Ferroelectrics at the ERL

Carol Thompson

Northern Illinois University

Argonne National Laboratory

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Collaborators at ANL

Materials Science Division
Matthew J. Highland
Paul Fuoss
Jeff Eastman
Dillon Fong
John Pearson

Advanced Photon Source
G. Brian Stephenson

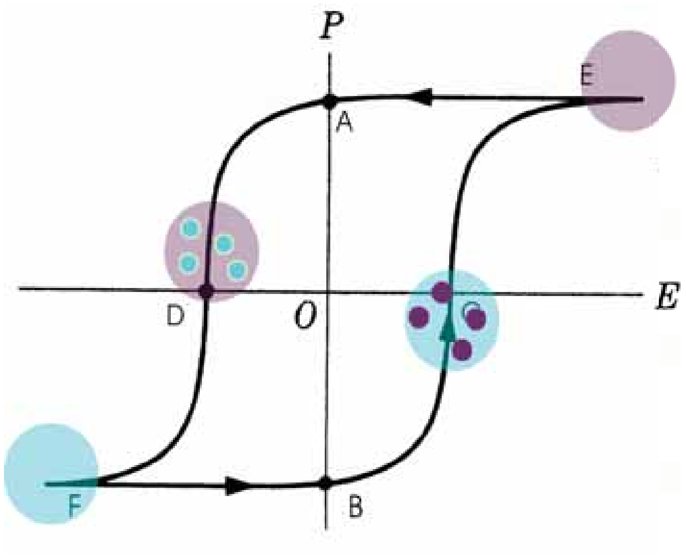
Physical Sciences and Engineering
Stephen K. Streiffer

Center for Nanoscale Materials
Ralu Divan
Jorg Maser
Martin V. Holt

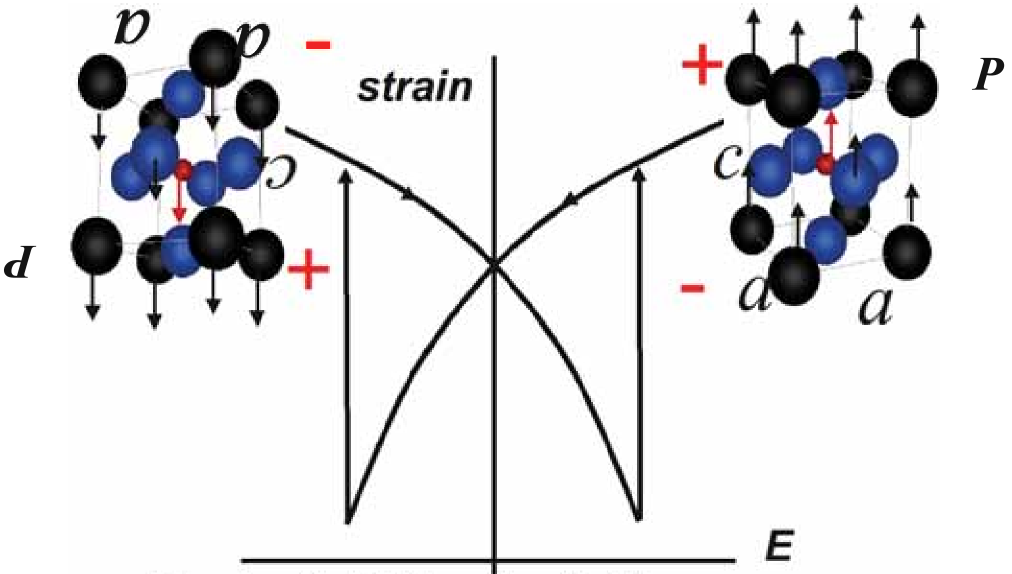
For my own work that may be presented here - Thanks to all these Argonne collaborators

Ferroelectrics – Switchable polar materials

- Structure-property relationships control:
    - dielectric, ferroelectric, piezoelectric, electrostrictive, pyroelectric and electro-optical properties
    - for actuators, sensors, electro-optical switches, non-volatile memory elements, hi-K dielectric, detectors…



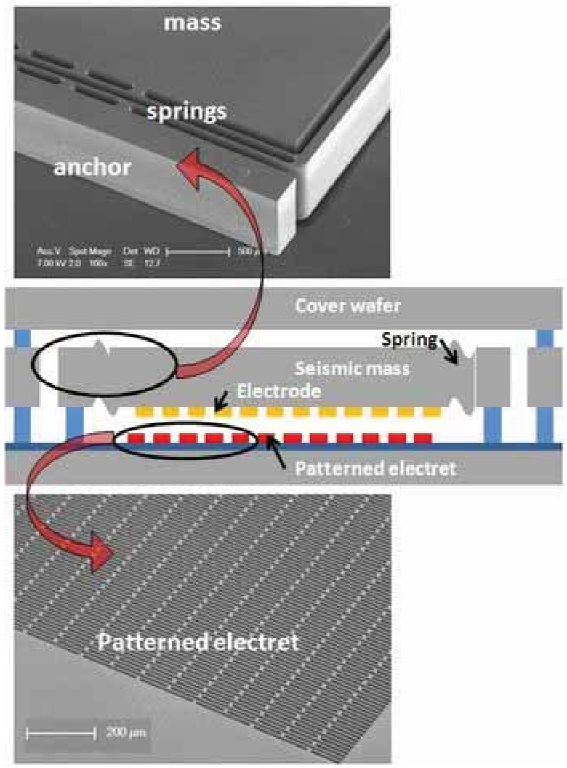
Polarization-field hysteresis loop and domain fractions



Strain-field 'butterfly' loop signature of piezoresponse and switching

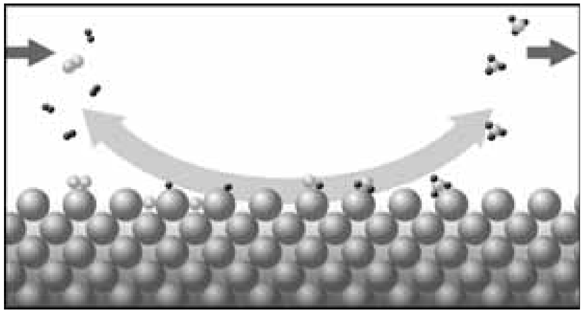
Future technology motivations - exploiting electrical/optical/mechanical/chemical/thermal couplings

Energy Harvesting



e.g., using vibrations - patterned electret designed as a voltage source for sensor. Image from http://www.memsinvestorjournal.com/2010/09/stable-patterned-electrets-for-mems-based-energy-harvesters.html by Mieke Van Bavel, et al.

Catalytic-activty



(schematic of catalysis from http://www.spaceflight.esa.int/impress/text/education/Catalysis/Commercial.html)

Memory elements

http:/www.ti.com Released 2011
Consumes 250x less power, write more than 100x faster, radiation resistant, lasts more cycles, than Flash-based devices

Issues:

- behavior of ultrathin films, e.g. switching, piezoelectricity
- surface charge compensation mechanisms
- how polarization influences interface/overlayer properties

Fundamental questions

- How are polarization, strain, and electric field coupled in time and in space on ultrafast time scales?
- How do domains walls respond on ultrafast time scales?
- How does film polarization affect chemistry at the surface / interface?
- Does the high electric field affect the atomic structure factors?

