Capacitors on Si with Diffusion Barrier Layer", Appl. Phys. Lett. **80**(19) (2002) 3599-3601.

A.H. Mueller, N.A. Suvorova, E.A. Irene, O. Auciello and J.A. Schultz, "Real Time Observations of Interface Formation for Barium Strontium Titanate Film on Silicon", Appl. Phys. Lett. **80** (2002) 3796-3798.

O. Auciello, A.M. Dhote, R. Ramesh, A. Mueller, and E.A. Irene, "Development of Materials Integration Strategies for Electroceramic Film-Based Devices via Complementary *In Situ* / *Ex Situ* Studies of Film and Interface Processes", International Symposium on the Applications of Ferroelectrics 2002 and 14th International Symposium on Integrated Ferroelectrics, Nara, Japan, May 28- June1 , 2002. Integrated Ferroelectrics, in press, 2003.

V. Nagarayan, A. Roytburd, A. Stanishevsky, S. Prasertchoung, T. Zhao, J. Mengailis, O. Auciello, and R. Ramesh, "Dynamics of Ferroelastic domains in Ferroelectric Thin Films", Nature-Materials **2** (2003) 43.

Invited Presentations (1st author quoted only)

Size Effects in Ferroelectrics: Lessons from In-Situ Studies of $PbTiO_3$ Thin Films, S. K. Streiffer, 11th U.S. - Japan Seminar on Dielectric and Piezoelectric Ceramics, Sapporo, Japan, Sept. 9-12, 2003.

In situ x-ray scattering studies of film growth and thickness effects on ferroelectricity in epitaxial lead titanate family of perovskites, O. Auciello, International Materials Conference, Cancun, Mexico, August 18-20, 2003.

In-Situ Studies of Size-dependent Behavior in Ferroelectric Thin Films, O. Auciello, ICMAT 2003 - International Conference on Materials for Advanced Technologies (ICMAT 2003) - Symposium J - Synchrotron Radiation for Advanced Materials Analysis and Processing, Singapore, June 29-July 4, 2003.

In-Situ Synchrotron X-ray Studies of the Processing and Physics of Ferroelectric Thin Films, G. B. Stephenson, Polar Oxides - Properties, Characterization, and Imaging, Capri, Italy, June 8-11, 2003.

In-Situ X-ray Studies of Growth and Phase Transitions in $PbTiO_3$, G. B. Stephenson, ONR Workshop on Epitaxial Heterogeneous Interfaces: Formation and Stability, Fish Camp, CA, May 4-8, 2003.

How Thin is Thin? In-Situ Studies of Ferroelectric Behavior and Domain Structures in $PbTiO_3$ Thin Films, S. K. Streiffer, Condensed Matter and Materials Physics Conference, April, 2003 in Belfast, Ireland.

In situ x-ray scattering studies of film growth processes and thickness effects on ferroelectricity in epitaxial $PbTiO_3$ and $Pb(Zr,Ti)O_3$ films, O. Auciello, 15th International Symposium on Integrated Ferroelectrics (ISIF), Colorado Springs, CO, March 2003.

In situ x-ray studies of 180° stripe domain formation and ferroelectricity in epitaxial $PbTiO_3$ thin films, J. A. Eastman, Symposium U: Ferroelectric Thin Films XI, Materials Research Society Fall 2002 Meeting, Boston, MA, December 2002.

Using the synchrotron for in situ studies of materials processing, Carol Thompson, Material Science with Synchrotron Radiation Workshop, 5th Canadian Light Source Users Meeting, Saskatoon, Canada, November 15, 2002.

X-ray scattering studies of thickness effects of ferroelectricity in epitaxial $PbTiO_3$ and $Pb(Zr,Ti)O_3$ films, G. B. Stephenson, 9th International Workshop on Oxide Electronics, St. Petersburg, FL, October, 2002.

In situ x-ray studies of vapor phase epitaxy of $PbTiO_3$, G. B. Stephenson, Seventh Int'l Conference on Surface X-ray and Neutron Scattering (SXNS-7), Lake Tahoe, CA, September 2002.

In situ x-ray scattering studies of growth and surface structure of $PbTiO_3$ films, Carol Thompson, 14th American Conf. on Crystal Growth and Epitaxy (ACCGE-14), Seattle, WA, August 2002.

In-situ synchrotron x-ray studies of growth processes and surface structure of perovskite ferroelectric thin films, O. Auciello, Synchrotron Radiation in Materials Characterization, XI International Materials Research Congress, Cancun, Mexico, August, 2002.

X-ray studies of nanoscale stripe domains and thickness effects on ferroelectricity in epitaxial $PbTiO_3$ films, G. B. Stephenson, Synchrotron Radiation in Materials Characterization, XI International Materials Research Congress, Cancun, Mexico, August, 2002.

