Local Polarization Switching and PFM Spectroscopy

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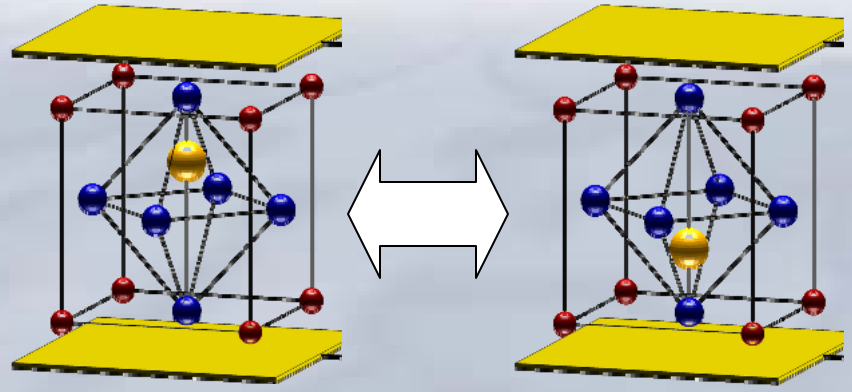
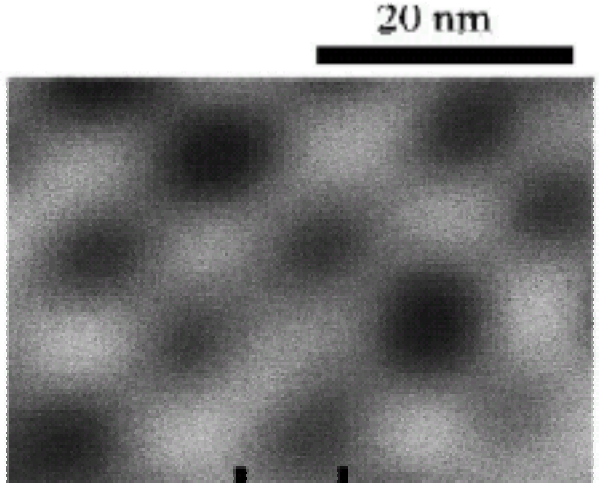
Ferroelectric Materials on the Nanoscale

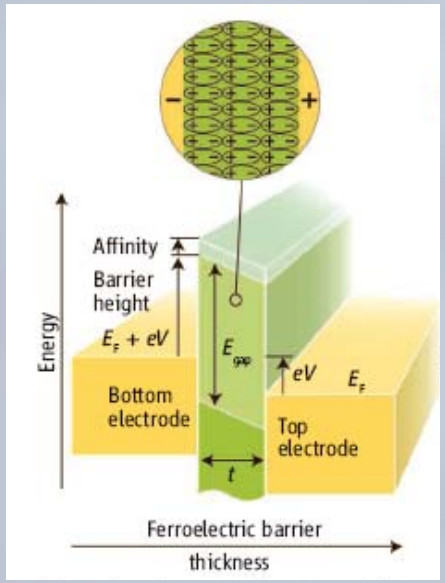


Perfect materials for information storage:

1. Non-volatile ferroelectric memories
   Fujitsy, Ramtron, TI
2. Data storage
   Samsung, Seagate, Intel
3. Resistive memories



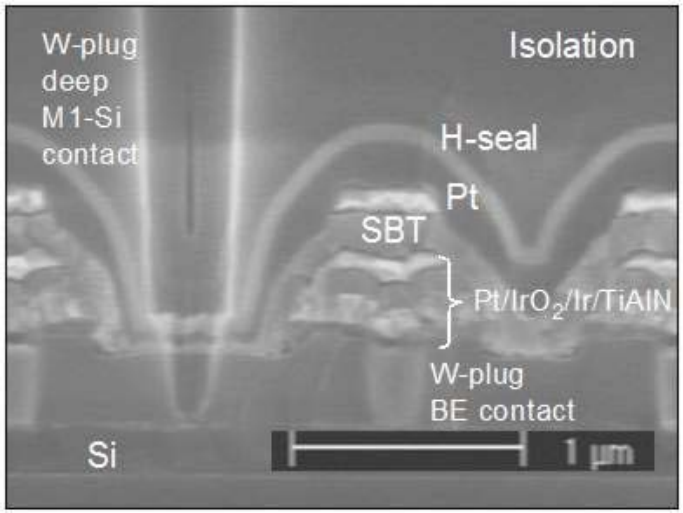
Cho et al., APL 2005

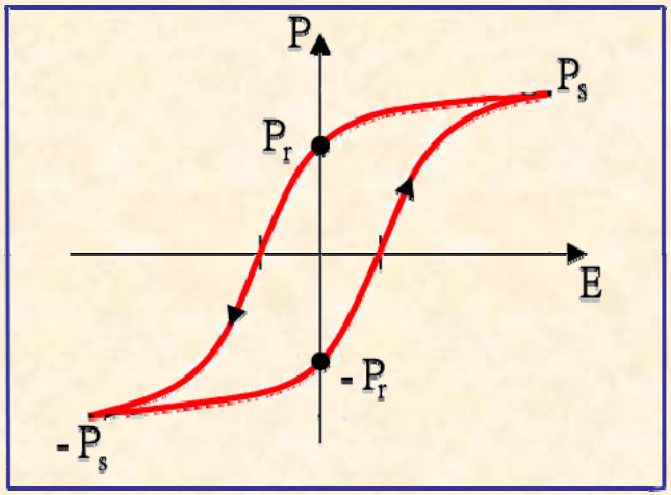


Kohlstedt and Tsymbal

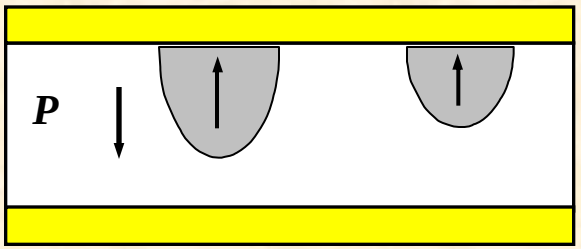
High speed: 50 ns vs 1μs – 1ms for Flash and EEPROM)
Low power: 1 pJ compared to 10 pJ-200 nJ for Flash and EEPROM
Endurance: 10^{12} cycles compared to 10^{6} for EEPROM
Scalable: 20 nm not a limit

Polarization Dynamics: Real and Ideal





Top electrode



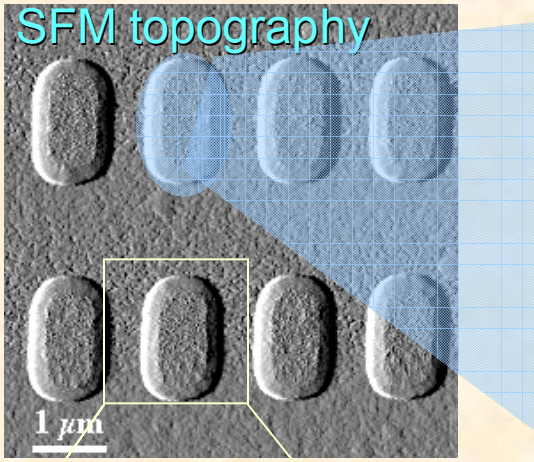
Bottom electrode

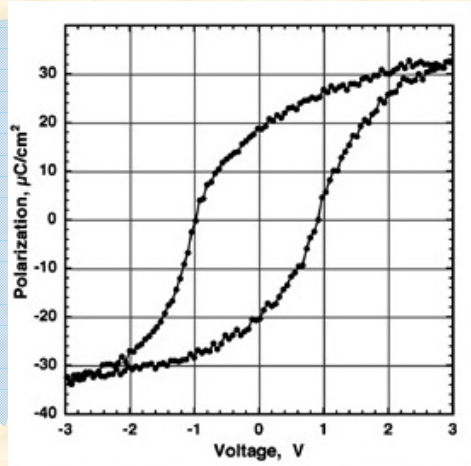
In macroscopic hysteresis measurements, measured is switchable polarization charge in a lcapacitor. This provides information (imprint, fatigue, etc) vital for ferroelectric devices. However, measurements are averaged over large area and this approach is inapplicable to nanoscale structures.

- What happens inside?
- Can we observe domain dynamics (wall motion and pinning)?
- Can we map switching behavior (domain nucleation)?

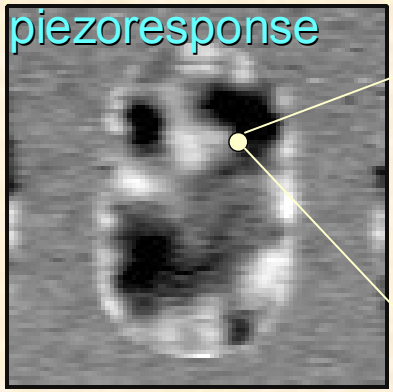
Characterization of Ferroelectric Capacitors

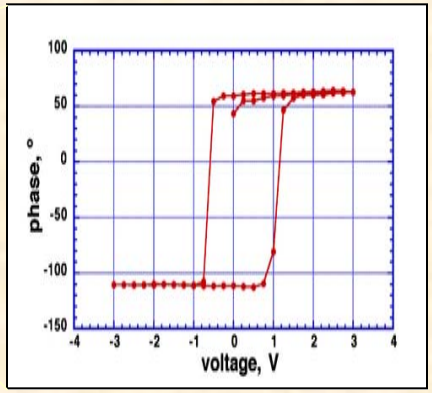
FeRAM PZT capacitors **Polarization loop**



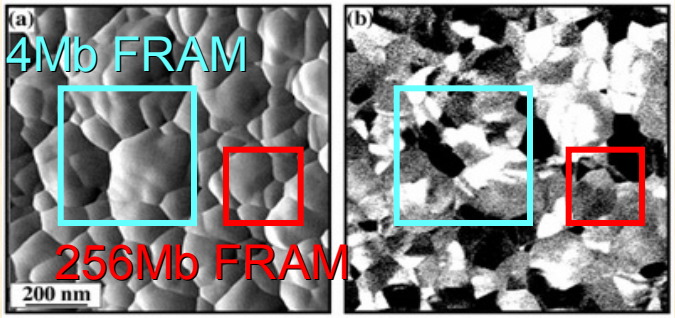


Minimum size of the capacitor that can be tested by a conventional technique is ~ 1 μm^2 (limited by the sensitivity of a current amplifier)





PZT inhomogeneity effect on FeRAM



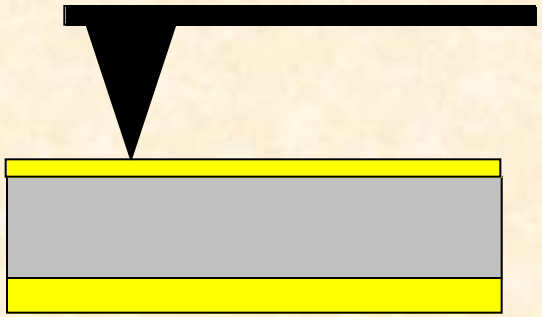
Origin of property variations:

- inhomogeneity of PZT layer
- mechanical stress
- etching damage

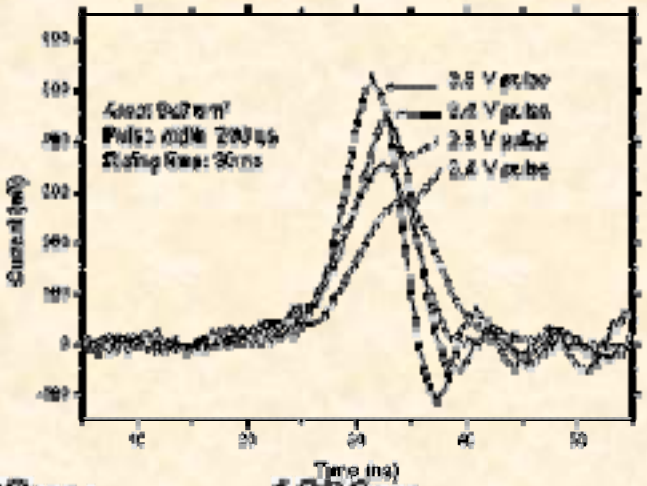
PFM allows a nano-insight into the μm size FeRAM capacitors to address the spatial variability of properties at nanoscale (< 10 nm)