Overview of this talk:
Potential Tickle/Probe Experiments

- Dynamics of ultrafast polarization switching and strain/polarization/field coupling
- Stripe domain dynamics
- Catalytic behavior and dynamics

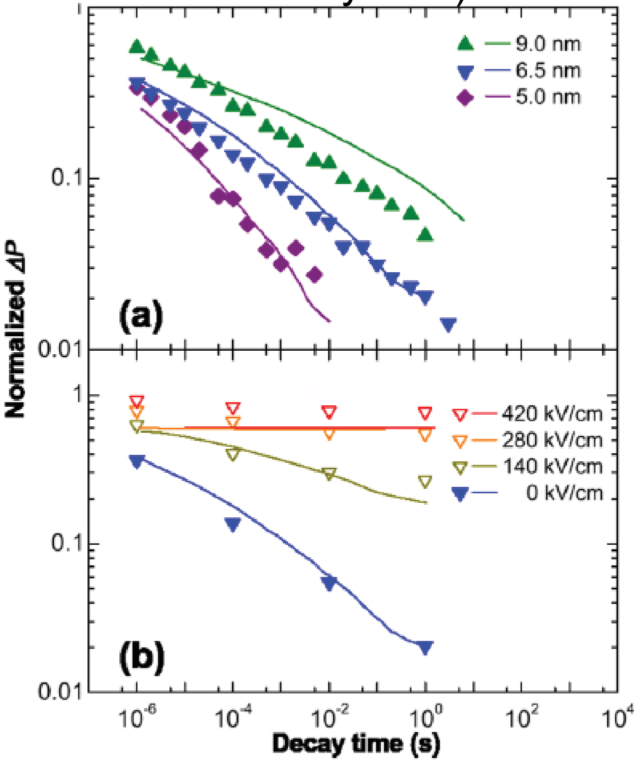
How to stimulate?

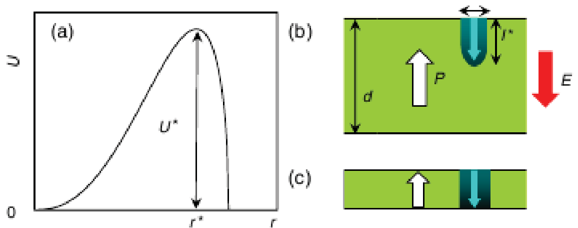
- Apply field with electrodes in small devices
- Apply field with THz light
- Apply strain using laser-induced shock

How else to study response and microstructure?

- Primary studies of switching are through electronic measurements (I-V, I-time, P-V, strain-V)
- Structural models and mechanisms are implicit in modelling of the data
    - Analysis - Indirect information on nucleation and growth
    - Suggests microscopic pictures – but no pictures.
        - *(n.b., complementary fast piezo-AFM methods are being developed and applied*
- X-ray imaging and diffraction techniques
    - additional structural information and potential for very non-ambient conditions

Example - using electrical measurements - Function of thickness/drive/time (epi SRO/BTO/SRO system)





Jo, et al, PRL 97, 247602 (2006)

Electrical measurements of switching times as function of capacitor size

Li, et al., Journal of lightwave technology 21, 3282 (2003)

Li, et al., APL 84, 1174 (2004)

- Intrinsic limit less than 70 psec – (still limited by circuit)
- Used semiconductor photoconductive swithc to produce fast rise time pulse

Volume fraction of switched material versus time for different capacitor sizes (C)

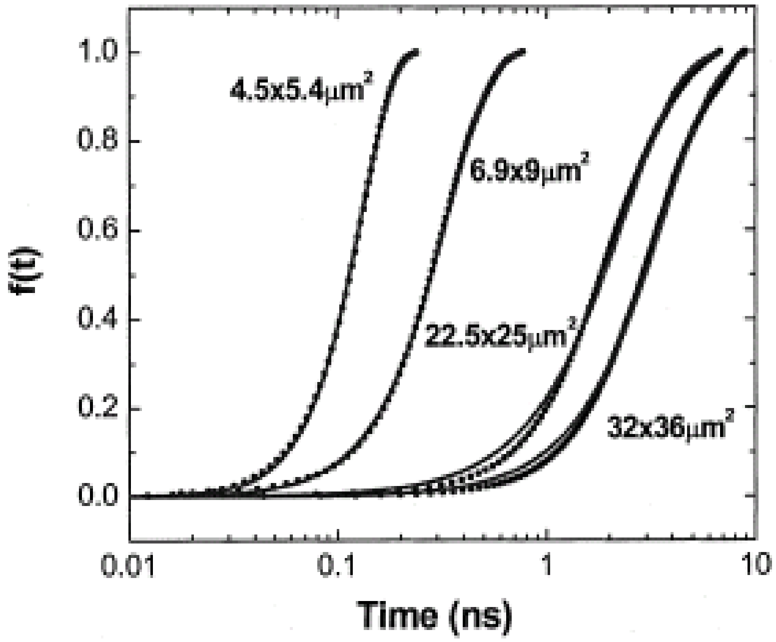
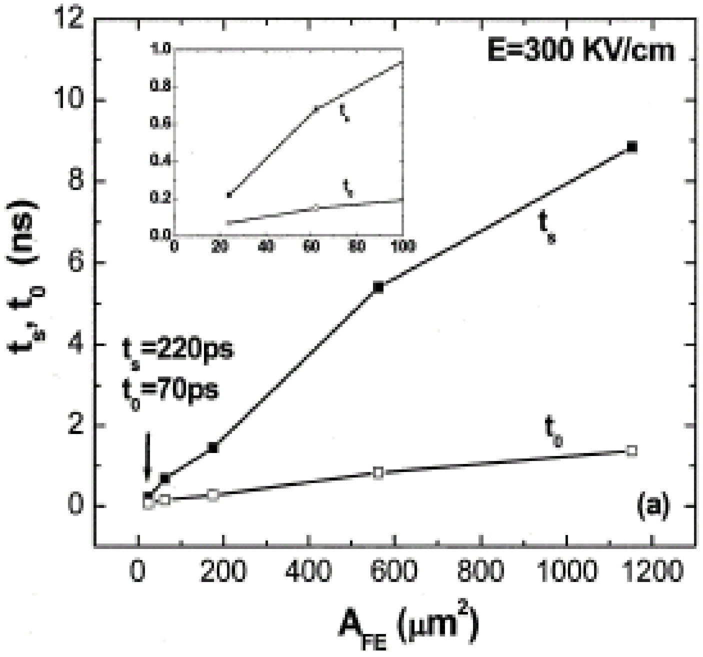


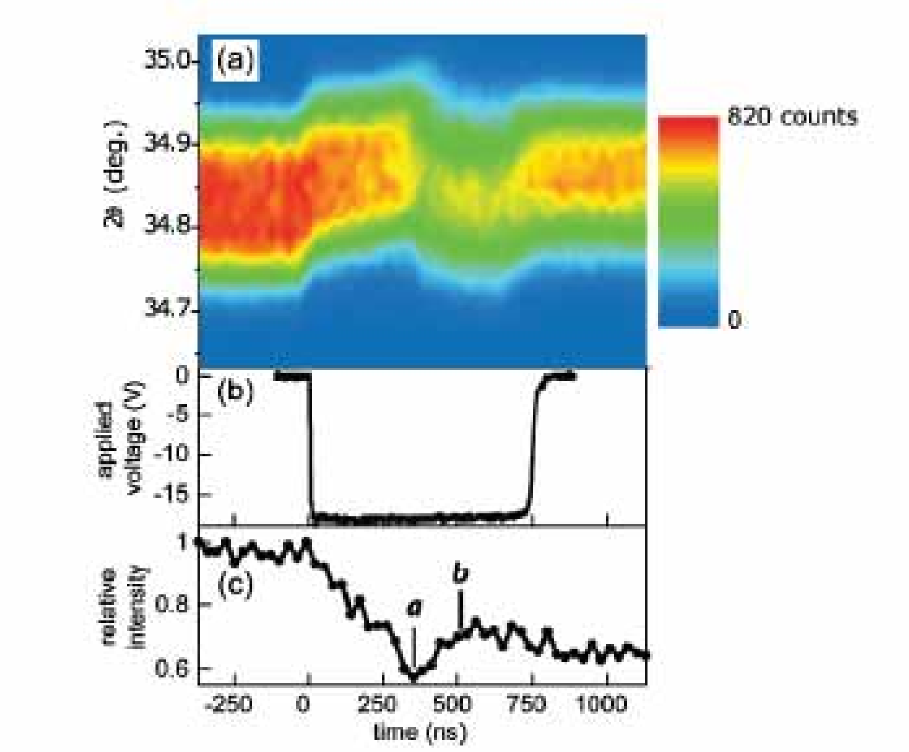
Fig. 9. Plots of measured (dot line) and fitted (solid line) $f(t)$ curves for various capacitor areas.