Invited Presentations

O. Auciello:

"Science and Technology of Ferroelectric Thin Films", Pan American Advanced Study Institute Rosario, Argentina, September 2002.

"*In situ* Studies of Ferroelectric Thin Film Growth via Synchrotron X-ray Scattering", International Conference on Materials, Cancun, Mexico, August 2002.

"Science and Technology of Ferroelectric Thin Films", European Materials Research Society Spring Meeting, Symposium on Advanced Materials for Microelectronics: Ferroelectrics and Low-K Materials, Strasbourg, France, July 2002.

"Studies of Ferroelectric Thin Film Synthesis via Complementary *In Situ* Characterization Techniques", International Union of Materials Research Societies Meeting, Xia, China, June 2002.

"Development of Materials Integration Strategies for Ferroelectric Memories via *In Situ* Analytical Methods", International Symposium on the Application of Ferroelectrics, Nara, Japan, July 2002.

In Situ Studies of Perovskite Film Growth and Interface Processes using Synchrotron X-ray Scattering Techniques", International Symposium on Integrated Ferroelecrtics, Colorado Springs, March 2003.

V. Dravid:

"Characterization of Nanostructured Materials", Lehigh Short Courses, Bethlehem, PA, June 2002

"Teaching Old Ceramics New Tricks: *Site-Specific Nanopatterning of Functional Inorganics"*, Gordon Research Conference, Meriden, NH, August 2002

"Nanotitration of Active Grain Boundaries", Electroceramics VIII conference, Rome, Italy, August 2002

"Electron Holography in Materials Science", Intl. Conf. On Electron Microscopy, Durban, South Africa, Aug-Sept. 2002

"Better Transparency and Conductivity through ALCHEMI", Intl. Conf. On Electron Microscopy, Durban, South Africa, Aug-Sept. 2002

"Site- and Shape-Specific Nanopatterning of Ceramics", Colloquium, University of Illinois at Urbana-Champaign, Sept. 2002.

"Nanopatterning of Addressable Functional Inorganic Nanostructures", Pan American Advanced Study Institute, Rosario, Argentina, September 2002.

"Miniaturized Bio-Nanosensor", IBM Watson Research Center, Yorktown Heights, NY, November 2002.

Role of Electron Microscopy in Nanotechnology, Intl. Conf on Inorganics, IIT Bombay, India, December 2002

Contributed Presentations (only speaker given)

X-Ray Observation of Ferroelectricity in Ultrathin Perovskite Films, D. D. Fong, 10th International Workshop on Oxide Electronics Conference Center St. Ulrich, Augsburg, Germany, September 11-13, 2003.

Ferroelectricity in Ultrathin $PbTiO_3$ Films, Dillon D. Fong, APS March Meeting, Austin, TX, March 3-7, 2003.

X-Ray measurements of the intrinsic surface structure of ferroelectric $PbTiO_3$ films, D. D. Fong, Symposium U: Ferroelectric Thin Films XI, Materials Research Society Fall 2002 Meeting, Boston, MA, December 2002.

Observation of 180° stripe domains in ferroelectric PbTiO_3 thin films, Carol Thompson, Fundamental Physics of Ferroelectrics, ÔWilliamsburg ConferenceÕ, Washington, DC, February 2002.

In situ synchrotron x-ray studies of metal-organic chemical vapor deposited $PbTiO_3$ thin films, S. K. Streiffer, Fundamental Physics of Ferroelectrics, Washington, DC, February 2002.

Patents

O. Auciello:
High-Dielectric Constant Alloy Oxide for New Generation of Integrated Circuit Gate Oxide and Magnetic Multilayers, application submitted on April 2003.

V. P. Dravid:
Multifunctional Nanosensors for bio-, chemical and gaseous sensing and diagnostics, October 2002.

Patterning Solid State Features Via Dip Pen Nanolithography with Sol-Based Inks"
NU 22008, Patent Application #60/341,614, Foreign filing - Yes

DPN printing with open tips; aperture pen nanolithography, NU 21009, "#083847-0208

Patent Application # 10-059,593, Foreign filing Yes

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1. Pearton, S. J., Abernathy, C. R., Overberg, M. E., Thaler, G. T., Norton, D. P., Theodoropoulou, N., Hebard, A. F., Park, Y. D., Ren, F., Kim, J., and Boatner, L. A., Wide Bandgap Ferromagnetic Semiconductors and Oxides, Journal of Applied Physics, in press (2002)

2. Norton, D. P., Kim, K. Christen, D. K., Budai, J. D., Sales, B. C., Chisholm, M. F., Kroeger, D. M., Goyal, A., and Cantoni, C., (La,Sr)TiO_3 as a conductive buffer for RABiTS coated conductors, Physica C, in press (2002).