NC STATE UNIVERSITY

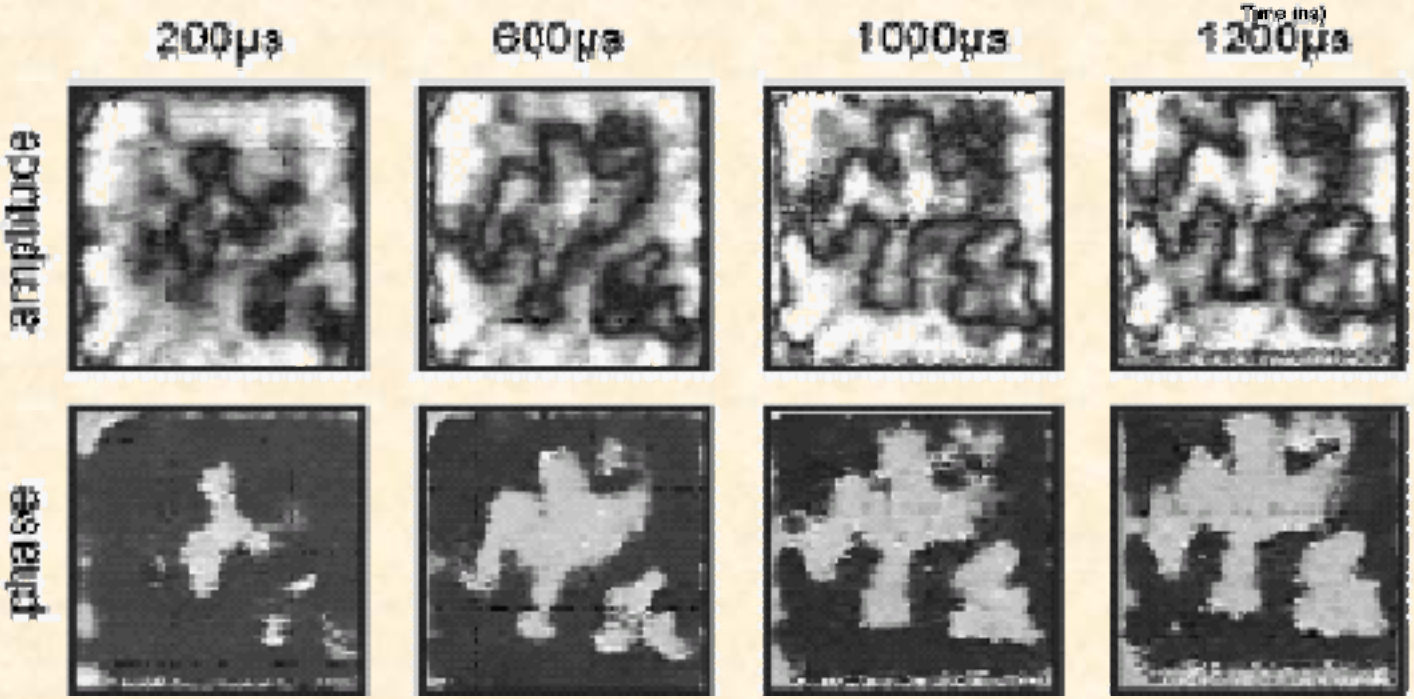
Switching in Ferroelectric Capacitors



- Uniform field
- Local detection
- Measure current

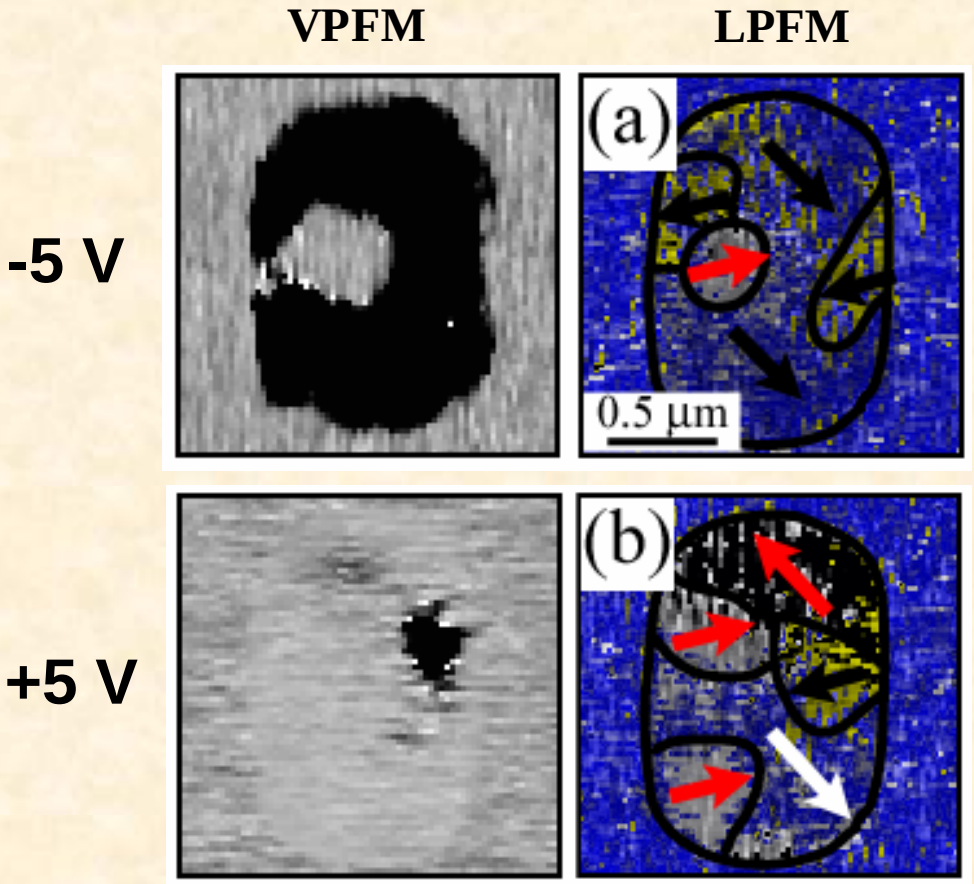


PFM and simultaneous switching current measurements

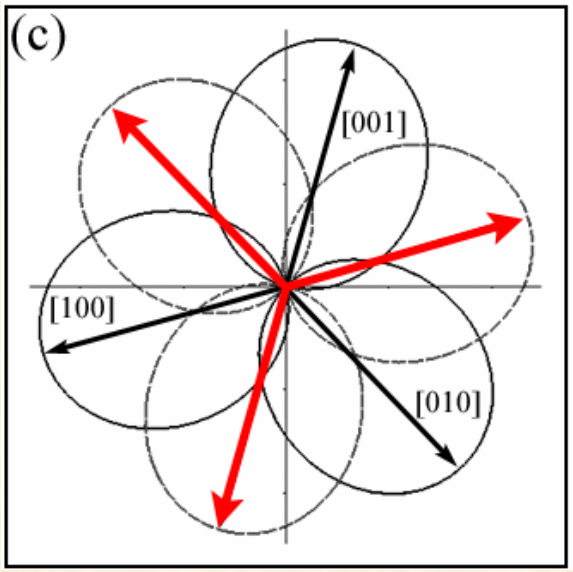


C. Dehoff et.al. Rev. Sci. Inst. **76**, 023708 (2005).

Orientational Imaging of Switching Process



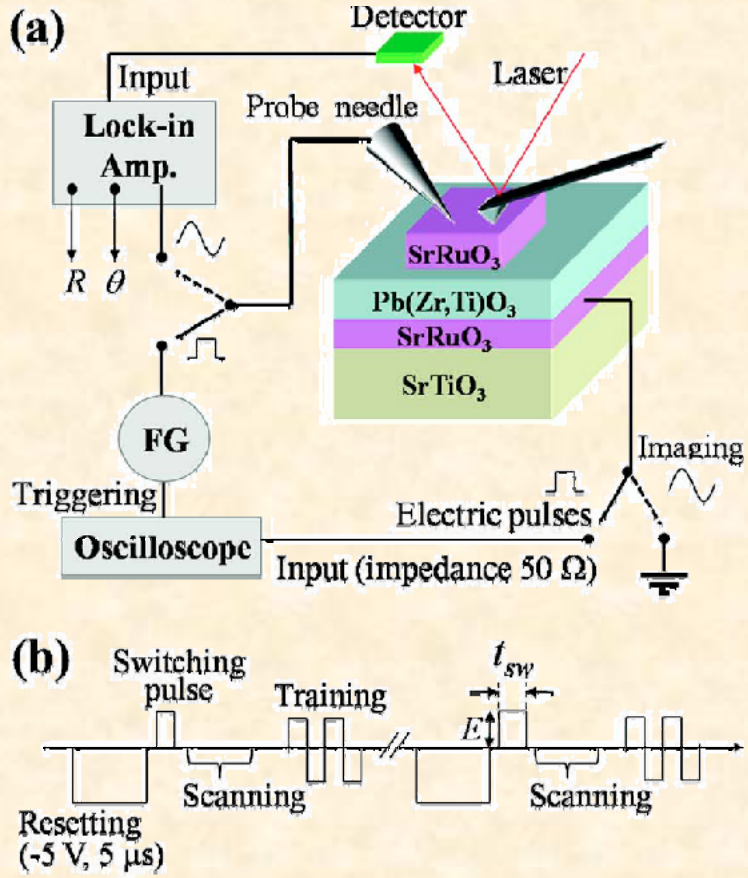
Projection of piezoelectric surfaces onto (111) plane

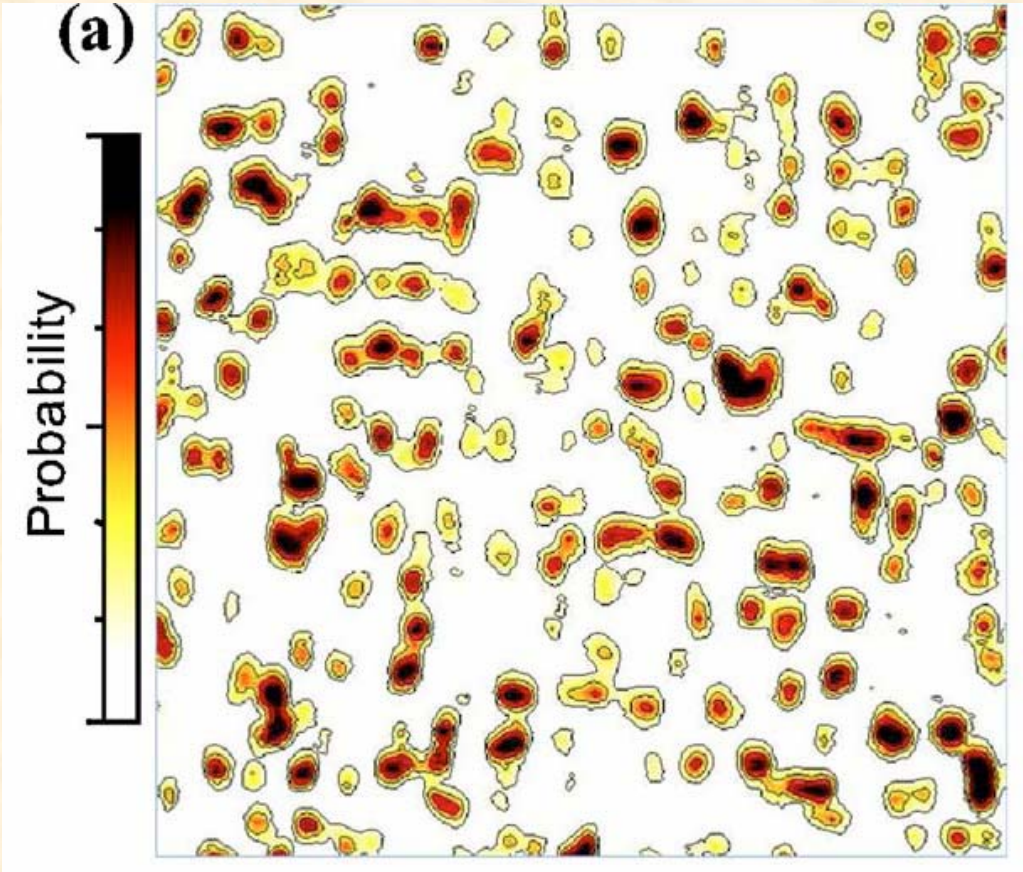


We can observe the evolution of ferroelastic domains inside the material

- Which domains switch and which do not
- Strains and degradation

Heterogeneous Nucleation in Capacitors

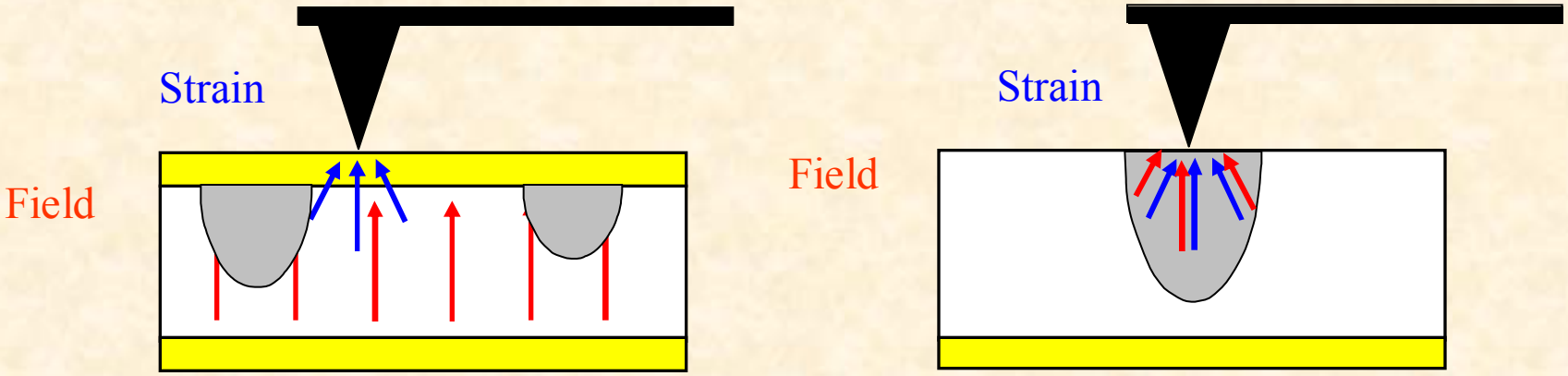




The nucleation sites in capacitors can be visualized directly.

D. J. Kim, J. Y. Jo, T. H. Kim, S. M. Yang, B. Chen, Y. S. Kim, and T. W. Noh, Appl. Phys. Lett. **91**, 132903 (2007)

Global vs. Local Polarization Dynamics



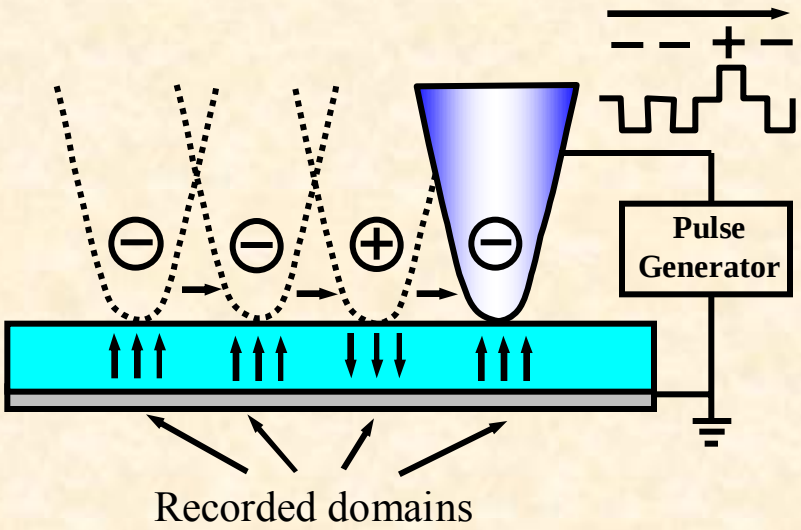
In top-electrode measurements, excitation is global and detection is local. Hence,

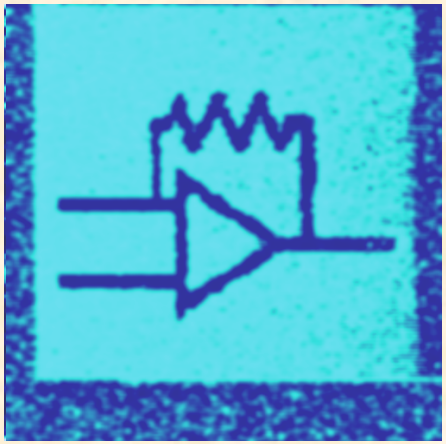
- Measurements are robust and are insensitive to tip state
- Resolution is limited by film thickness (clamped) or electrode thickness (free)
- Nucleation proceeds at intrinsic nucleation sites and cannot be controlled

In tip-electrode measurements, excitation is local and detection is local. Hence,

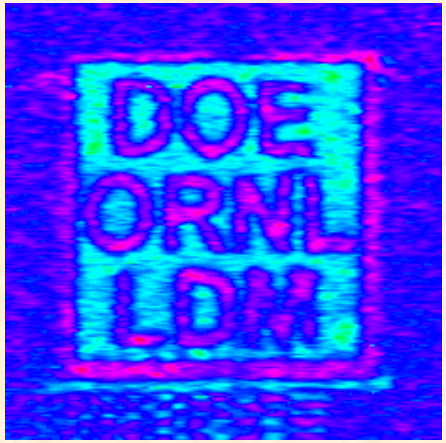
- Measurements are very sensitive to tip state
- Resolution is limited by the tip radius of curvature/contact area
- Nucleation proceeds at the tip location and can be controlled

Manipulating Polarization on the Nanoscale



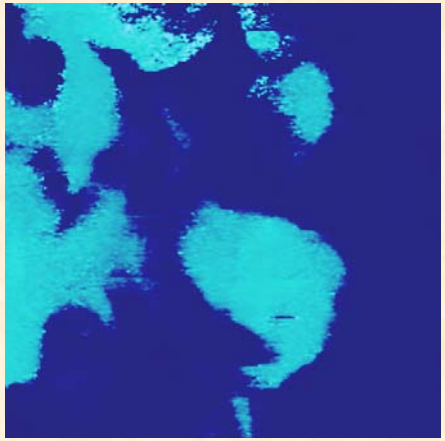


Simple shapes



Text

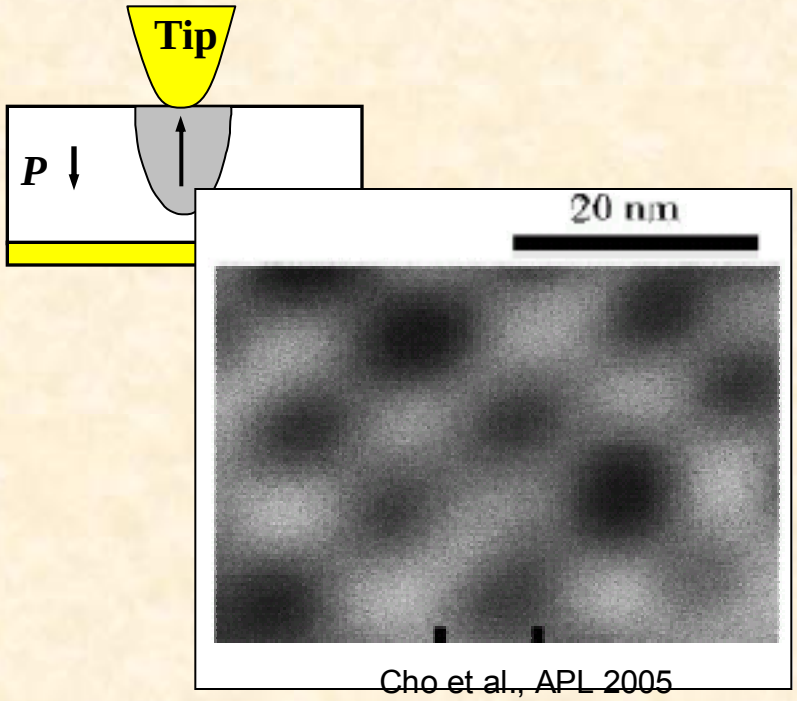
Images



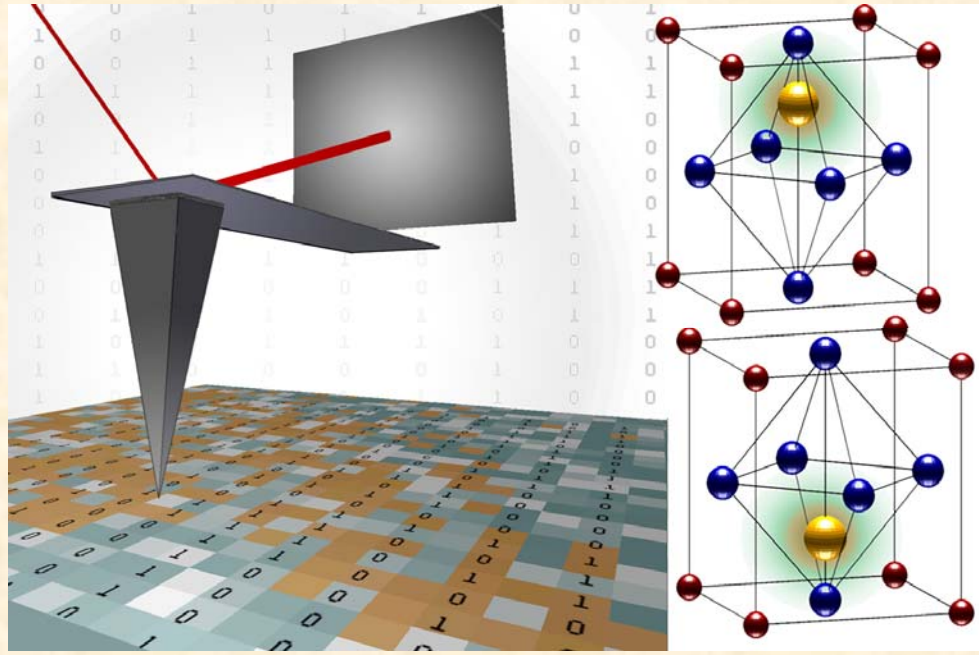
Domain dynamics

PFM of Ferroelectric Materials

In ferroelectric materials, polarization can be manipulated by the electric field.