Switching time versus capacitor size

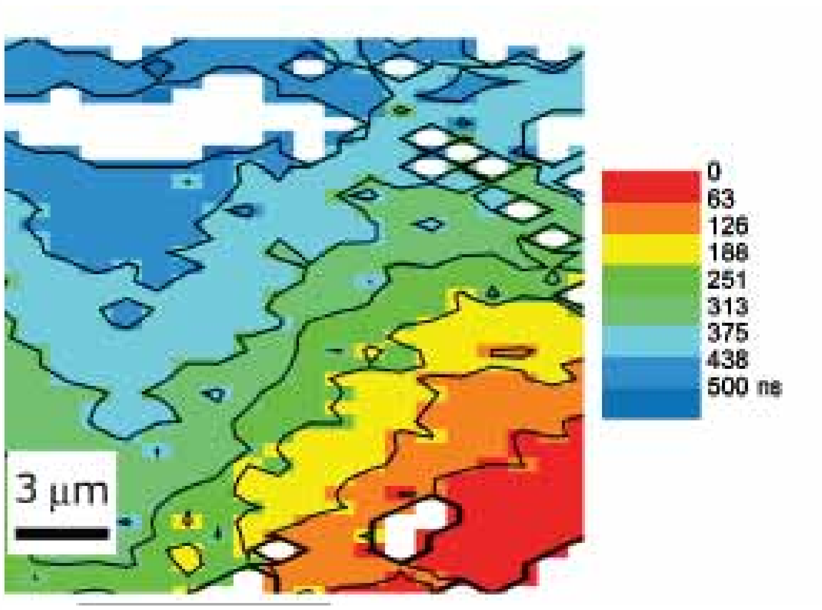


Time and spatial examination of ferroelectric switching (Evan's group)

Grigoriev, et al., PRL 96, 187601 (2006)



Time resolved diffraction of 002 Bragg peak under application of electtric field. Shows piezoresponse, then switch.

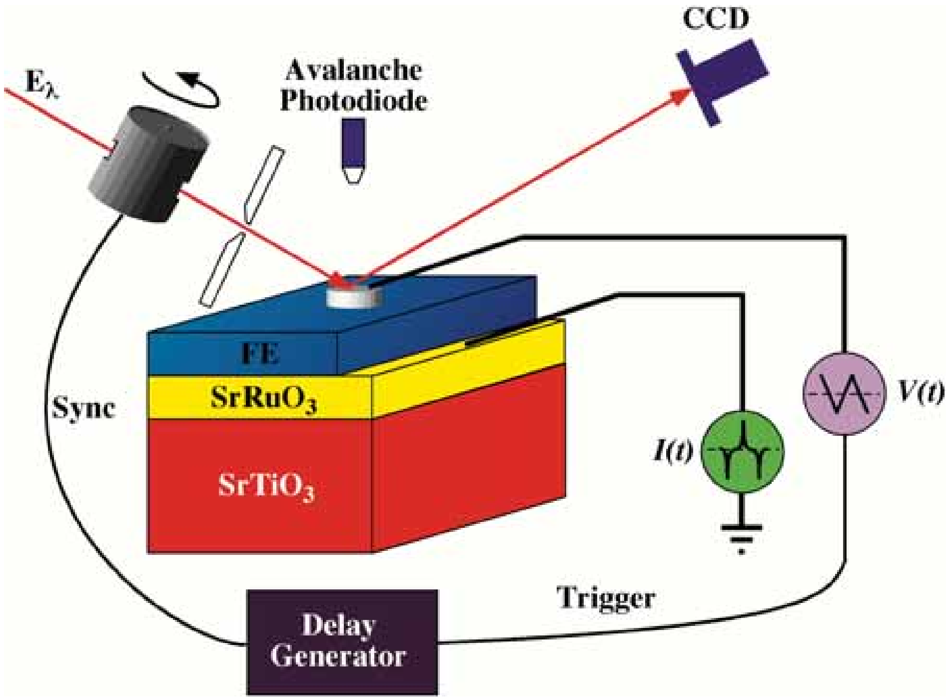


Polarization switching times in a 20umx20um piece of the thin film PZT capacitor as domain wall passes through. Capacitor is 200um diameter, SRO/400nm PZT/SRO thin film.

Stroboscopic methods for ferroelectrics - schematics

Electrical stimulation of device synchronized/delayed so that sample is in particular electrical state during collection of scattering/fluorescence signal

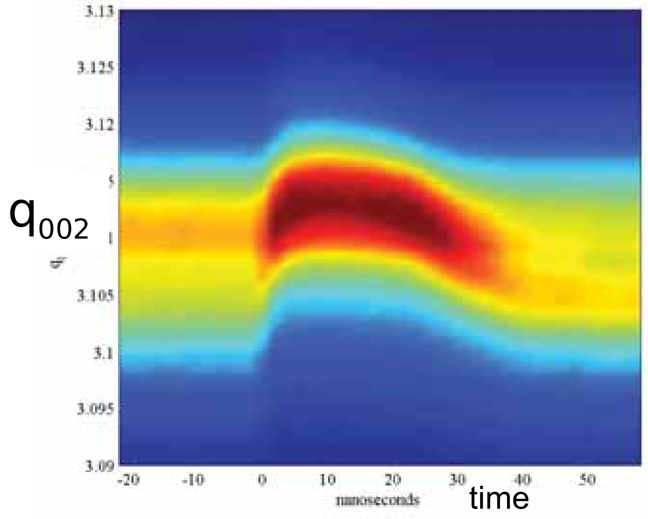
Requires: Synchronized timing of particular piece of electrical signal with respect to the photons