3. Sigman, J., Norton, D. P., Christen, H. M., Fleming, P. H. and Boatner, L. A., Antiferroelectric behavior in symmetric $KNbO_3$/$KTaO_3$ superlattices, Physical Review Letters, Volume 88, Number 9, p. 097601-1, 2002.

4. Norton, D. P.; Pearton, S.J.; Christen, H.M.; Budai, J.D., Hydrogen-assisted pulsed-laser deposition of epitaxial CeO_2 films on (001)InP, Applied Physics Letters, Volume 80, Issue 1, 2002, Pages 106-108.

Invited Presentations

Epitaxi of Complex Oxides on Dissimilar Substrates, Florida Chapter of the America Vacuum Society, Orlando, Florida, March 2002

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1. J. Sigman, H. M. Christen, P. H. Fleming, L. A. Boatner, and D. P. Norton, "Evidence for Antiferroelectric Behavior in $KNbO_3/KTaO_3$ Superlattices," Materials Research Society Symposium Proceedings 720, H6.4 (2002).

2. P. Galinetto, E. Giulotto, G. Samoggia, V. Trepakov, S. Kapphan, and L. Boatner, "Effect of Li-Dipoles in $K_{1-x}Li_xTa_{1-y}NbyO_3$: A Raman Study," Ferroelectrics 272, 87-92 (2002).

3. "Effects of Co implantation in $BaTiO_3$, $SrTiO_3$, and $KTaO_3$," J. S. Lee, Z. G. Khim, Y. D. Park, D. P. Norton, J. D. Budai, L. A. Boatner, S. J. Pearton, R. G. Wilson, R.G., Electrochemical and Solid-State Letters, Volume 6, Issue 4, 2003, Pages J1-J3

4. "Properties of Mn-implanted $BaTiO_3$, $SrTiO_3$, and $KTaO_3$," D. P. Norton, N. A. Theodoropoulou, A. F. Hebard, J. D. Budai, L. A. Boatner, S. J. Pearton, R. G. Wilson, R.G., Electrochemical and Solid-State Letters, Volume 6, Issue 2, 2003, Pages G19-G21

5. V. Trepakov, P. Galinetto, E. Giulotto, G. Samoggia, M. Savinov, V. Vikhnin, S. Kapphan, L. Jastrabik, and L. Boatner, "Recent Developments in $K_{1-x}Li_xTa_{1-y}Nb_yO_3$ Investigations," Ferroelectrics 267, 221-228 (2002).

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7. Jaime A. Li, E. A. Akhadov, Jeff Baker, L. A. Boatner, D. Bonart, J. Fritsch, S. A. Safron, U. Schröder, J. G. Skofronick, and T. W. Trelenberg, "Surface Structure and Dynamics of $KTaO_3$ (001)," The Physical Review B (accepted for publication).

8. W. Jiang, W. J. Weber, S. Thevuthasan, and L. A. Boatner, "Effect of ion irradiation in cadmium niobate pyrochlores," Nuclear Instruments and Methods in Physics Research B (accepted for publication).

9. D. P. Norton, J. D. Budai, L. A. Boatner, J. S. Lee, Z. G. Khim, Y. D. Park, M. E. Overberg, S. J. Pearton, and R. G. Wilson, "Ferromagnetism in Cobalt-Implanted ZnO," Applied Physics Letters," (submitted for publication).

Invited Presentations

1. David Norton, J. Sigman, Hans Christen, Pam Fleming, Lynn Boatner, and Mark Reeves, "Evidence for Antiferroelectric Behavior in $KNbO_3/KTaO_3$ Superlattices," Presented at the 2002 Spring MRS Meeting, San Francisco, CA April 1-5, 2002.

2. J. G. Skofronick, T. W. Trelenberg, E. A. Akhadov, S. A. Safron, D. H. Van Winkle, L. A. Boatner, and F. A. Flaherty, "A Study of the Surface Properties of the Mixed Crystal $KTa_xNb_{1-x}O_3$ (KTN) Using Helium Atom Scattering," Presented at the Annual APS March Meeting 2002, Indianapolis, Indiana, March 18-22, 2002.

3. Hyung-jin Bae, Jennifer Sigman, D. P. Norton, L. A. Boatner, "Treatment of (100) $KTaO_3$ for Atomically Flat Surfaces," Presented at the 2002 Fall Meeting of the Materials Research Society, Boston, MA, December 2-6, 2002.