Cho et al., APL 2005



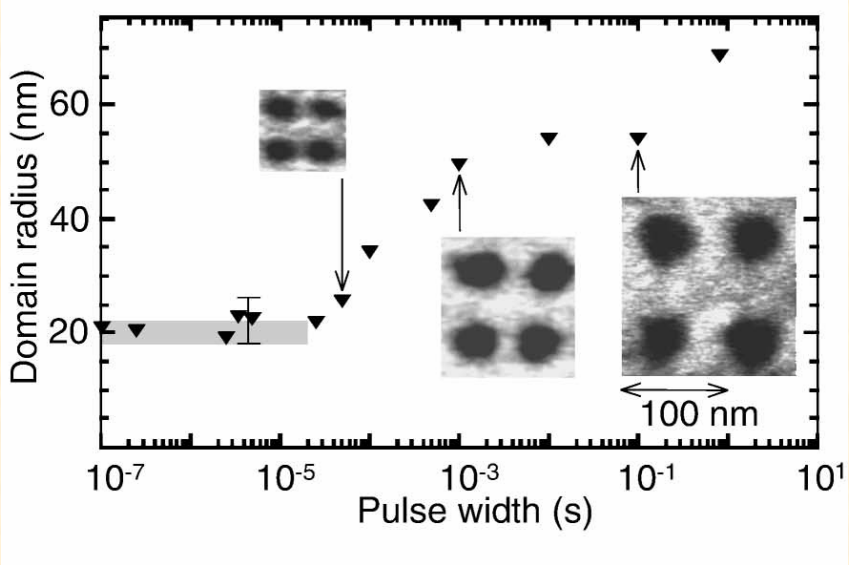
Applications:

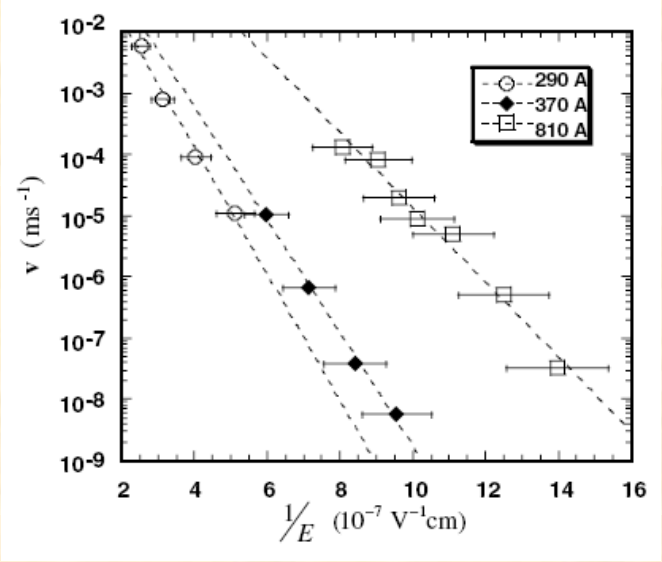
- High density data storage
- Ferroelectric lithography

Fundamental science:

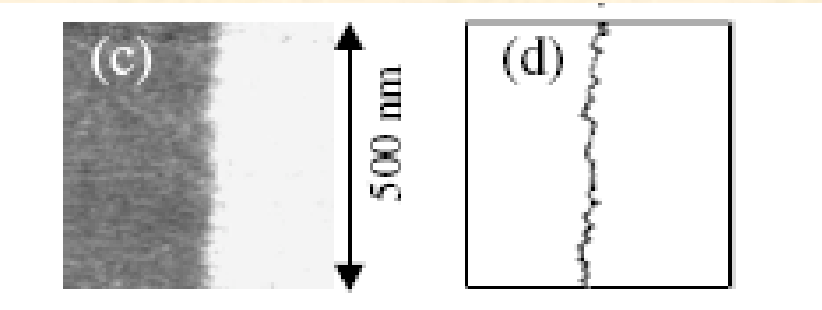
- Physics of polarization switching
- Nucleation
- Wall motion

Domain Growth Kinetics





$$v \sim \exp - \frac{R}{k_B T} \left(\frac{E_0}{E} \right)^{\mu},$$

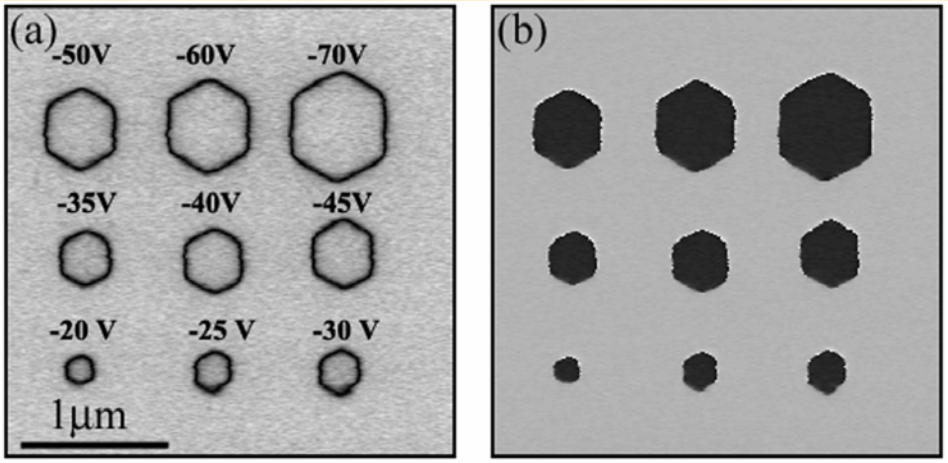


- Domain growth kinetics can be described as domain wall motion in disordered media
- Kinetics yields information on disorder type
- Similar information can be obtained from wall roughness

P. Paruch, T. Giamarchi, and J.-M. Triscone Phys. Rev. Lett. 94, 197601 (2005).

T. Tybell, P. Paruch, T. Giamarchi, and J.-M. Triscone, Phys. Rev. Lett. **89**, 097601 (2002).

Domain Growth



Bias dependence of domain size:

Activation energy α:

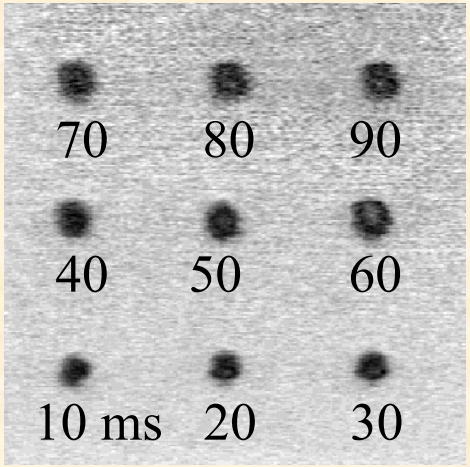
$2x10^3$ kV/cm (20 V) and 50kV/cm (100 V)

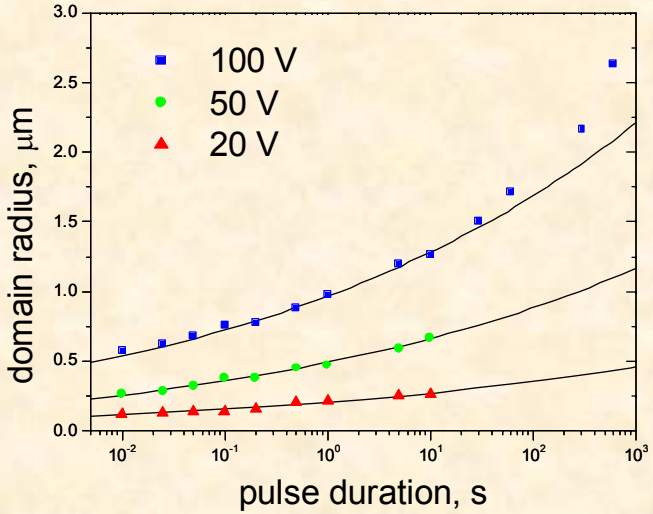
Minimal domain radius:

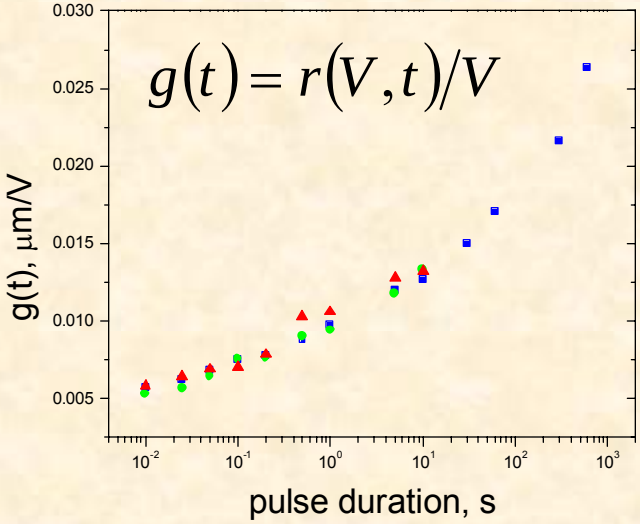
r_0 = 17 nm (20 V) and 110 nm (100 V)

A. Gruverman et al, Appl. Phys. Lett. **87,** 082902 (2005).

Time dependence of domain size

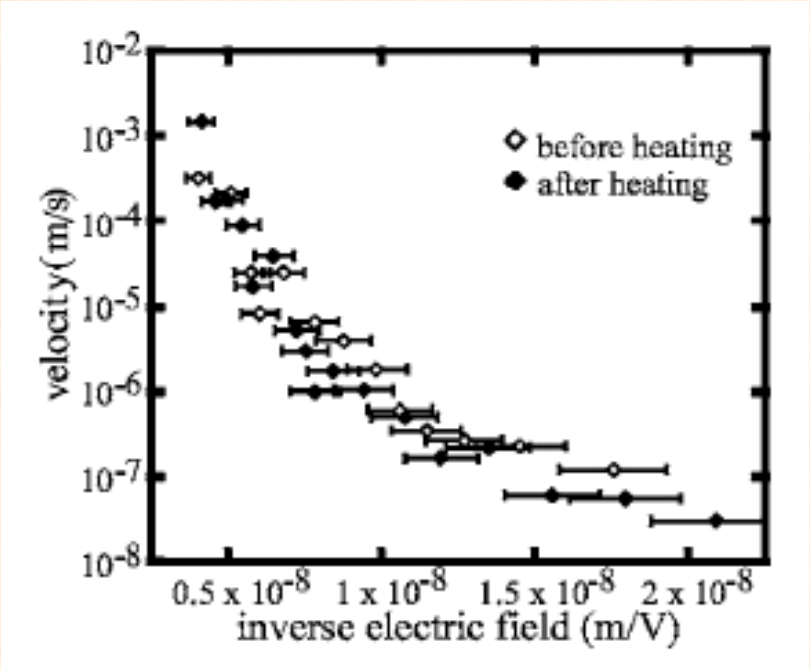




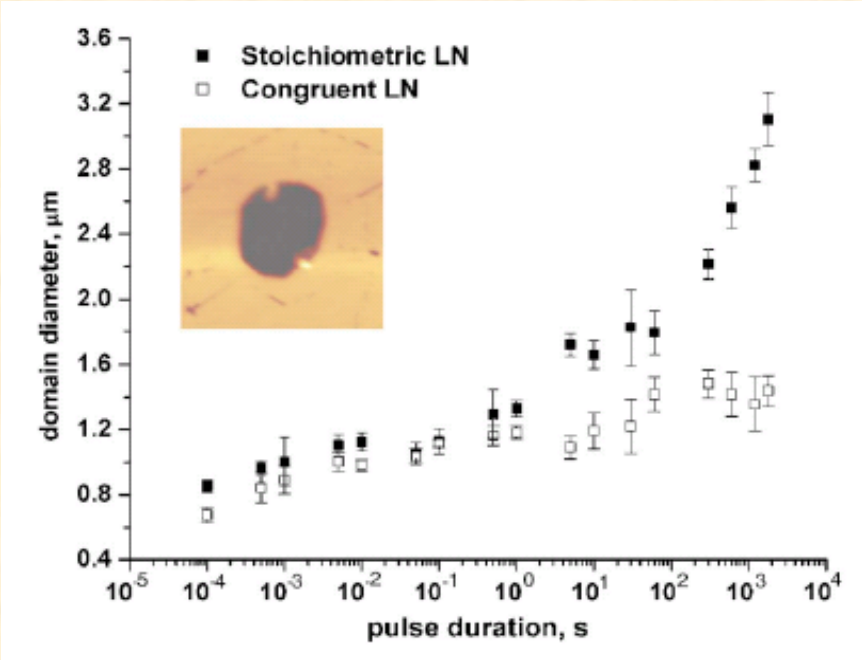


- Domain growth kinetics can be described by universal scaling curve
- For small times, $g(t) \sim \ln(t)$

Effect of Defects on Domain Growth



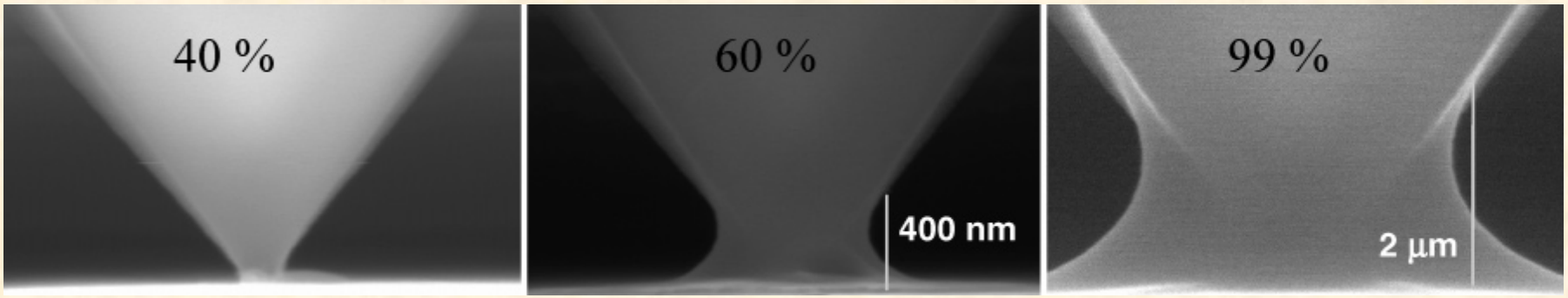
P. Paruch et al, Appl. Phys. Lett. **88**, 162907 (2006)



A. Agronin et al, Appl. Phys. Lett. **88**, 072911 (2006)

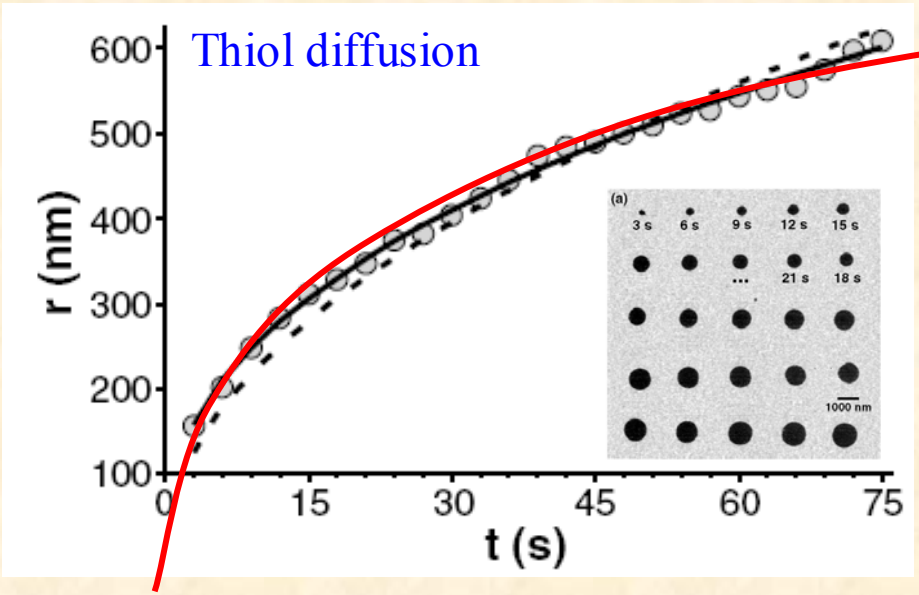
- Defects inhibit domain growth (pinning)

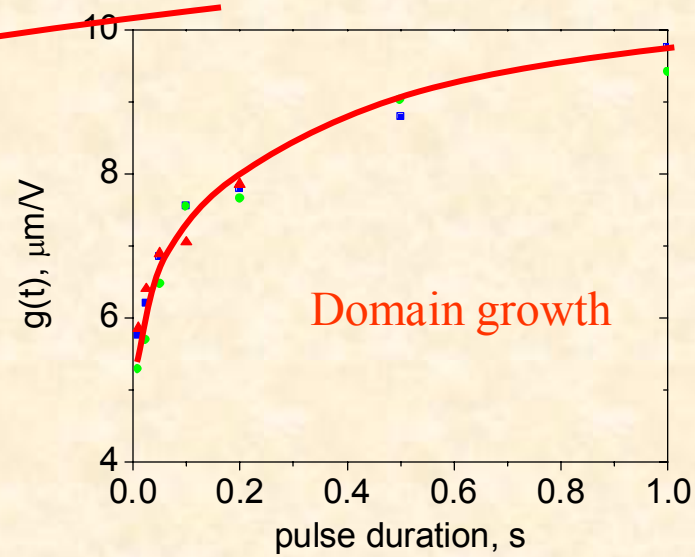
Note of caution:



- There is a meniscus at the tip-surface junction
- The 2D diffusion gives rise to similar kinetic laws

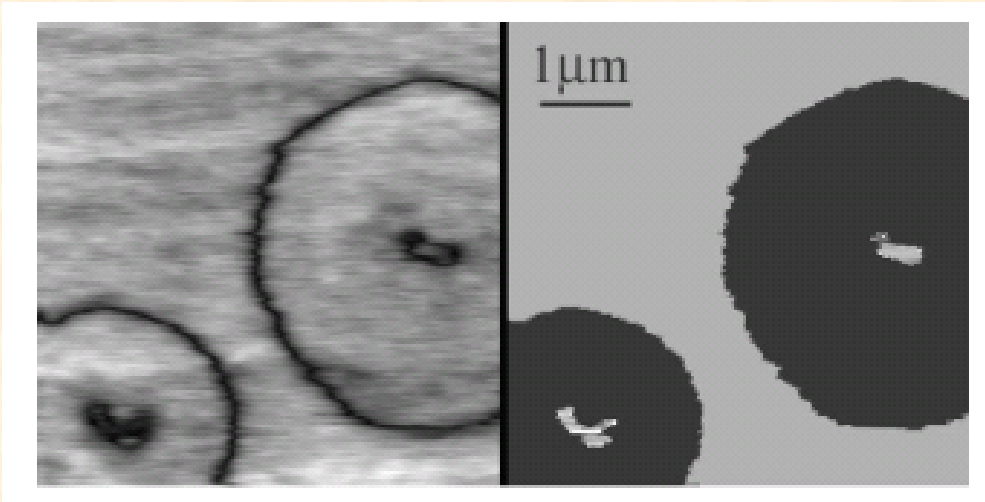
Langmuir **21**, 8096-8098 (2005)



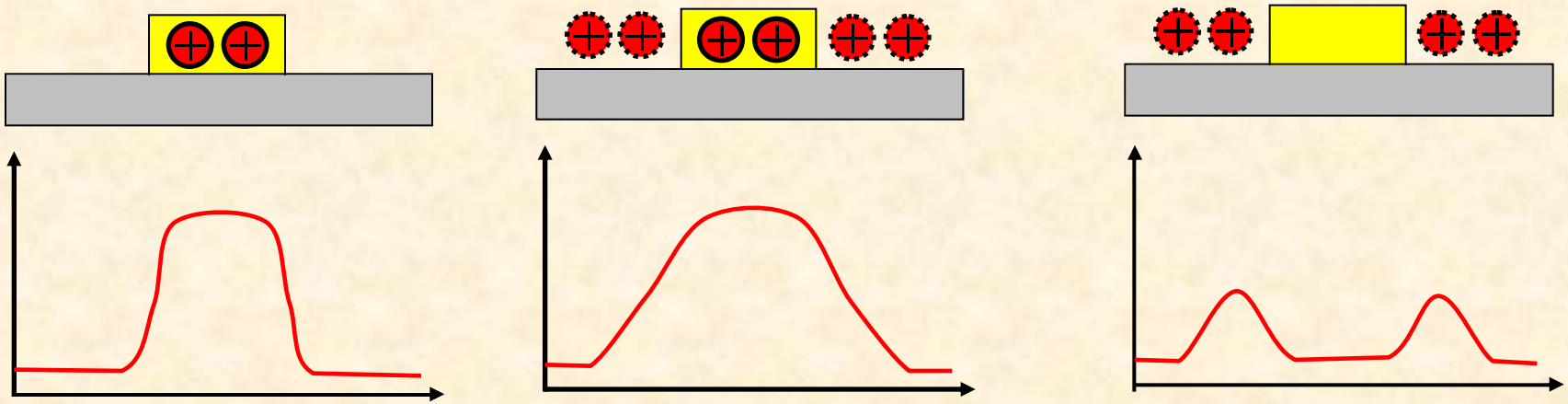


P. E. Sheehan, L. J. Whitman, W.P. King, and B.A. Nelson, Appl. Phys. Lett. **85**, 1589 (2004)

Adsorbed Water Effects on PFM

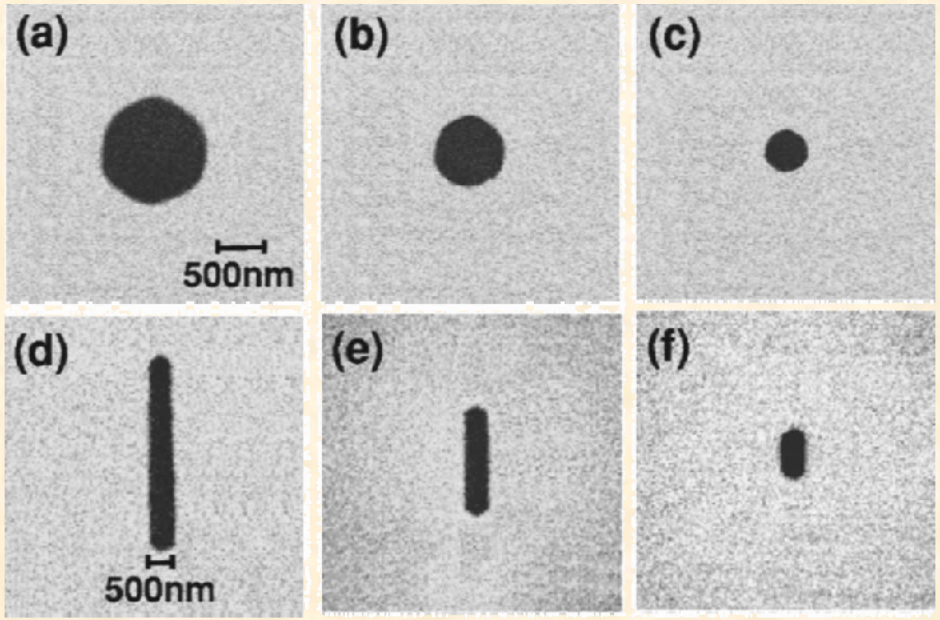


S. Bühlmann, E. Colla, and P. Muralt, Polarization reversal due to charge injection in ferroelectric films, Phys. Rev. B 72, 214120 (2005)

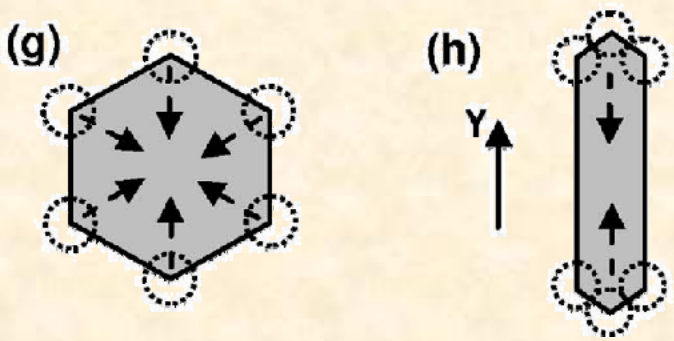


Formation of "bubble" domains, previously attributed to ferroelectroelastc switching, is actually due to surface charge dynamics!

Domain Relaxation Kinetics

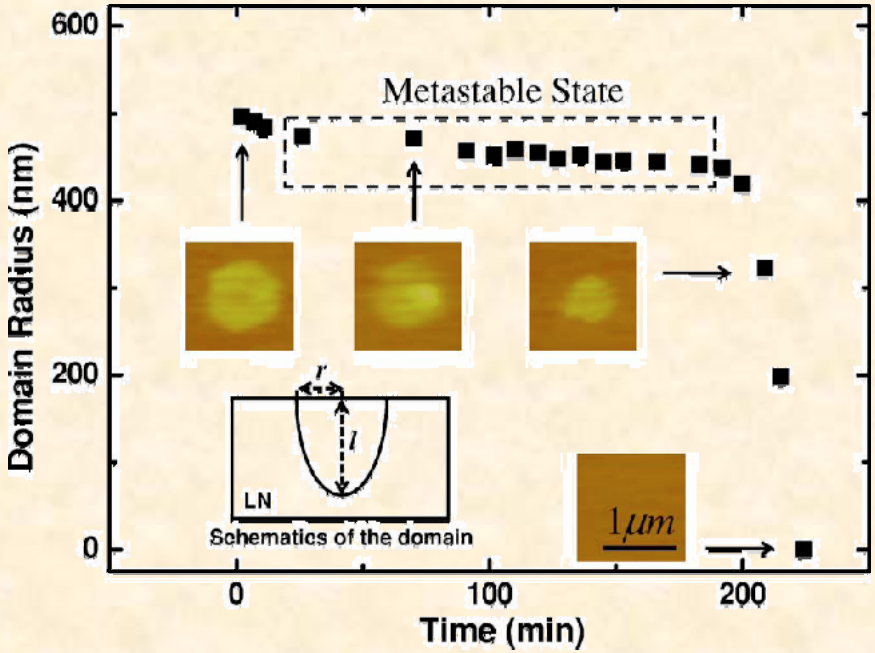


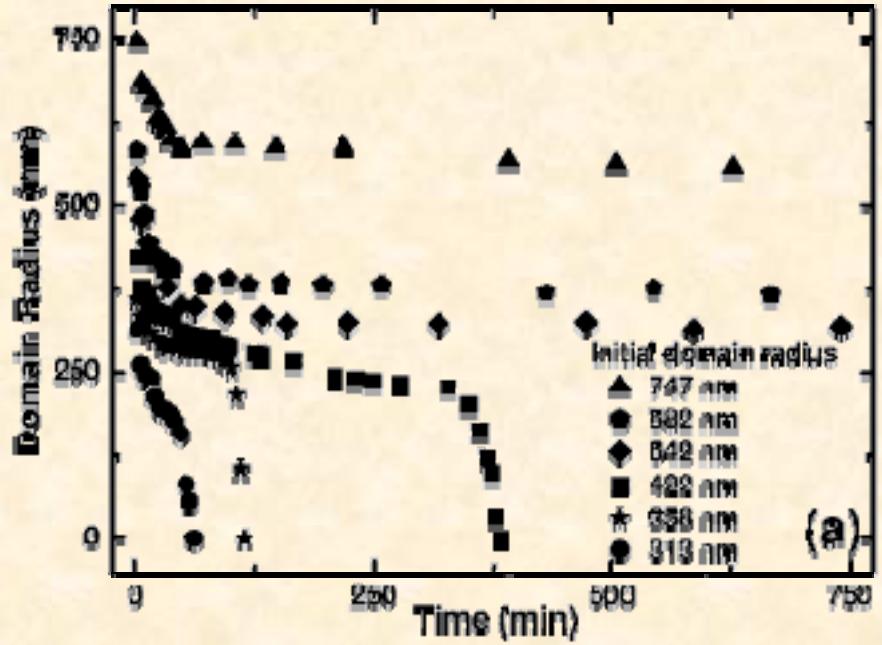
- Domain relaxation is driven by the corners
- Relaxation can be fast at high temperatures
- Relaxation depends on the screening processes (air vs. vacuum)
- Relaxation can be minimized by increasing density of pinning sites – e.g. by ion implantation



X. Liu, K. Kitamura, and K. Terabe, Appl. Phys. Lett. **89**, 142906 (2006).

Domain Relaxation Kinetics



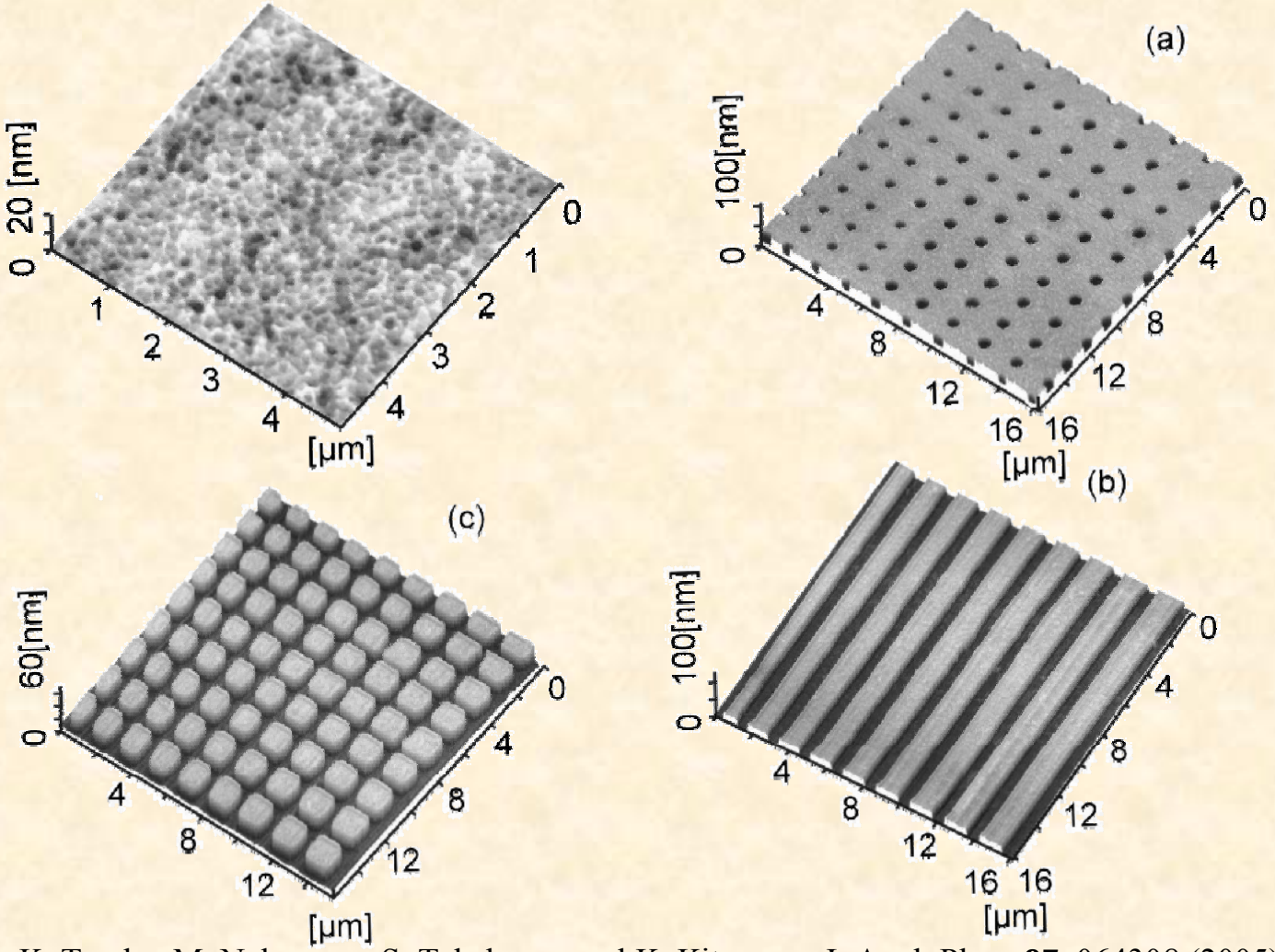


- Relaxation has two stages
- Slow stage is shrinking of the penetrating domain
- Fast stage is vertical shrinkage
- Retention time is domain size and thickness dependent
- Data agrees well with Molotskii model assuming weak pinning