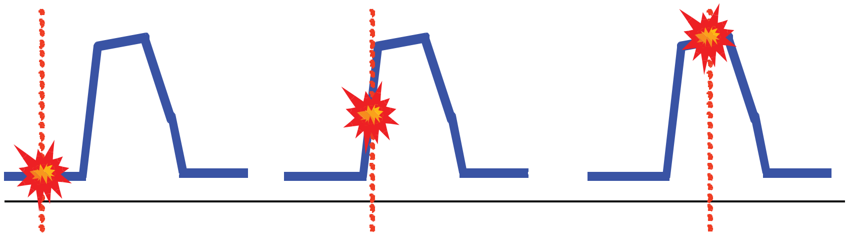


1st generation device

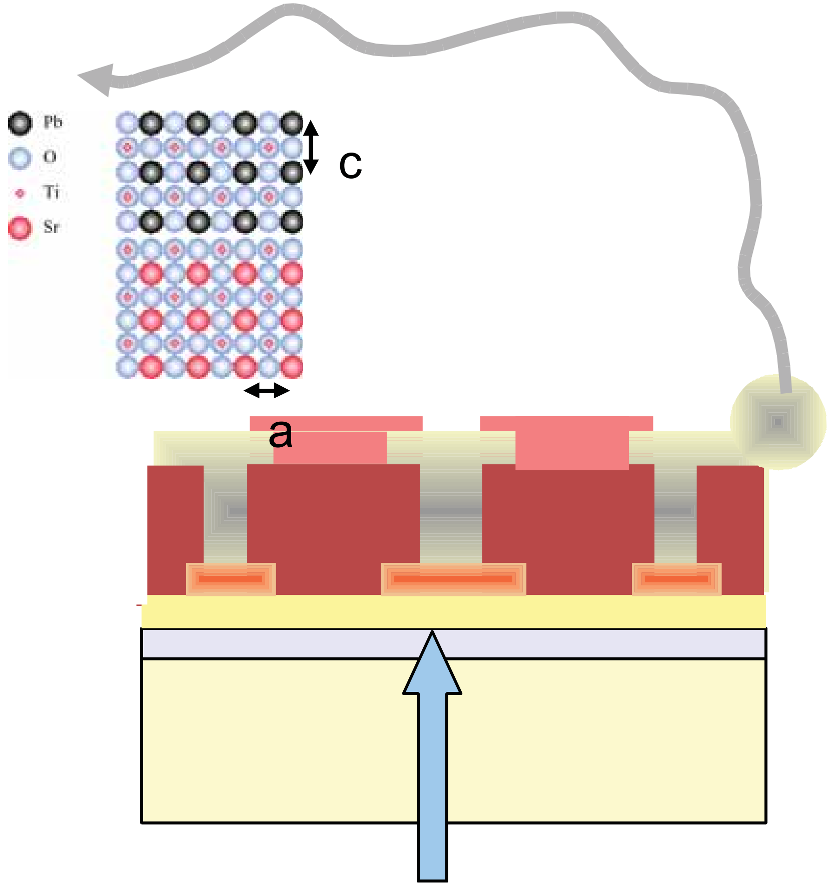
250nm thick $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$/SRO/STO

~100um diameter pad, RC time constant ~10nsec





2nd Generation Device
(almost 'all oxide' epitaxial heterostructure)



10 to 20 um
diameter capacitors

Packaging

🟥 4th Photoresist (thin protective)

🟥 3rd Photoresist (thick 7-8um dielectric layer)

▨ Al (fill vias and make connections (2um))

🟧 Cu (40 nm) ←

oxide epitaxial heterostructure

🟨 $PbTiO_3$ (20-30nm OMVPE)

⬜ $SrRuO_3$ (20-30 nm sputtered)

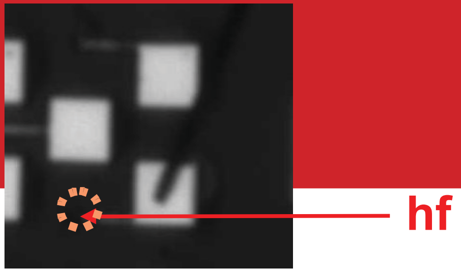
🟨 $SrTiO_3$ (100 substrate)

Device Processing steps
('2nd' generation device)

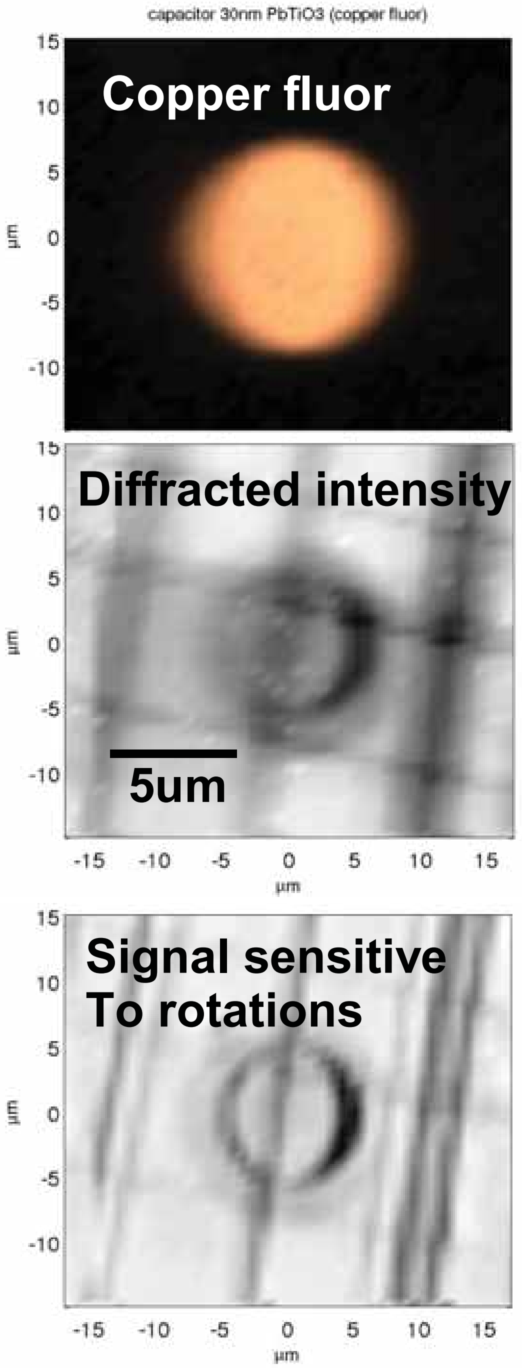
- Wire-bond Al wire to gold chip carrier pads
- Mount sample in chip carrier
- 4th and final photoresist to protect dielectric surface
  - stripping resist - aluminum electrode pads
- 3rd photoresist
  - pattern aluminum, etch excess aluminum
- 2um Al (sputtered)
  - conformal into 8um deep x 15um wide vias
- 2nd photoresist
  - Thick dielectric layer
- 1st photoresist
  - Pattern copper, etch excess Cu (chem etch)
- 40nm Cu (evaporated)
- Cleave 10mmx10mm to 4 samples.
- 20-30nm PbTiO3 (OMVPE)
  - In chamber that we use for x-ray scattering experiments on OMVPE growth and ultrathin PTO films
- 30-40nm SrRuO3 (sputter)
- Etch SrTiO3 surfaces normal processing to ensure single TiO2 termination
- Start (100) SrTiO3 substrates

🟥	4th Photoresist (thin protective)
🟥	3rd Photoresist (thick 7-8um dielectric layer)
▨	Al (fill vias and make connections (2um))
🟧	Cu (40 nm)
🟨	$PbTiO_3$ (20-30nm OMVPE)
⬜	$SrRuO_3$ (20-30 nm sputtered)
⬜	$SrTiO_3$ (100 substrate)