4. David Norton, J. Sigman, Hans Christen, Pam Fleming, Lynn Boatner, and Mark Reeves, "Evidence for Antiferroelectric Behavior in $KNbO_3/KTaO_3$ Superlattices," Presented at the 2002 Spring MRS Meeting, San Francisco, CA April 1-5, 2002.

5. J. G. Skofronick, T. W. Trelenberg, E. A. Akhadov, S. A. Safron, D. H. Van Winkle, L. A. Boatner, and F. A. Flaherty, "A Study of the Surface Properties of the Mixed Crystal $KTa_xNb_{1-x}O_3$ (KTN) Using Helium Atom Scattering," Presented at the Annual APS March Meeting 2002, Indianapolis, Indiana, March 18-22, 2002.

6. J. Sigman, D. P. Norton, H. M. Christen, P. H. Fleming, and L. A. Boatner, "Evidence for Antiferroelectric Behavior in $KNbO_3/KTaO_3$ Superlattices," Presented at the 30th Annual Symposium of the Florida Chapter of the American Vacuum Society & the 20th Annual Meeting of the Florida Society for Microscopy, Orlando, Florida, March 10 – 12 (2002).

7. W. Jiang, W. J. Weber, S. Thevuthasan, and L. A. Boatner, "Effect Ion Irradiation in Cadmium Niobate Pyrochlores," presented at the 104th Annual meeting of the American Ceramic Society, St. Louis, M April 28 – May 1, 2002.

Publications

B.T. Liu, K. Maki, Y. So, V. Nagarajan, R. Ramesh, J. Lettieri, J.H. Haeni, D.G. Schlom, W. Tian, X.Q. Pan, F.J. Walker and R.A. McKee, "Epitaxial La-doped SrTiO3 on silicon: A conductive template for epitaxial ferroelectrics on silicon", *Appl. Phys. Lett.*, in press (2002).

R.A. McKee, F.J. Walker and M.F. Chisholm, "Physical Structure and Inversion Charge at a Semiconductor Interface with a Crystalline Oxide", *Science* **293**, 468(2001).

A.Lin, X. Hong, V. Wood, A.A. Verevkin, C.H. Ahn, R.A. McKee, F.J. Walker and E.D. Specht "Epitaxial Growth of $Pb(Zr_{0.2}Ti_{0.8})O_3$ on Si and its Nanoscale Piezoelectric Properties", *Appl Phys Lett* **78**, 2034(2001).

Invited Presentations

Interfacial Structure of Crystalline Oxides on Semiconductors,
The American Physical Society, March 2002.

Publications

G.L. Brennecka, W. Huebner, B. Tuttle and P. Clem, "Use of Stress to Produce Highly-Oriented Tetragonal Lead Zirconate Titanate (PZT 40/60) Thin Films and Resulting Electrical Properties," J. Amer. Ceram. Soc., submitted

Invited Presentations

B.A. Tuttle, D.Williams, M.A. Rodriguez, J.S. Wheeler, D.McCallum, B. Nowak and W.R. Olson, "Comparison of Bulk and Thin Film High Zr Content PLZT Dielectrics," 105th Annual American Ceramic Society Meeting, Nashville, TN April 30, 2003.

B.A. Tuttle, J. Wheeler, G. Jamison, D. Williams, D. Wheeler, J. Cesarano and P. G. Clem, "Dielectric Materials for Fuel Cell Vehicles and Pulsed Discharge Applications, Dielectric Materials and Components for Pulsed Power Applications Workshop, Arlington, VA June 2-3, 2003.

Contributed Presentations

D. P. Williams, B.A. Tuttle, J.S. Wheeler, M.A. Rodriguez, and W.R. Olson, "Electrical Properties of High Zirconia Content PLZT Thin Films," 105th Annual American Ceramic Society Meeting, Nashville, TN April 28, 2003.

B. A. Tuttle, D. Williams, P.G. Clem, D. Wheeler, G. Jamison, P. Yang, W. R. Olson and J.S. Wheeler, " Evaluation of Two Thin film Capacitor Families," The 27th Annual International Conference on Advanced Ceramics & Composites," Cocoa Beach, FL, January 23, 2003.

D. Williams, B. Tuttle, P.G. Clem, D. Wheeler, G. Jamison, P. Yang, W. R. Olson and J.S. Wheeler, " Robocasting of High Zr Content PLZT Ceramics," The 27th Annual International Conference on Advanced Ceramics & Composites," Cocoa Beach, FL, January 23, 2003.

D.P. Williams, B.A. Tuttle, J. Cesarano, M. Rodriguez and P. Clem, "High Zr Content Capacitors for High Energy Density Applications," 14th Annual Rio Grande Symposium on Advanced Materials, Albuquerque, NM, October 21, 2002.