Y. Kan, X. Lu, H. Bo, F. Huang, X. Wu, and J. Zhu, Appl. Phys. Lett. **91**, 132902 (2007)

From Domain Patterns to Nanostructures

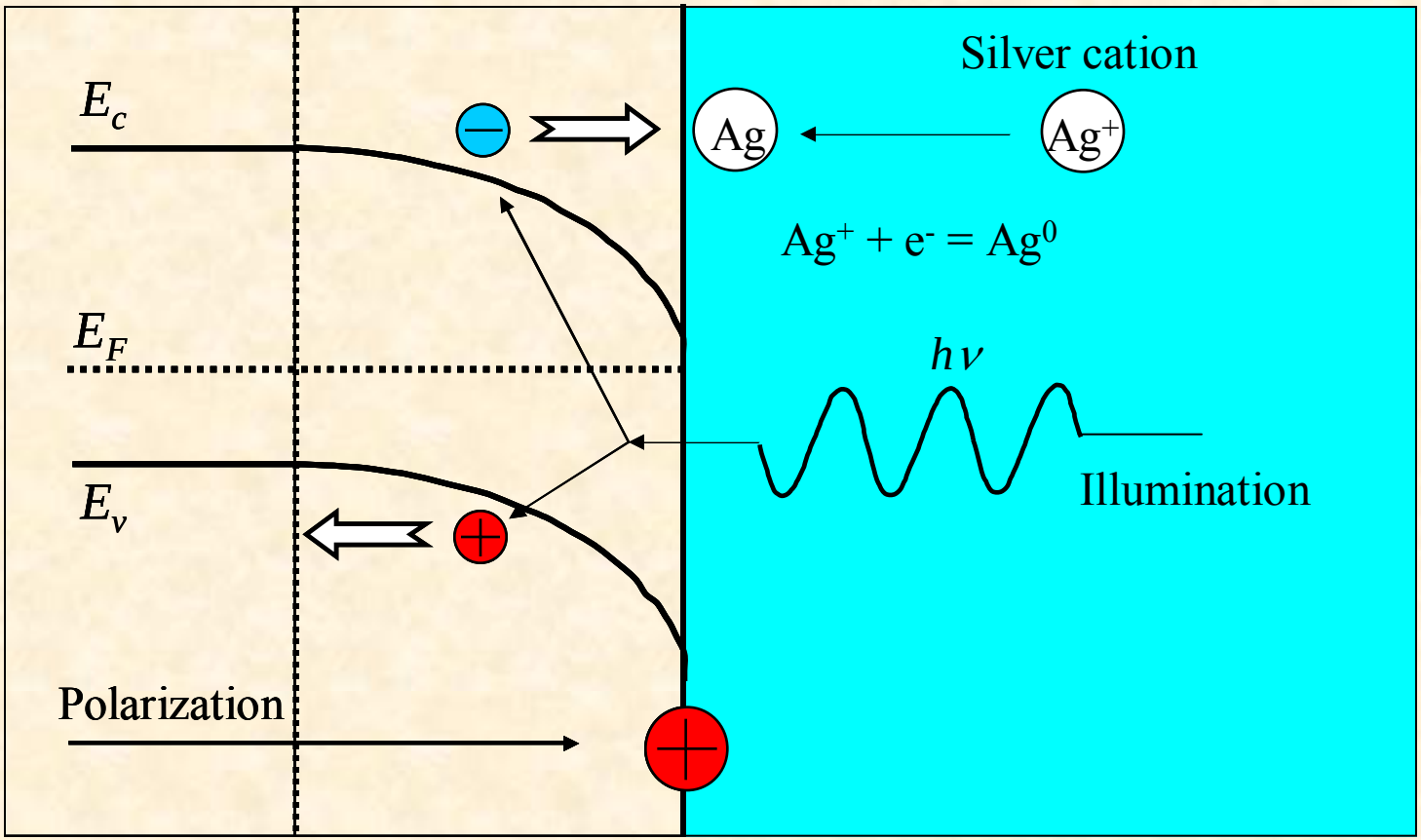
- Etching rate of ferroelectric material is dependent on domain orientation
- Etching produces relatively flat (2 nm roughness for 70 nm etching depth) surfaces



X. Liu, K. Terabe, M. Nakamura, S. Takekawa, and K. Kitamura, J. Appl. Phys. **97**, 064308 (2005)

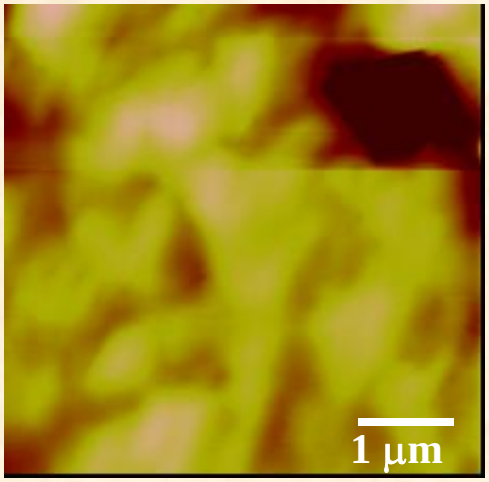
Photoelectric Phenomena in Ferroelectrics

Perovskite titanates ($SrTiO_3$, TiO_2) are often photoactive
(photocatalysis, photoreduction of metals, water photodissociation)

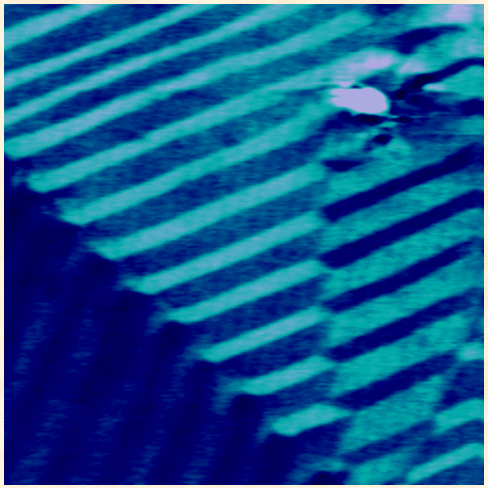


- **Reduction occurs on c^+ domains**
- **Oxidation occurs on c^- domains**

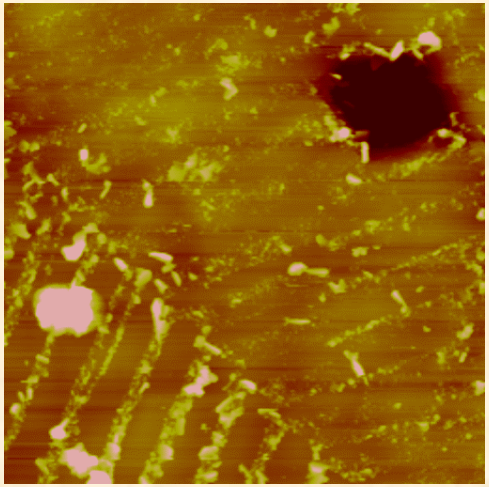
Domain-controlled Deposition



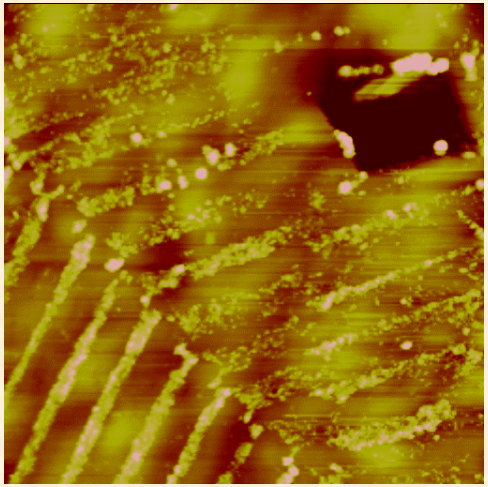
Surface topography



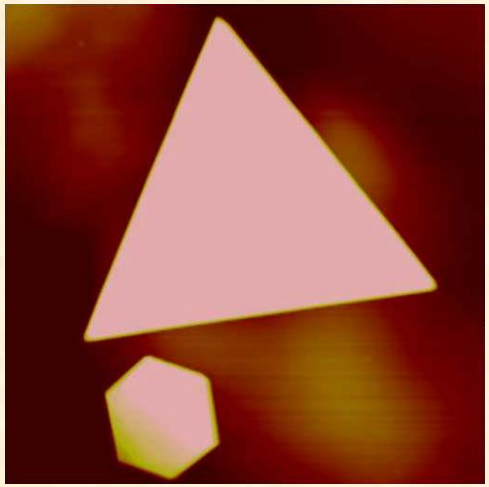
Piezoresponse



Ag deposition



Pd deposition

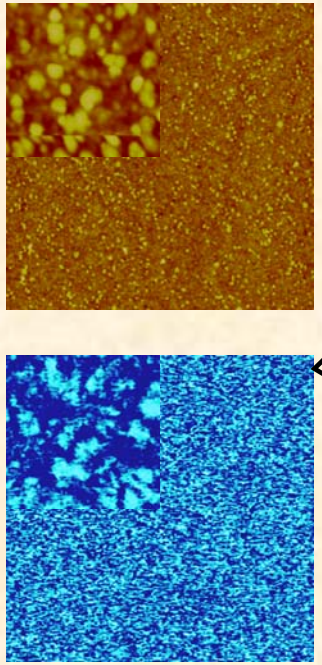


Au deposition

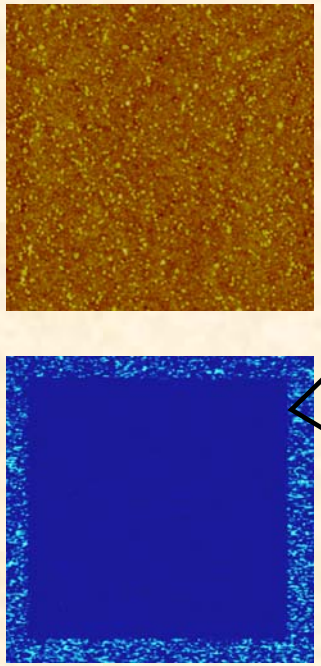
Deposition process can be repeated many times:

⇒ Successive deposition of several metals is possible

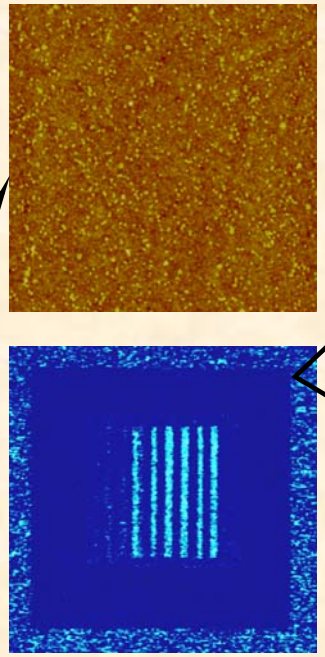
Domain-controlled Deposition: PZT



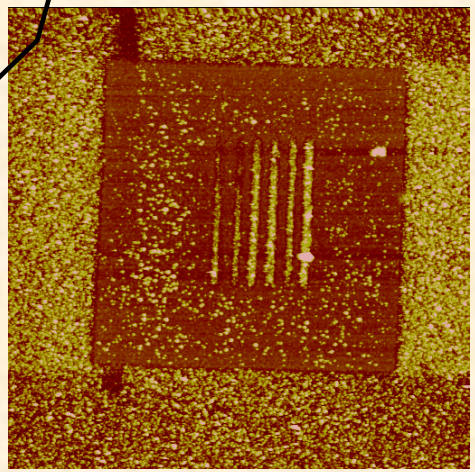
Sol-gel PZT thin film on $Si/SiO_2/Pt$



A uniform area is poled with a 10 V tip voltage



Local regions are switched with tip voltages of -10



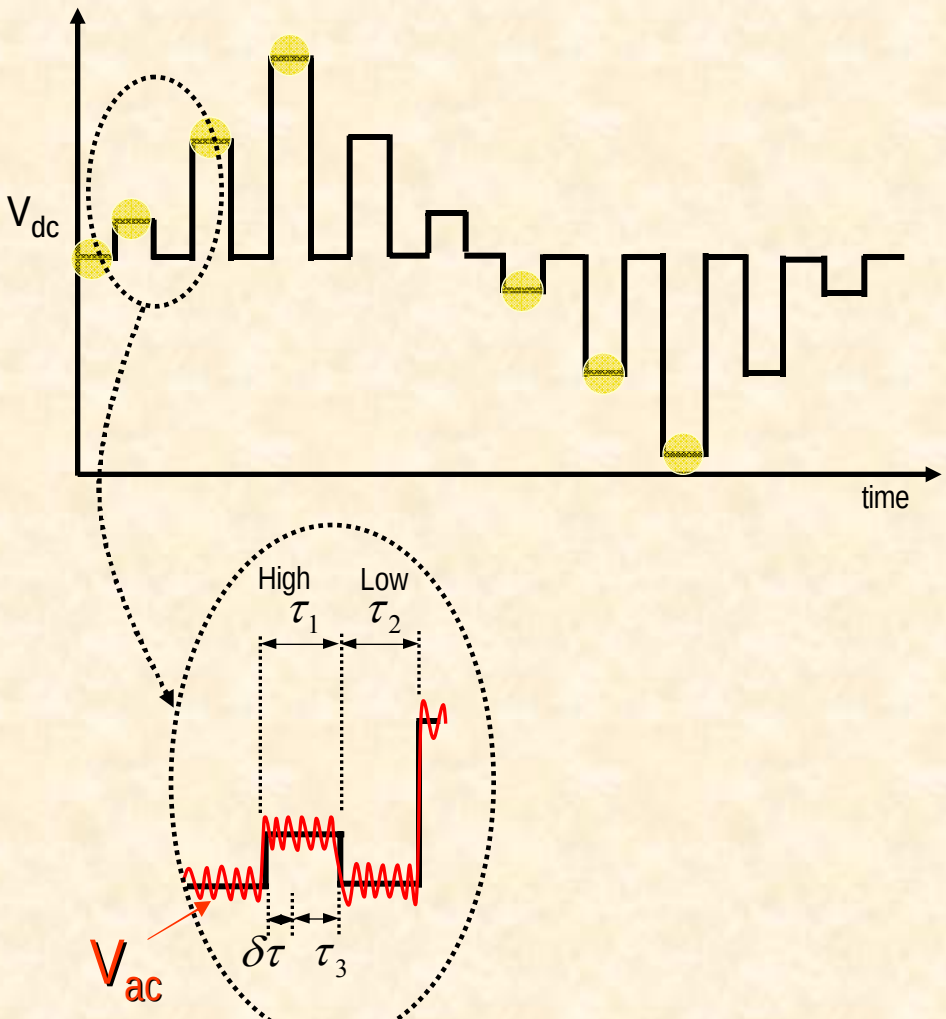
Ag deposited from 0.1 M $AgNO_3$, white light Xe source, 300W, 30 min

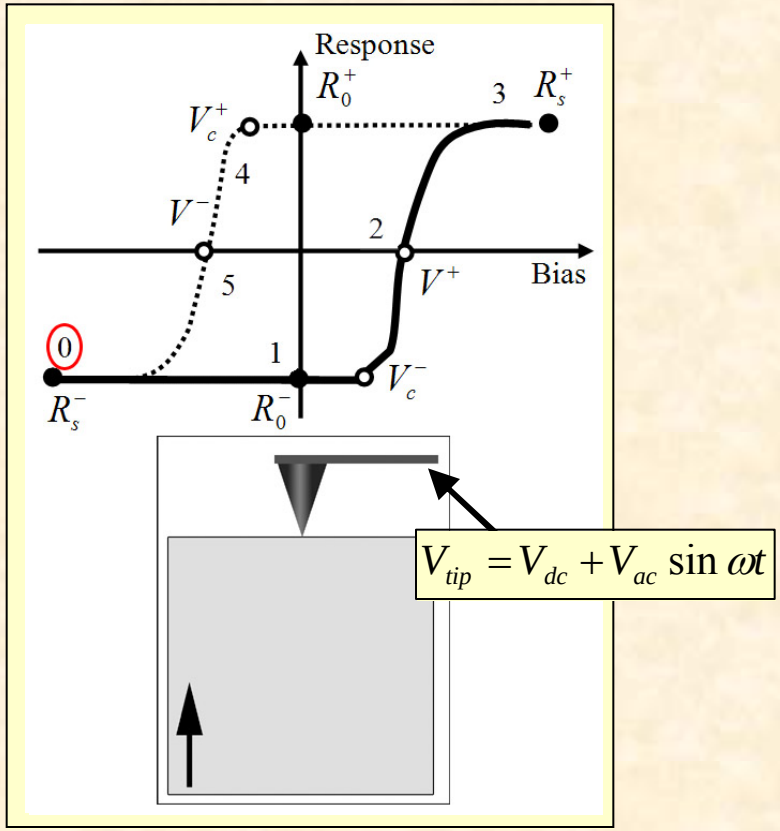
Spectroscopy in PFM

Spatially resolved studies of bias-induced domain formation enables applications such as data storage and lithography, and provides insight into physics of switching phenomena

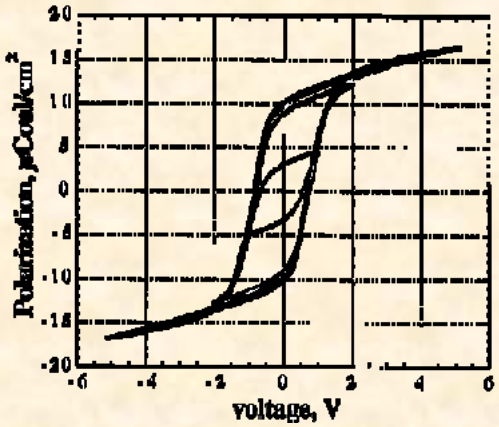
However, the time scales involved are very significant (~days per point). Is there an alternative?