Device

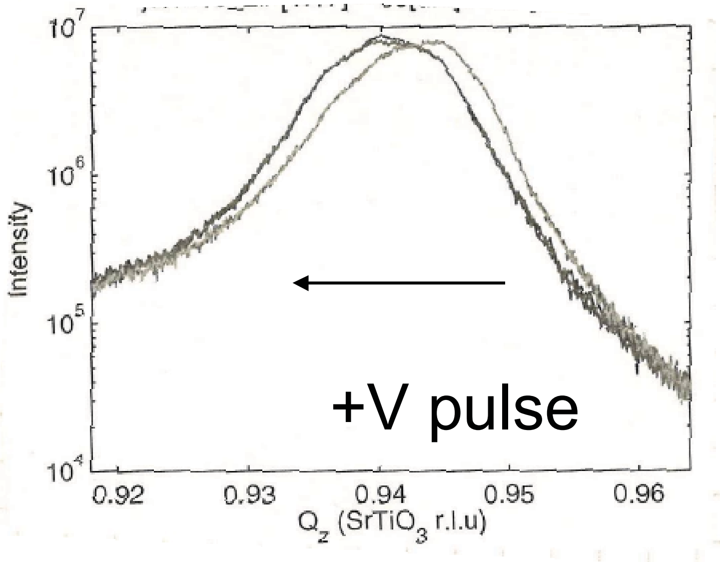


- Device parameters
  - ~30 nm PbTiO3 film
  - ~15 um diameter cap
  - ~8 pf capacitance
  - Ok, this sample is twinned (relaxed)
    - (maybe stresses during my cleaving of sample)
- Imaging conditions
  - Zone plate - ~80nm spot size
  - 002 PbTiO3 peak (about 18° theta)
- n.b. for these devices
  - Edge of pad affects film
    - Initial analysis
      - Appears to be related to rotation,not polarizaiton reductio
    - Also found in non-twinned samples as well as at 1st step in processing (only Copper)

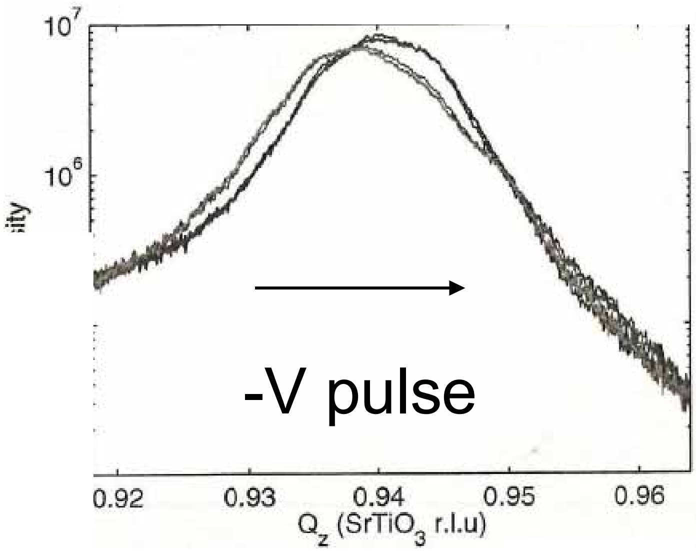


Preliminary X-ray Results taken with ~10nsec steps (RC < several nsec) 80nm spot size: Piezoresponse (+V pulse, -V pulse)

Thompson, et al. unpublished



+V pulse



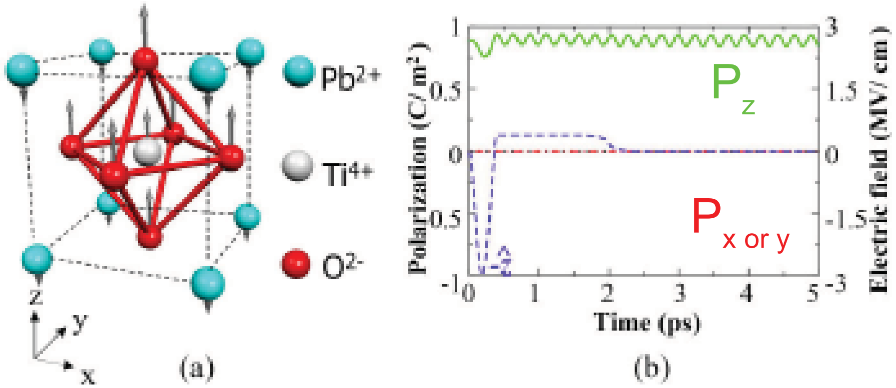
-V pulse

002 PTO peak shift
piezo-response

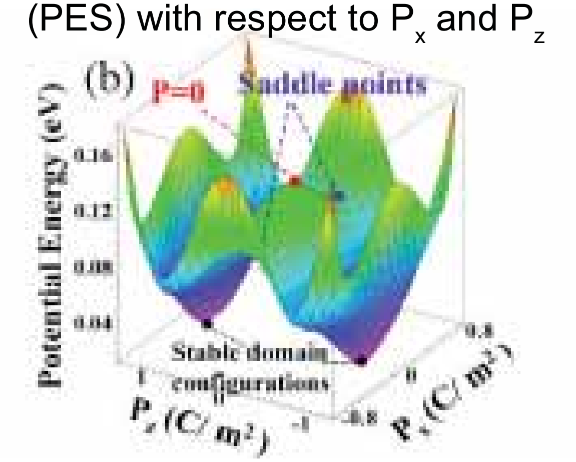
Can THz pulses be used to switch without electrodes?

Qi, et al. PRL 102, 247603 (2009) [THEORY]

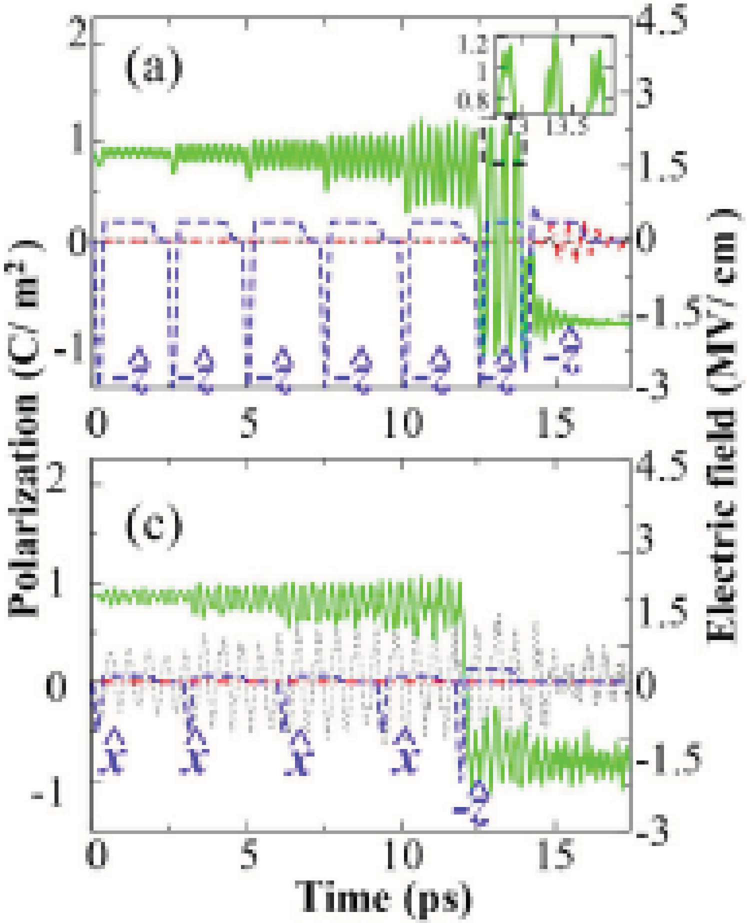
Time-dependent lattice response to a single asymmetric THz pulse alone Z



Follow microscopic path using Lattice potential energy surface (PES) with respect to P_x and P_z



P_z and $P_{x\ or\ y}$ Response of Polarization to synchronized THz pulses



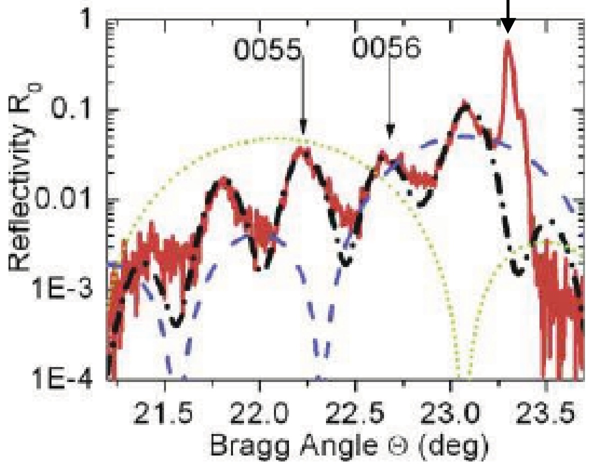
Apply Strain From Laser Pulse: Polarization and Strain Coupling