Piezoresponse Force Spectroscopy

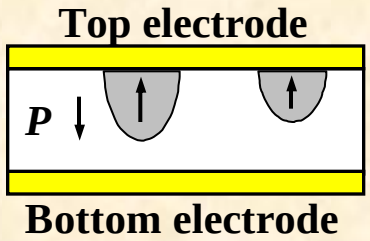




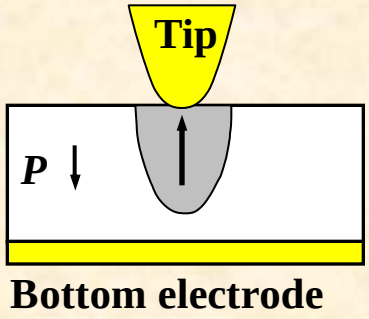
Spectroscopy in PFM

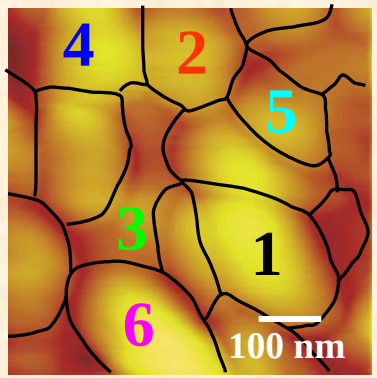


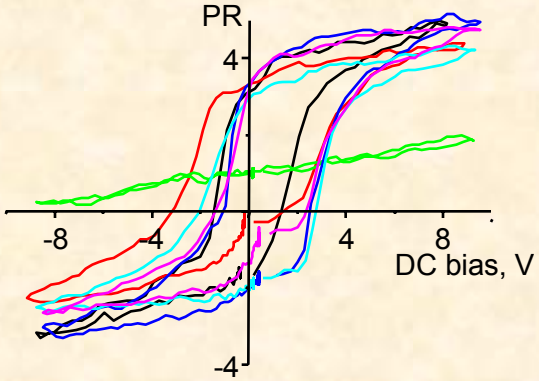
Macroscopic Hysteresis



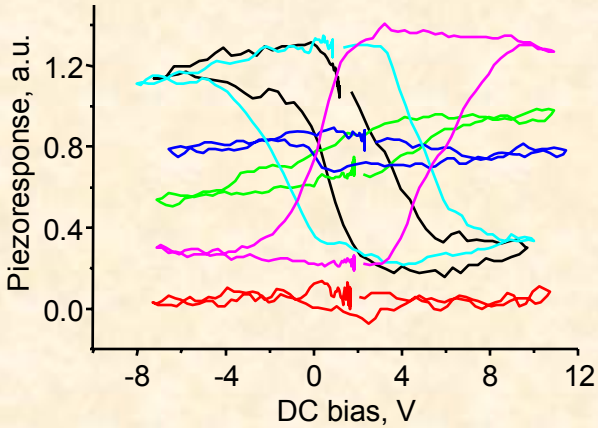
Local Hysteresis







Vertical response



Lateral response

Grain 1: Ferroelectric, large P_{out}, left P_{in}

Grain 2: Ferroelectric, large P_{out}, zero P_{in}

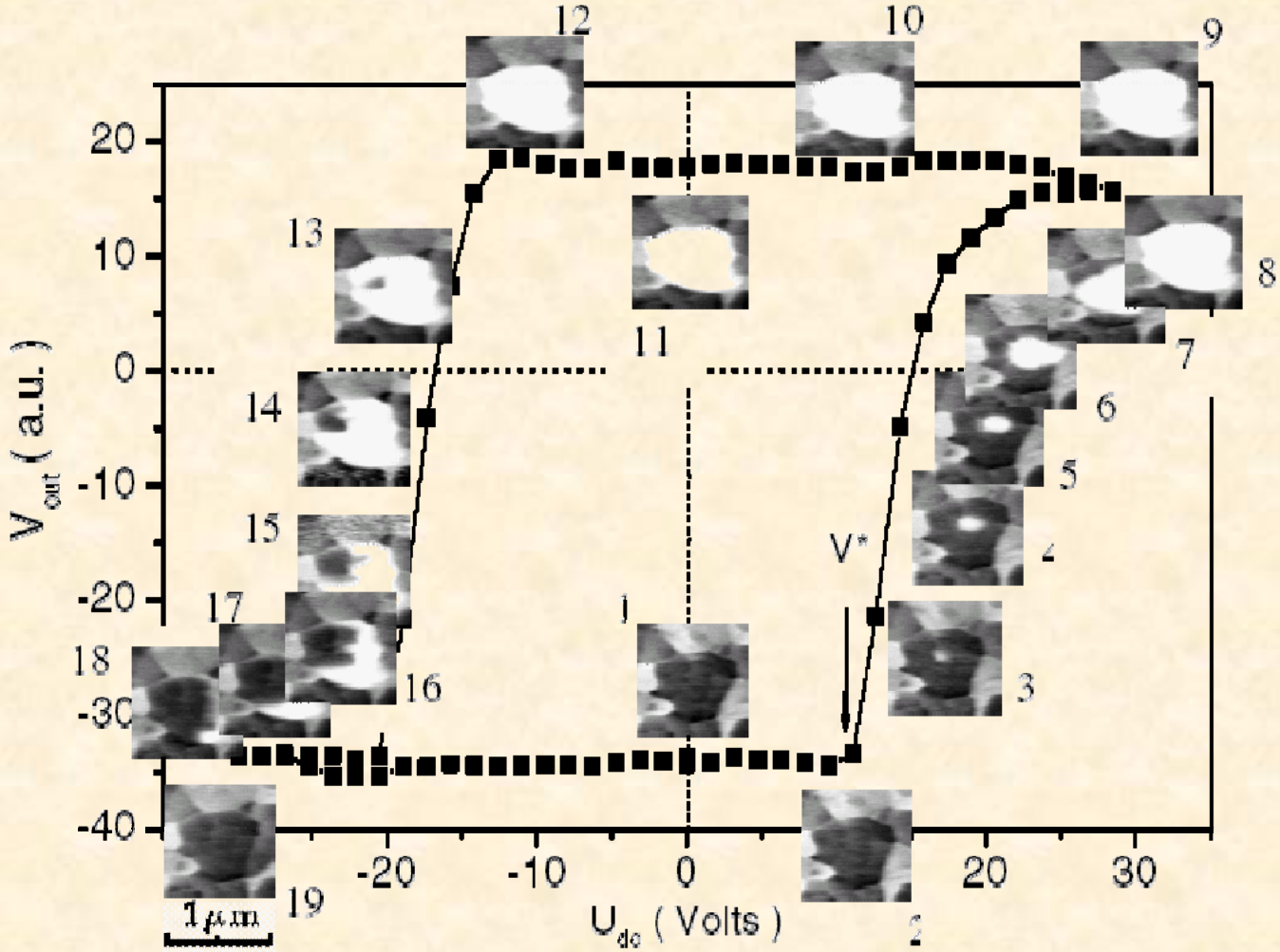
Grain 3: In-plane or non-ferroelectric

Grain 6: Ferroelectric, large P_{out}, right P_{in}

Single point hysteresis loop measurements are limited:

- not enough statistical data
- not clear how relate to microstructure

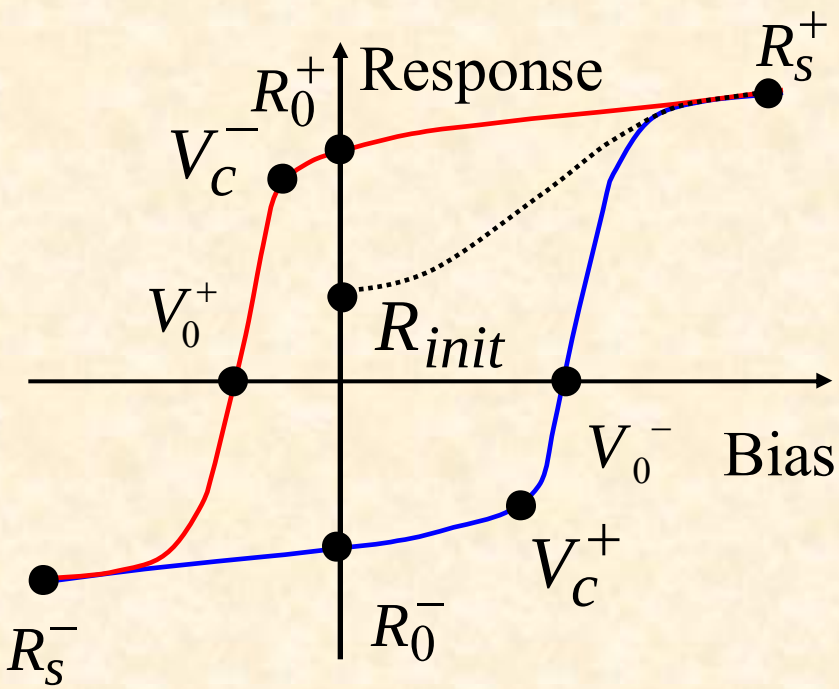
PFM Spectroscopy and Lithography



Kholkin et. al. MRS Proceedings Symp. O, Fall 2004

Ferroelectric polarization switching can be probed on a nanoscale within a single grain. PFM imaging on each stage allows visualization of a growing domain.

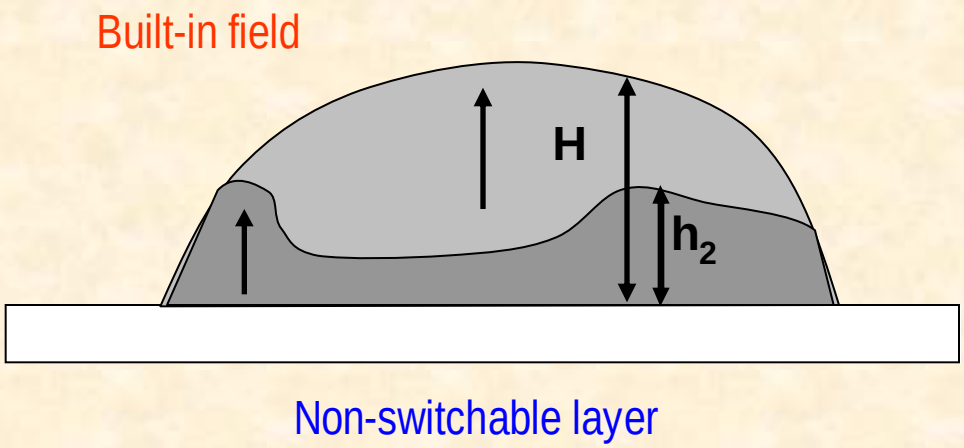
Data Analysis in SS-PFM

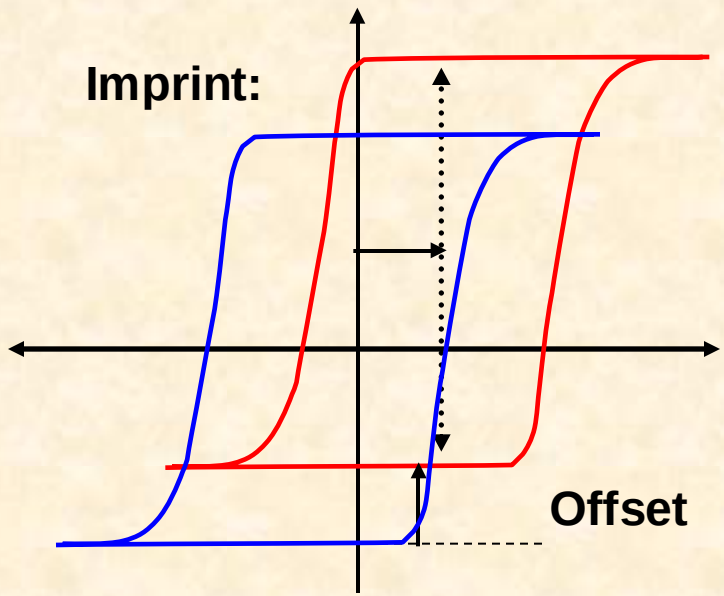


R_{init}	PFM image
V_0^+	Positive coercive bias
V_0^-	Negative coercive bias
V_{c0}^+ , V_{c0}^-	Nucleation bias
$\mathrm{Im} = \frac{V_0^+ + V_0^-}{2}$	Imprint
R_0^+ , R_0^-	Remanent polarization
R_S^+ , R_S^-	Saturated response
$R_m = R_s^+ - R_s^-$	Switchable polarization
$A_s = \int_{-\infty}^{+\infty} \left(R^+(V) - R^-(V)\right) dV$	Work of switching

1. **Statistical analysis**
2. **Direct curve fitting**

Two Layer Model

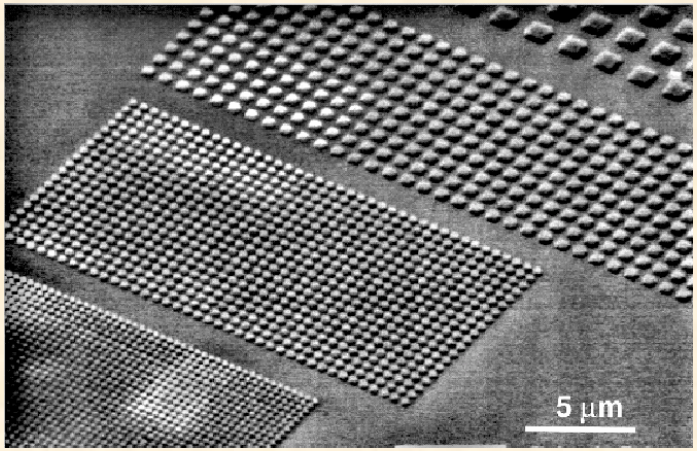


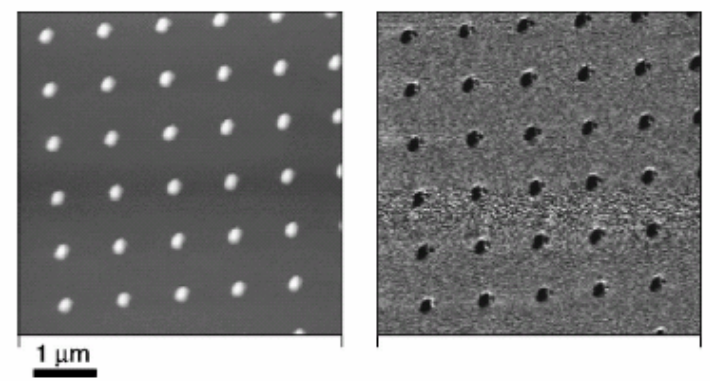


Material properties:

1. Material has layers with frozen and switchable polarization
2. Switchable layer has built-in electric field
3. Frozen layer results in the vertical shift of hysteresis loop
4. Built-in field results in lateral shift

Phenomenological Theory for Loop Formation





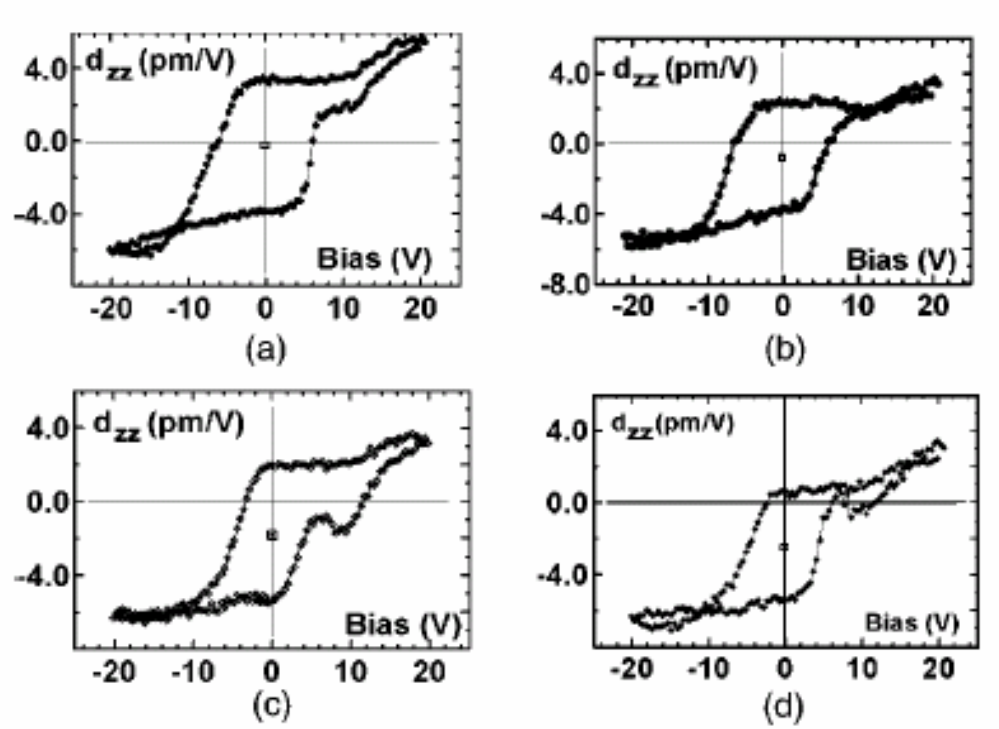


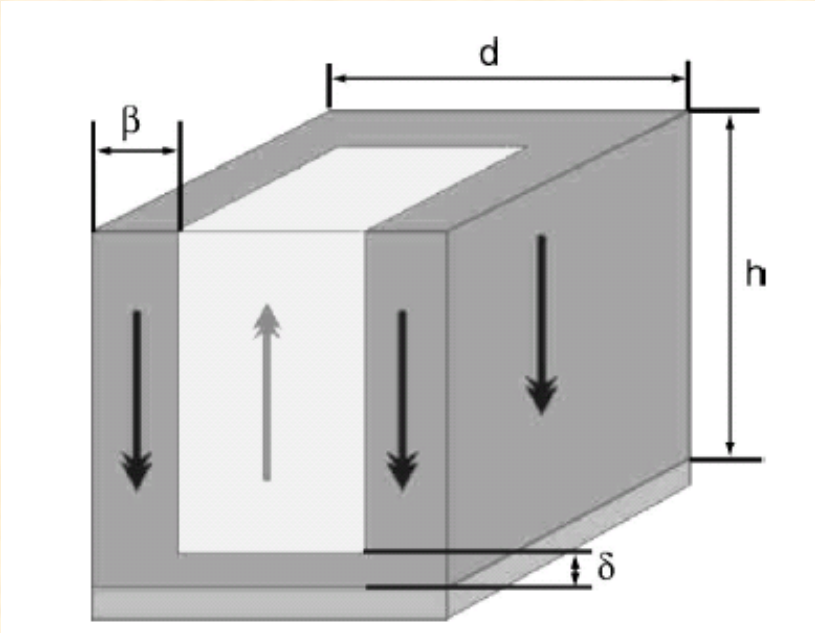
FIG. 1. Remanent piezoelectric hysteresis loops of PZT cells with: (a) 1000, (b) 500, (c) 250, and (d) 100 nm lateral size.