Schmising, et al., PRL 98, 257601 (2007),
also figures from
Schmising, et al. Z. Kristallogr. 223, 283 (2008).
Schmising, et al., Physics Procedia 3, 333 (2010)

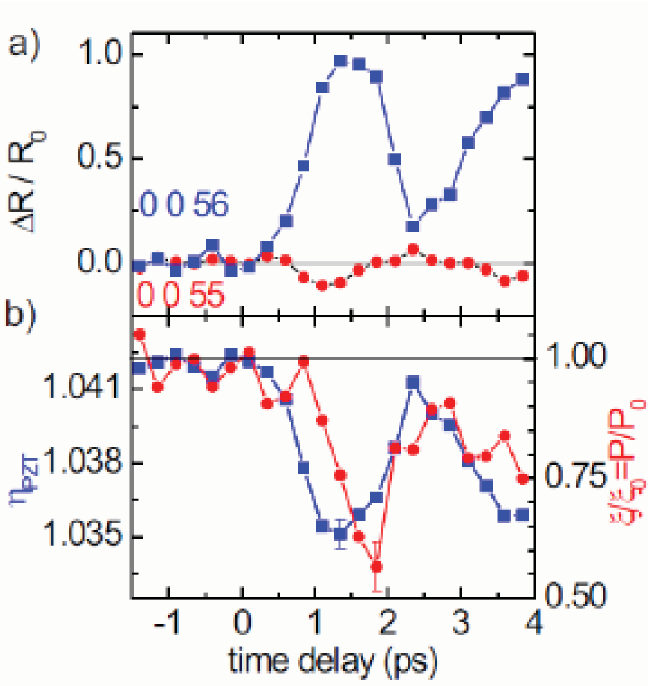
- Photogenerated uniaxial stress (from 50fsec laser pulse) propagating through 15 period 15period PZT(5nm) /SRO(6nm)
- Intensities of 2 x-ray reflectivity SL peaks are used to extract polarization and tetragonality
- Surprise – time delay of soft-mode response w.r.t. Tetragonal strain change.

Static 00L reflectivity and fit

STO (002)



Reflectivity Intensity changes in (0 0 56) and (0 0 55) superlattice reflections



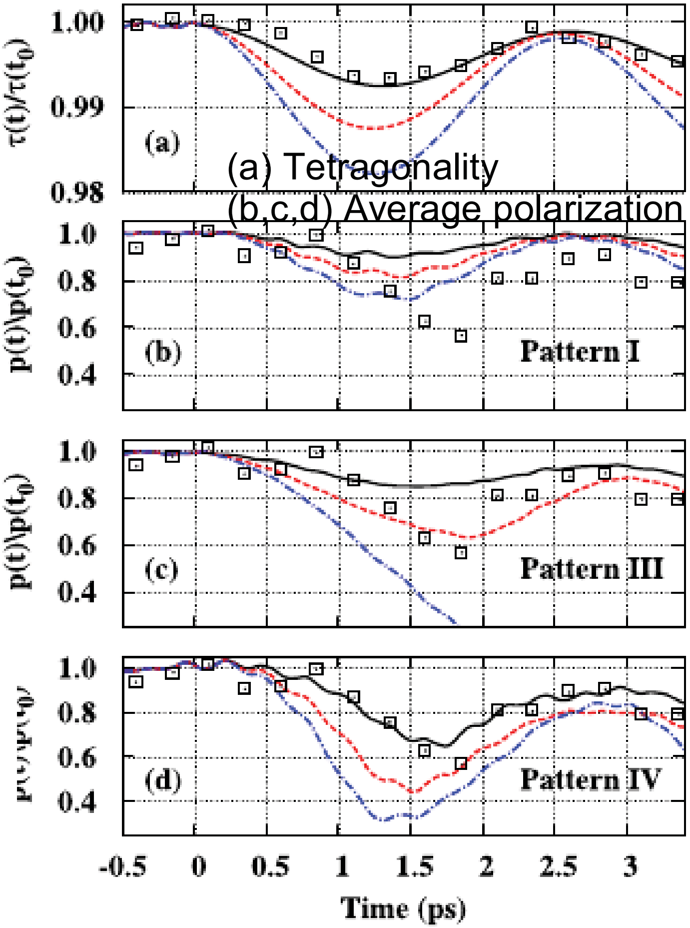
Polarization and Strain coupling surprises – heterogeneity issues?

Ponomareva and Bellaiche, PRL 101, 197602 (2008) [theory]

- Expt - Time delay of soft-mode response w.r.t. tetragonal strain
  - reduction of the polarization until soft-mode catches up
    - strong deviation from a coupling law between polarization and strain.
- Ponomareva and Bellaiche 1st principles calculations suggested
  - “slow breathing” of dipolar inhomogeneities
    - explained all the experimental results
  - Switching occurs – and average structures shows an 'effective' 'delay'.

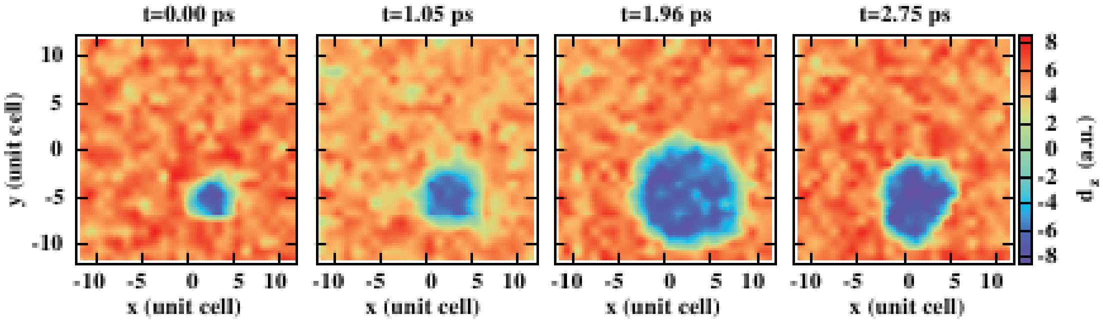
Time structure of various breathing mode patterns

(squares from Schmising data)

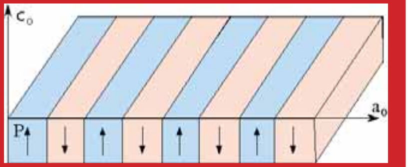


(a) Tetragonality

(b,c,d) Average polarization

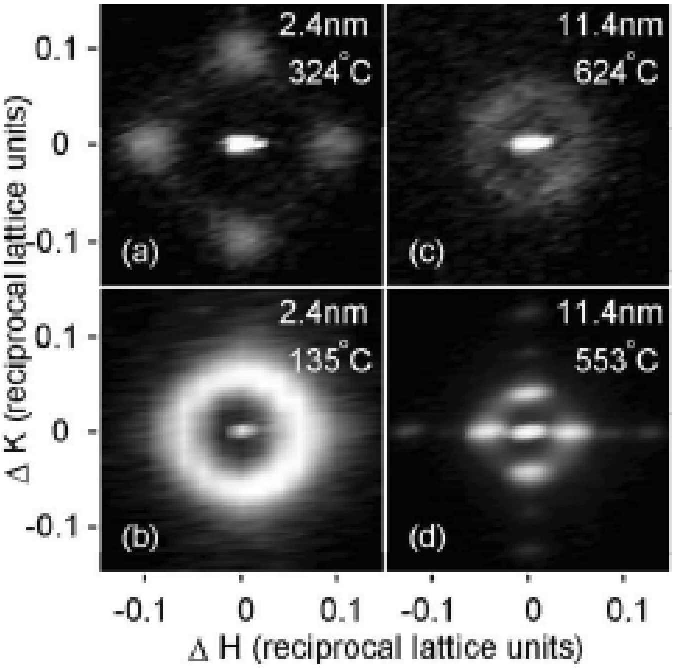


Dynamics of stripe domain – Temperature/Thickness



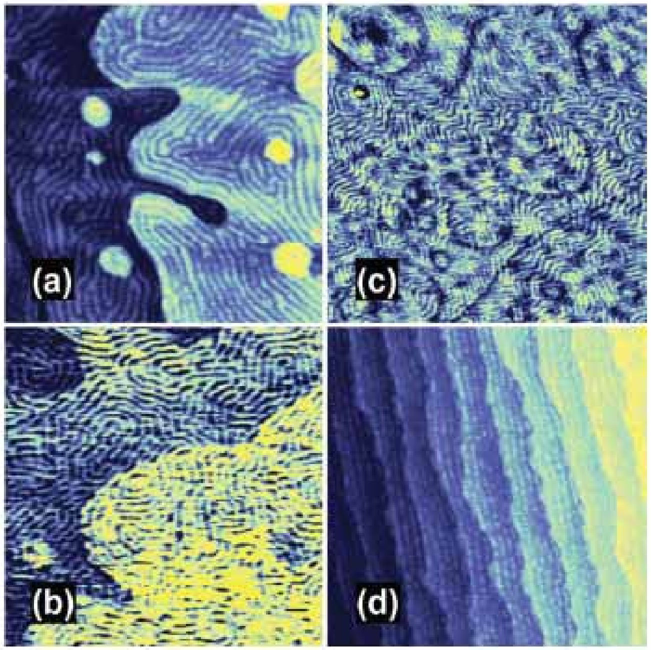
Thompson, et al. APL 93, 182901 (2008)

- Low temperature stripe domains are static
- However – at high temperature they may be dynamic
- Study equilibrium dynamics of domains using coherent x-rays



Satellites due to stripe domains around (304) PTO

180° stripe domains in thin $PbTiO_3/SrTiO_3$



500x500nm These AFM images show terraces and the fine structure of the 180o stripe domains

PTO thickness
(a),(b), (d), 10nm thick PTO/STO
(c) 5nm thick PTO/STO

Catalysis

Example Volcano plot - oxygen reduction activity

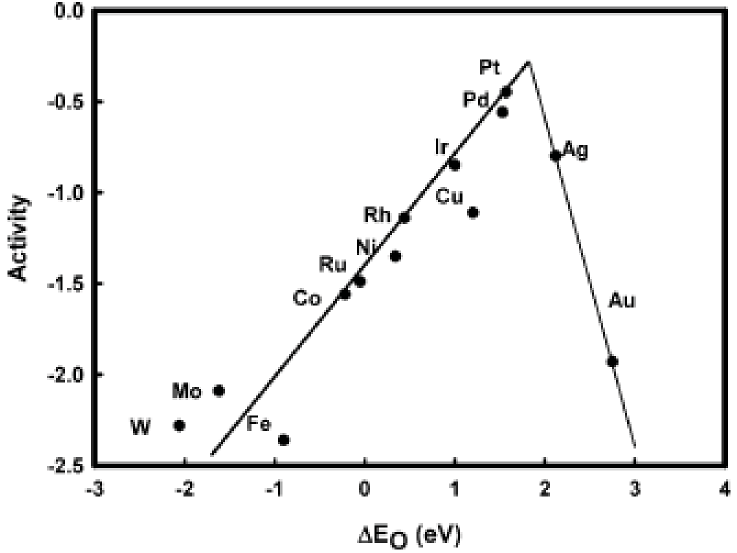
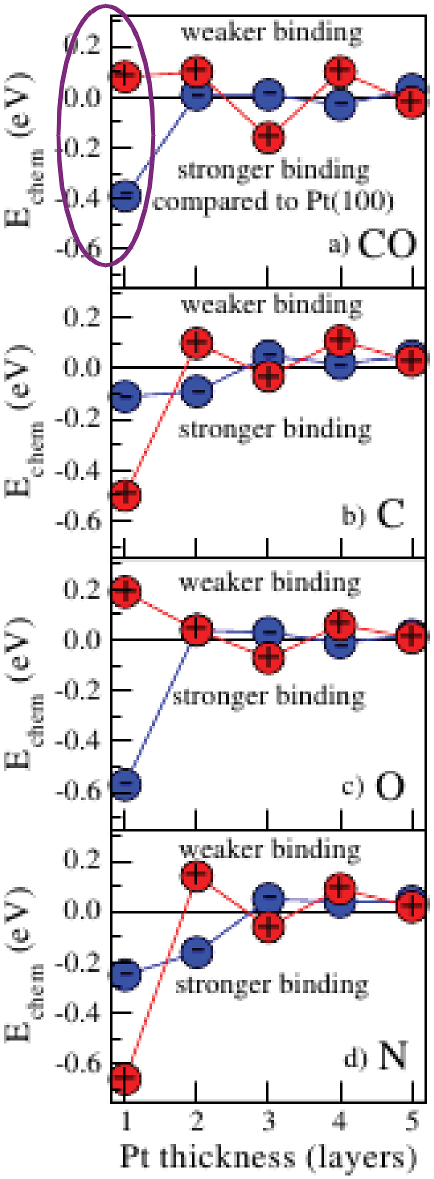


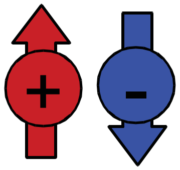
Figure 4. Trends in oxygen reduction activity (defined in the text) plotted as a function of the oxygen binding energy.

J. K. Nørskov, et al.,17886, J. Phys. Chem. B 108, 17886 (2004)

- Catalytic activity – the sweet spot
    - Too weak chemisorption leads to not enough species around to react
    - Too strong chemisorption and the reactant doesn't leave (blocking sites)
- Turnover time can be long, e.g. milliseconds
- Many orders of magnitude in activity improvement theoretically possible – we are far from the fundamental limit

Polarization control of catalytic reactions





Kolpak, et al. PRL 98, 166101 (2007) [THEORY]

- Polarization orientation strongly affects catalytic activity of Pt overlayer – allows possibility of electrically tuning activity or selectivity

- If polarization can be dynamically cycled, can turnover rate be increased?

Calculations - Chemisorption energies for CO, O, C, and N as function of polarization direction (+ or -) and Pt thickness for the PbO/Pt interfaces.

Summary

A variety of scientific questions in ferroelectric materials could be addressed by "tickle-probe" experiments:

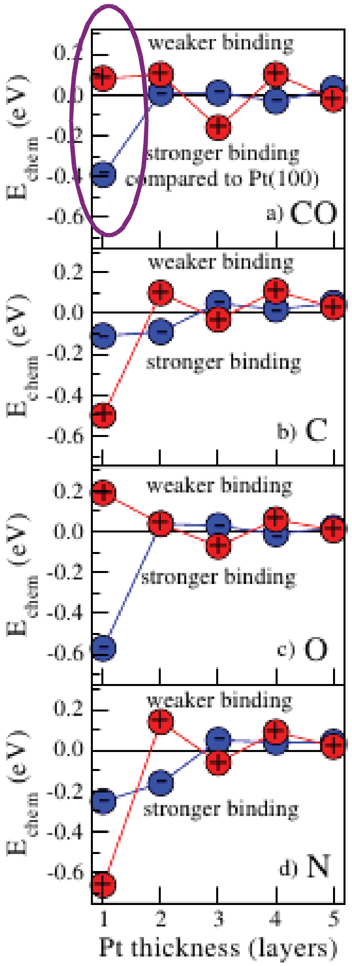
- Dynamics of ultrafast polarization switching and strain/polarization/field coupling
- Stripe domain dynamics
- Catalytic behavior and dynamics

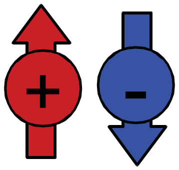
Several methods to stimulate the sample would allow high rep rate experiments:

- Apply field with electrodes in small devices
- Apply field with THz light
- Apply strain using laser-induced shock

Polarization control of ferroelectric – dynamic control of catalytic activity

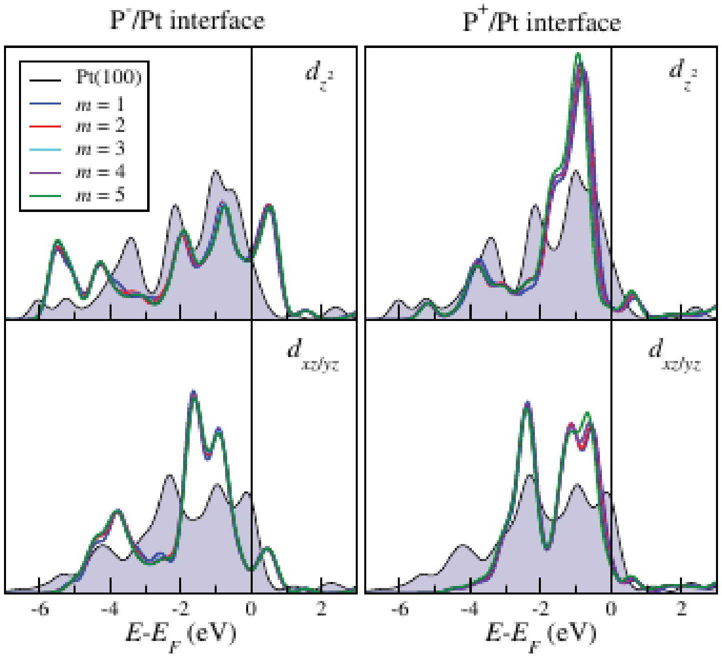
Calculated - Chemisorption energies for CO, O, C, and N as function of polarization direction (+ or -) and Pt thickness for the PbO=Pt interfaces.





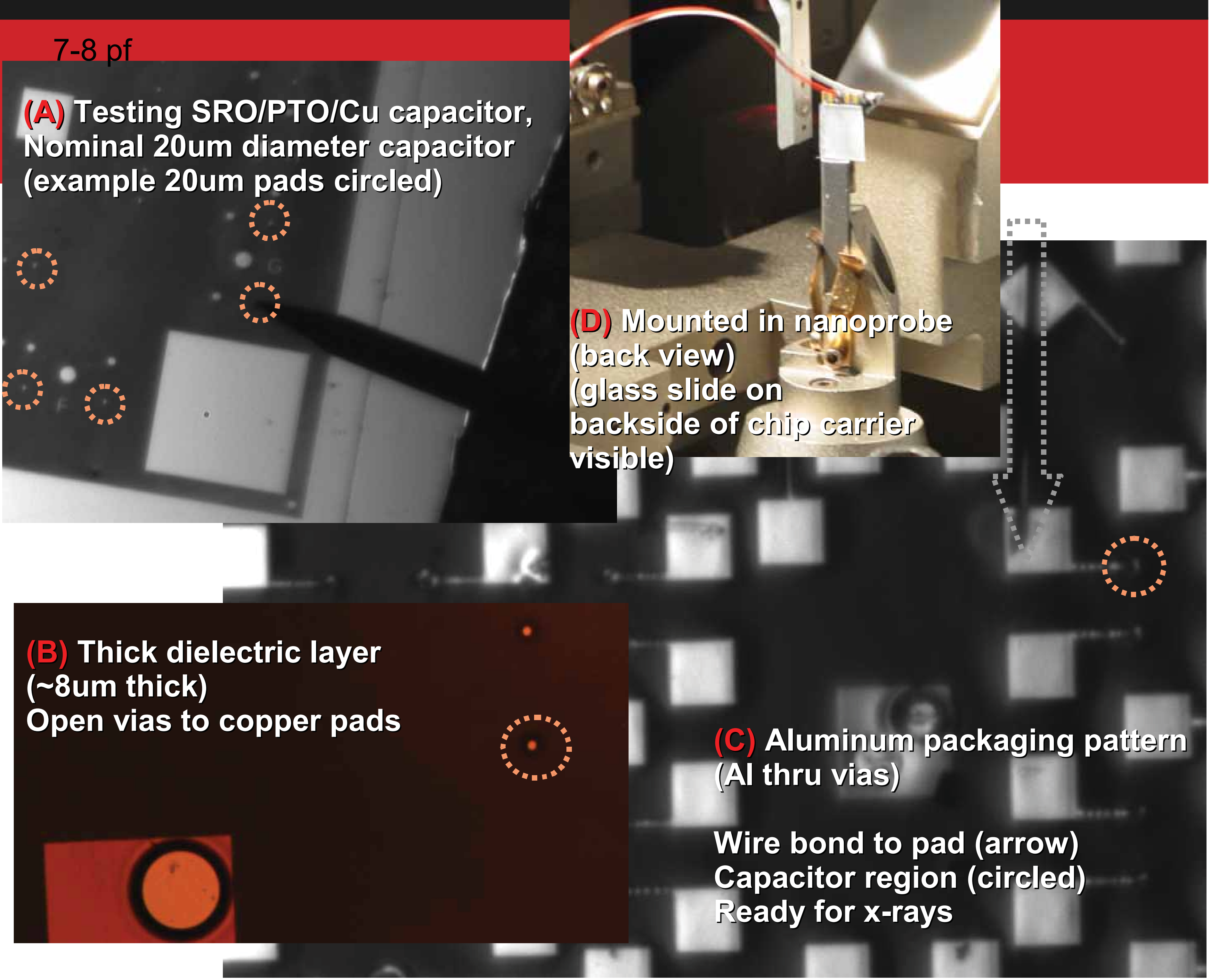
- Catalytic activity – the sweet spot
  - Too weak chemisorption leads to not enough species around to react
  - Too strong chemisorption and the reactant doesn't leave (blocking sites)

Platinum d_{z2} and $d_{xz/yz}$ DOS as a function of PbTiO3 film thickness for one monolayer of Pt above the P+(left) and the P- (right) PbO-terminated PbTiO3. (Gray shaded is bulk Pt (100))



Alexie M. Kolpak, et al. PRL 98, 166101 (2007) [theory – Rappe group]

7-8 pf



**(A) Testing SRO/PTO/Cu capacitor,
Nominal 20um diameter capacitor
(example 20um pads circled)**

**(D) Mounted in nanoprobe
(back view)
(glass slide on
backside of chip carrier
visible)**

**(B) Thick dielectric layer
(~8um thick)
Open vias to copper pads**

**(C) Aluminum packaging pattern
(Al thru vias)**

**Wire bond to pad (arrow)
Capacitor region (circled)
Ready for x-rays**