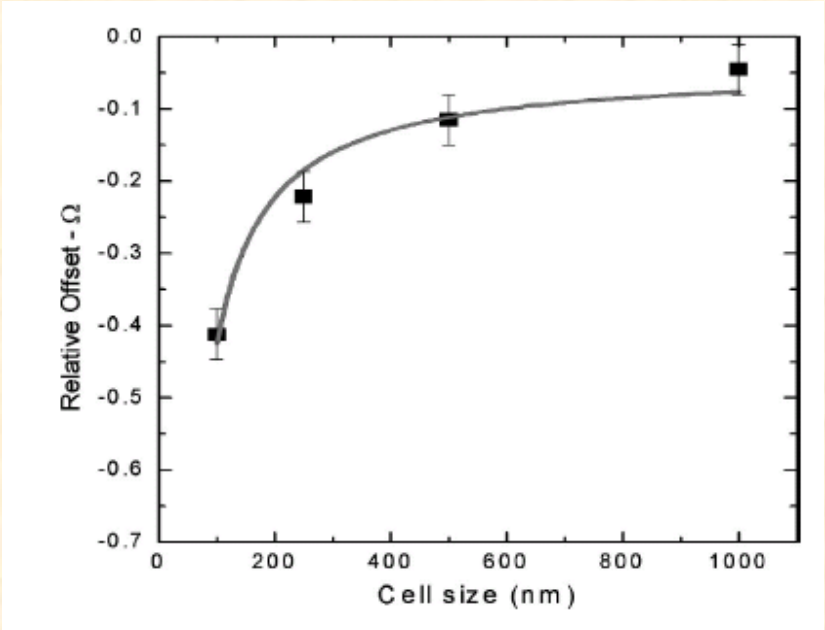
- Shift along voltage axis provides a measure of internal field: **Imprint**
- Shift in vertical direction provides information on the regions with frozen polarization

M. Alexe, C. Harnagea, D. Hesse, and U. Gösele, *Polarization imprint and size effects in mesoscopic ferroelectric structures*, Appl. Phys. Lett. 79, 242 (2001)

Phenomenological Theory for Loop Formation

Alexe model: vertical shift of hysteresis loop is due to the presence of polar non-switchable region





Vertical shift: $$\Omega = \frac{1}{2}\frac{(1-\beta/d)^2(1-\delta/h)-1}{(1-\beta/d)^2(1-\delta/h)+1}$$

Fitting parameters: $\delta = 15 \pm 8\ nm$ $\beta = 69 \pm 7\ nm$

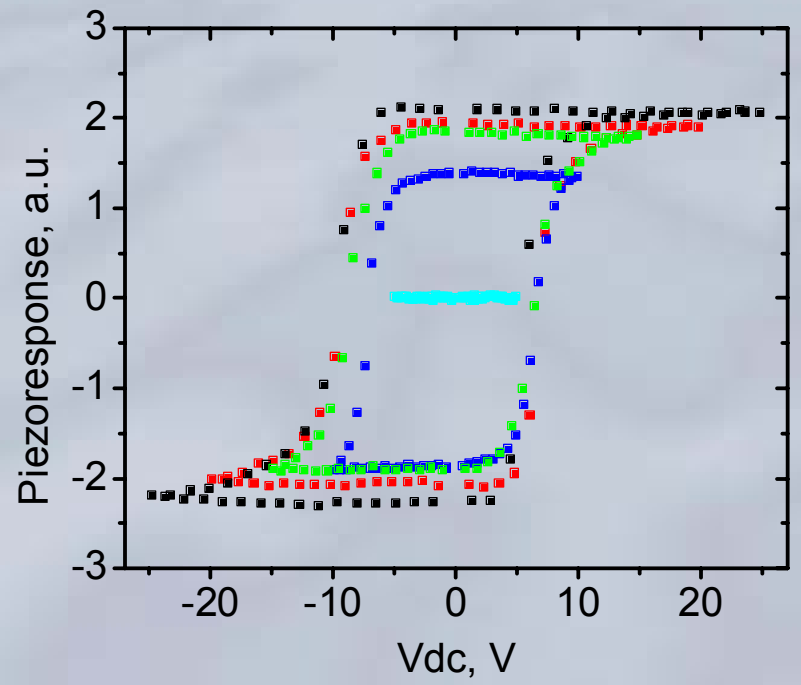
Large regions with "frozen" polarization

Ferroelectric nanostructures are an extremely complex system (defects, edges, size effects).

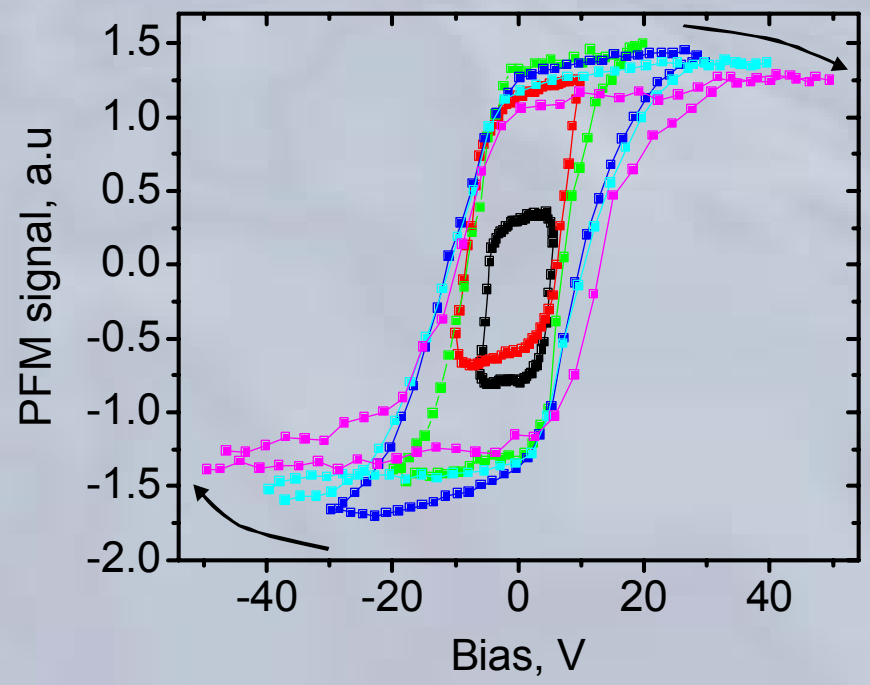
How does switching proceed in high-quality epitaxial films with low defect concentration?

Hysteresis Loops in Epitaxial Ferroelectrics

Epitaxial $BiFeO_3$
(R.Ramesh, UC Berkeley)



Epitaxial PZT
(M. Alexe, MPI)

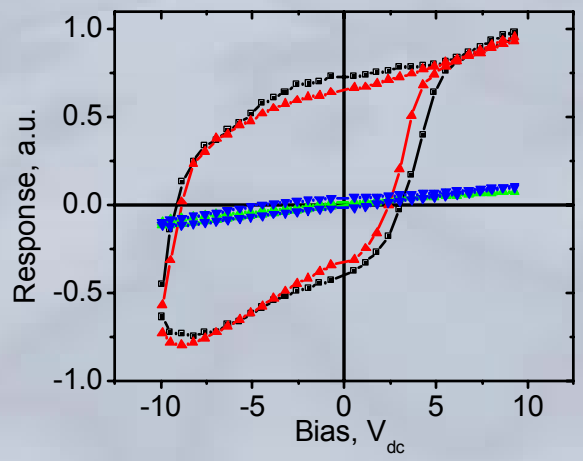


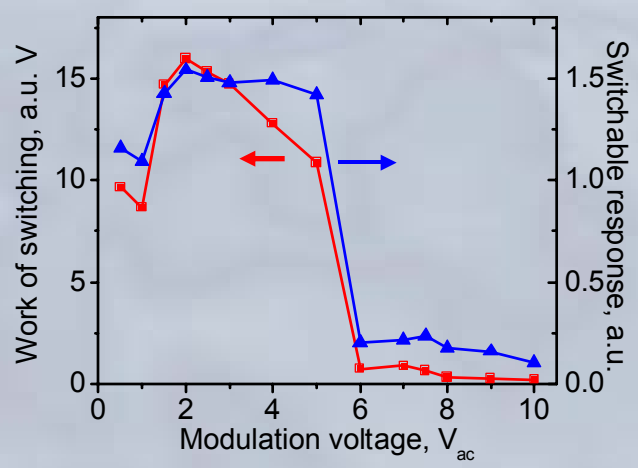
In ideal films, the behavior of hysteresis loop with bias suggests the mechanism:

1. Domain nucleates at certain finite bias
2. After nucleation, domain grows
3. Domain wall is strongly pinned (no relaxation when bias is off)
4. Clamping can be important

Effect of Imaging Conditions on Hysteresis Loops

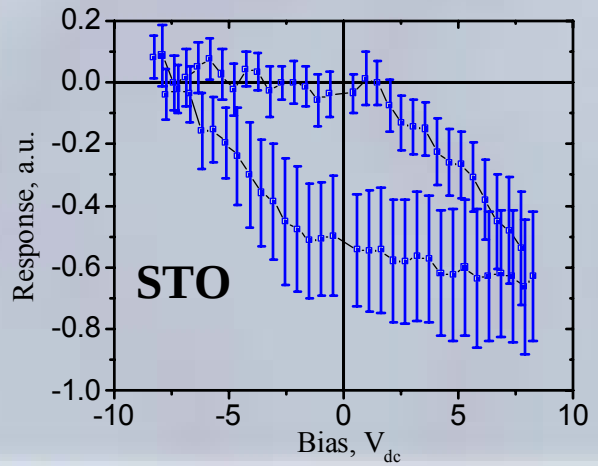
Effect of modulation bias

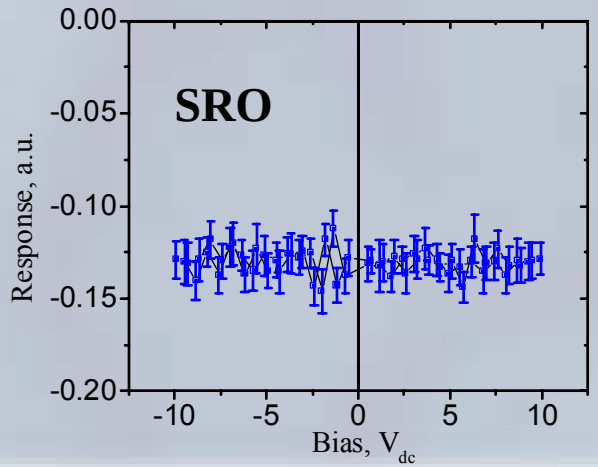




Loops are reproducible for driving voltages below coercive bias, and collapse above

Response on non-piezoelectric surface



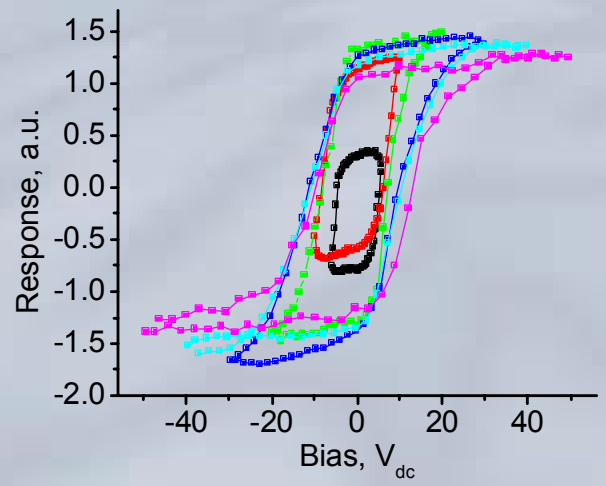


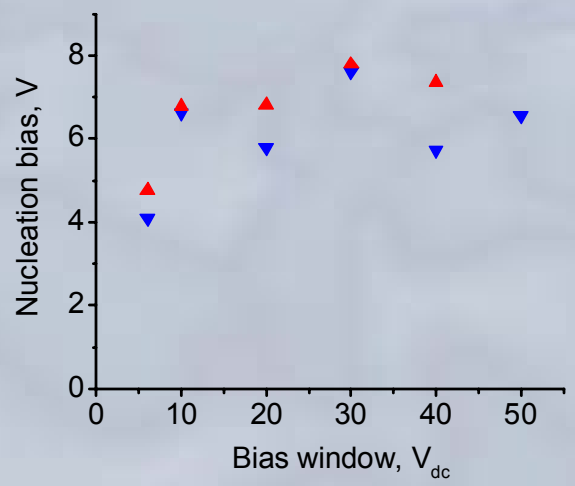
Sometimes, non-zero response is observed on non-ferroelectric surfaces.

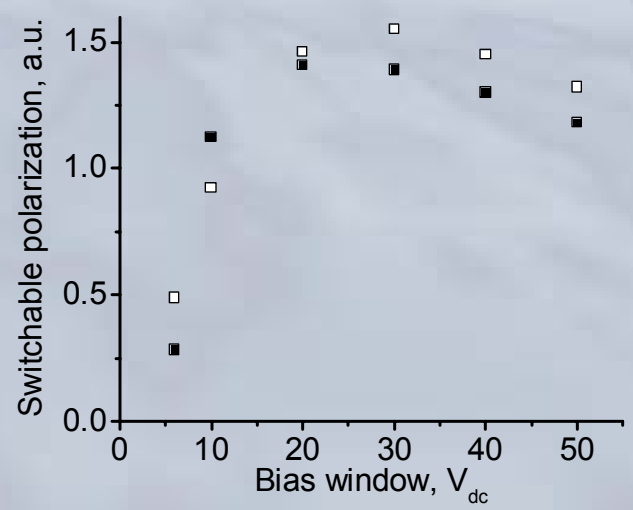
- Electrochemistry?
- Electrocapillary effects?
- Surface ferroelectricity?

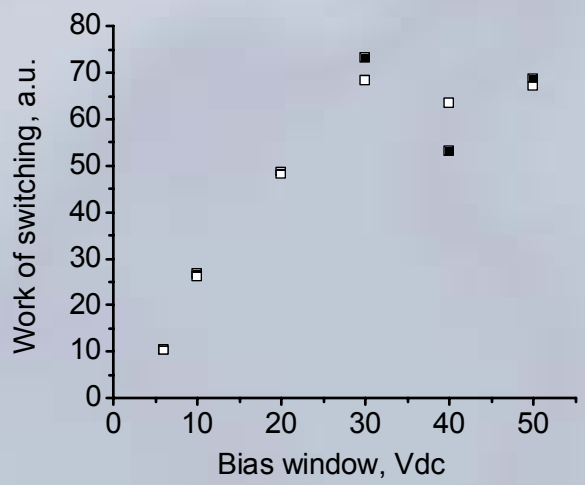
Effect of Imaging Conditions on Hysteresis Loops

Effect of bias window









The evolution of loops with bias window has three phases:

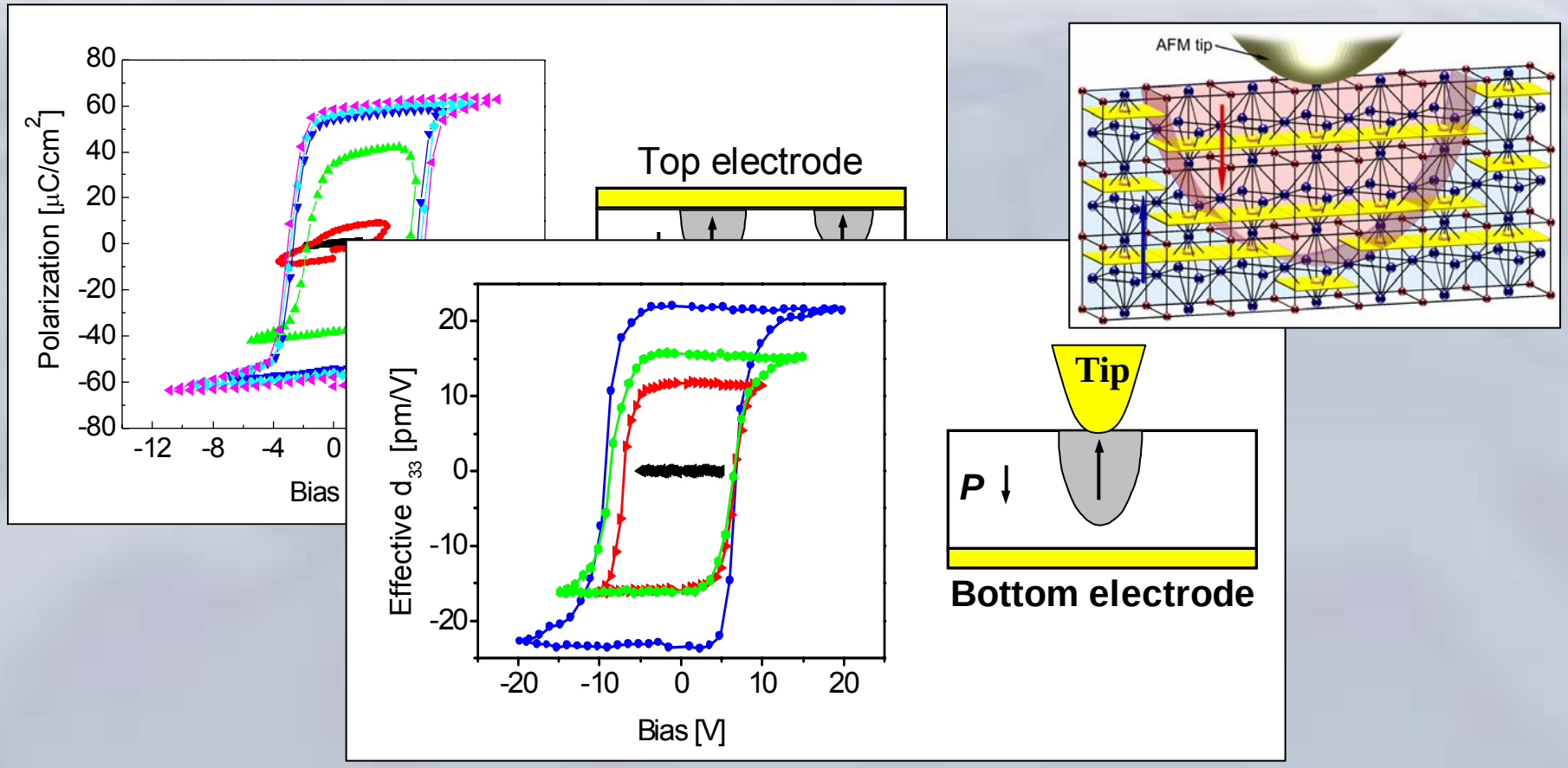
- Closed (no switching)
- Partial switching (domain size smaller then signal generation volume)
- Saturated (domain size larger then signal generation volume)

For some materials, “anomalous” behavior is observed at large biases

Loop parameters evolve as:

- Nucleation biases can be determined for partial and saturated loops
- Work of switching can be determined only for saturated loops

Local Polarization Dynamics: Piezoresponse Force Spectroscopy



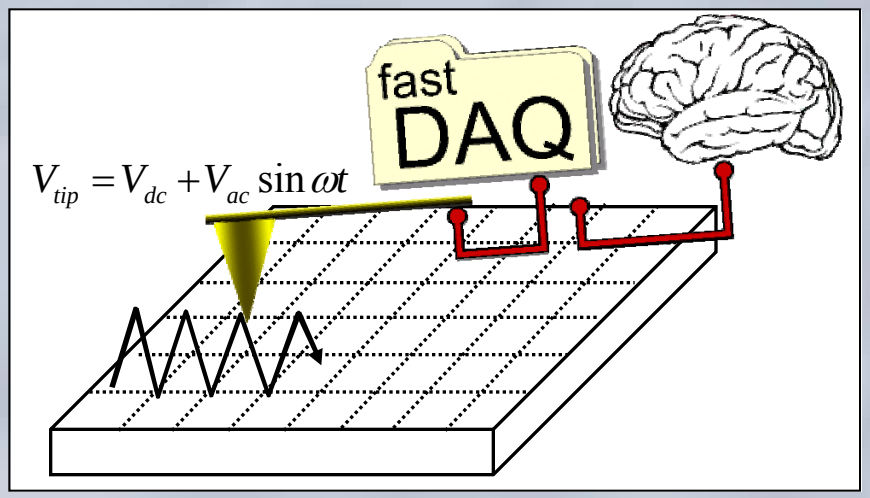
Mechanisms for local and macroscopic switching:

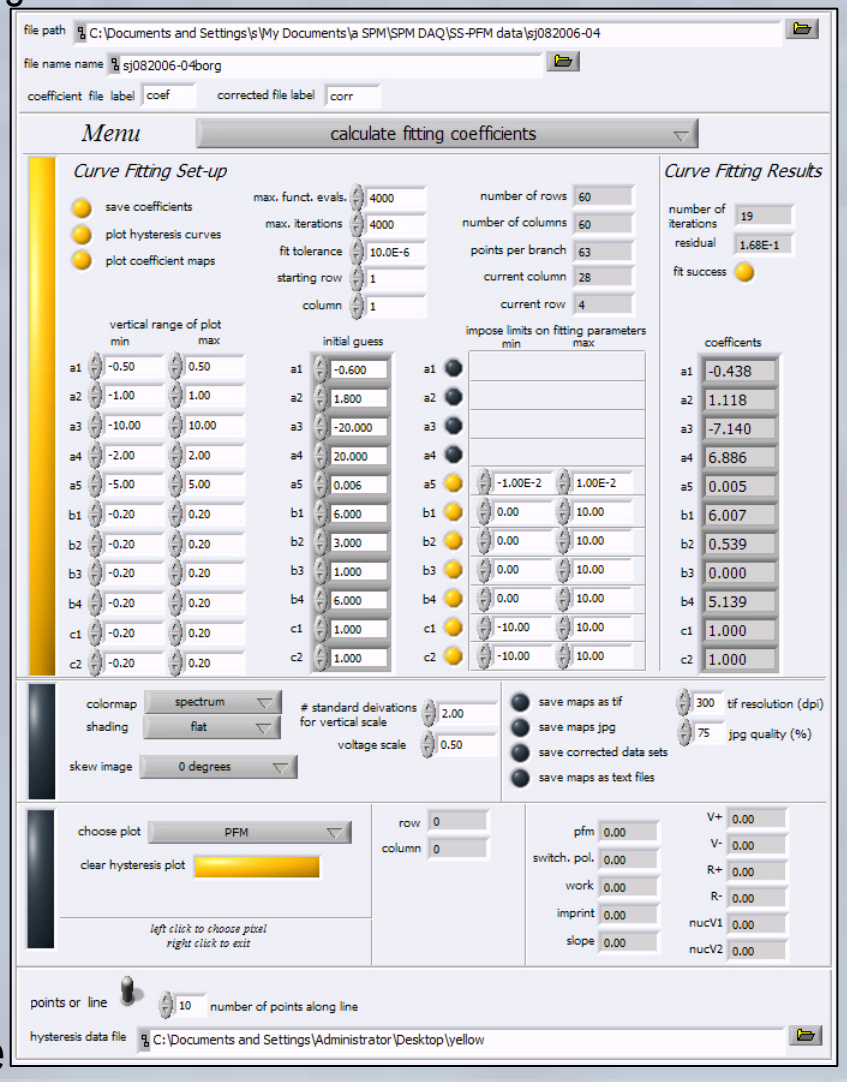
1. Domain nucleates at certain finite bias
2. Domain wall is strongly pinned (no relaxation when bias is off)
3. Characteristic biases are close - similarity in mechanisms?

Challenge 1: Can we develop the theory describing hysteresis loop formation in PFM?
Challenge 2: Can we study spatial variability of switching behavior to link it to structure?

Switching Spectroscopy Piezoresponse Force Microscopy

Key development: Two order of magnitude increase in data acquisition from single point spectroscopy to spatially resolved imaging

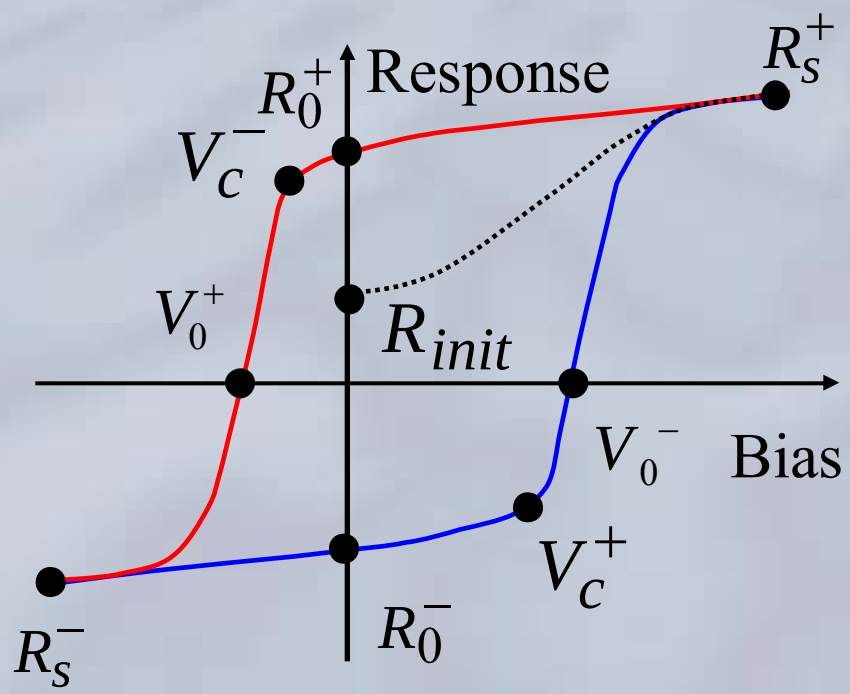




SS-PFM capabilities

- Static parameters
  - local imprint and coercive bias
  - work of switching map
- Dynamic parameters
  - local nucleation bias
- Correlation of switching behavior with microstructure

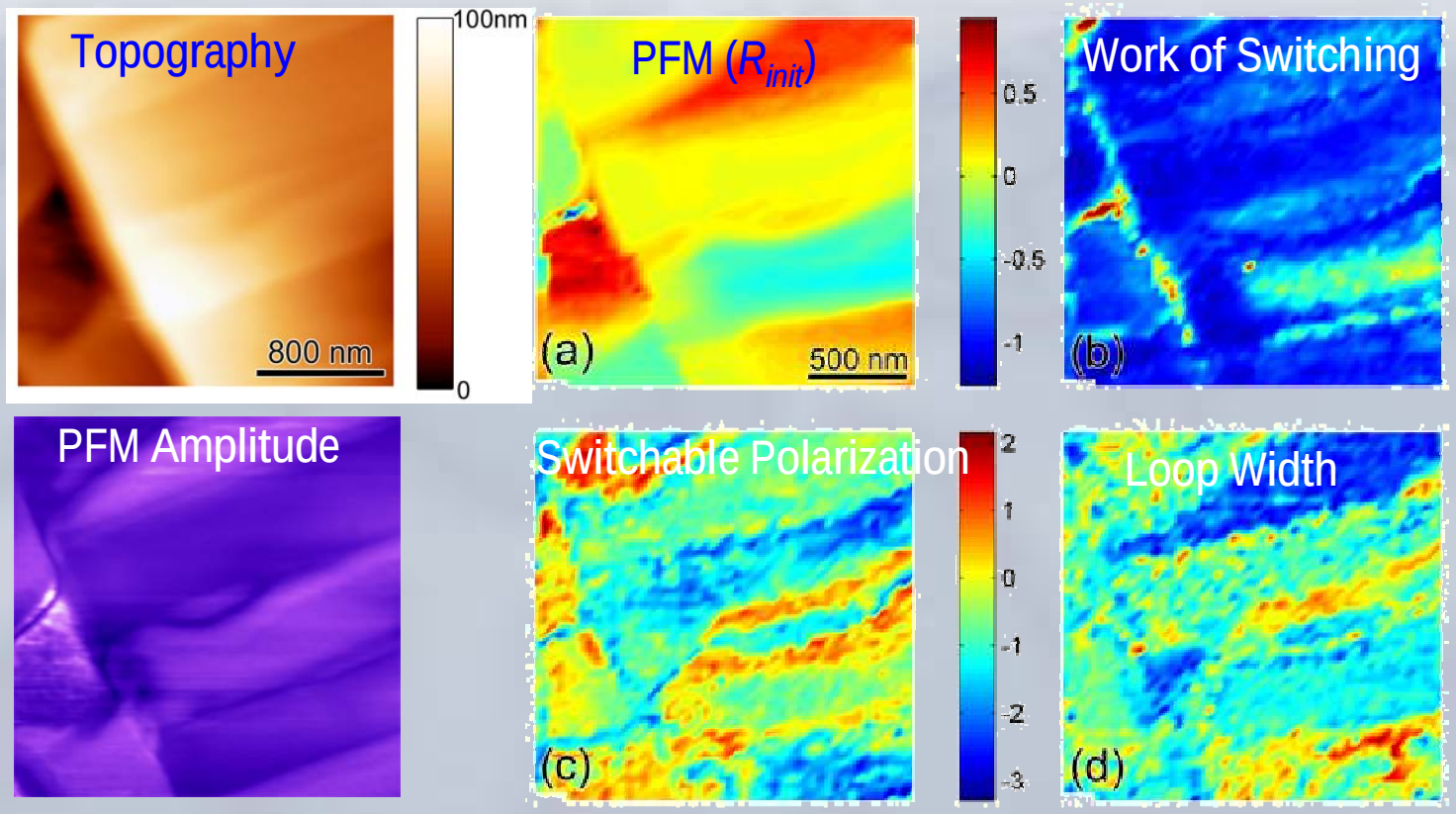
Data Analysis in SS-PFM



R_{init}	PFM image
V_0^+	Positive coercive bias
V_0^-	Negative coercive bias
V_{c0}^+, V_{c0}^-	Nucleation bias
$\mathrm{Im} = \frac{V_0^+ + V_0^-}{2}$	Imprint
R_0^+, R_0^-	Remanent polarization
R_S^+, R_S^-	Saturated response
$R_m = R_s^+ - R_s^-$	Switchable polarization
$A_s = \int_{-\infty}^{+\infty} \left(R^+(V) - R^-(V)\right) dV$	Work of switching

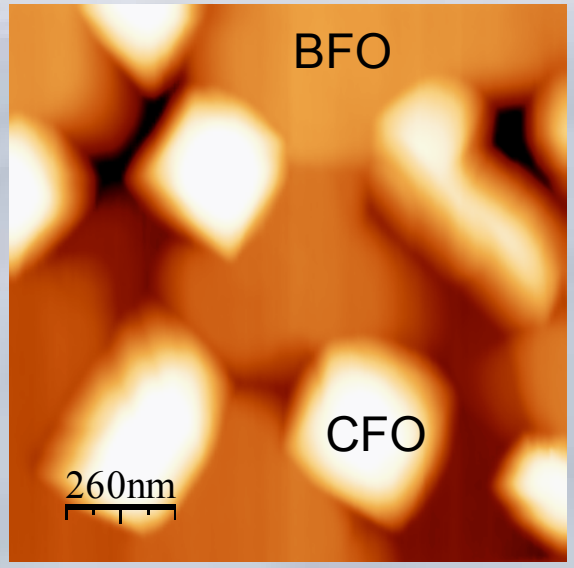
1. **Statistical analysis**
2. **Direct curve fitting**

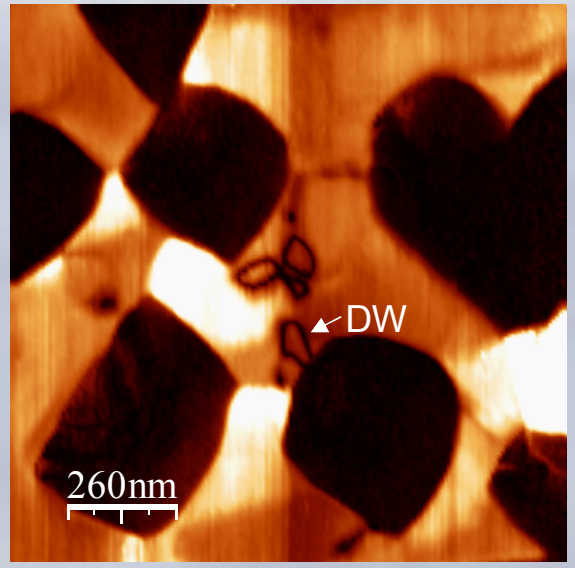
SS-PFM of Polycrystalline PZT

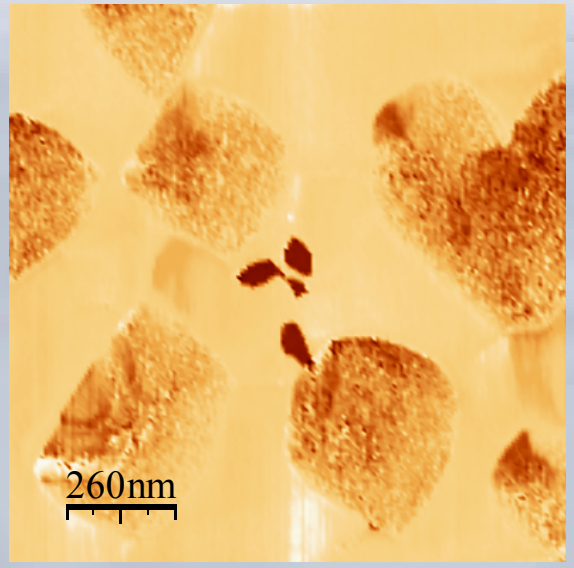


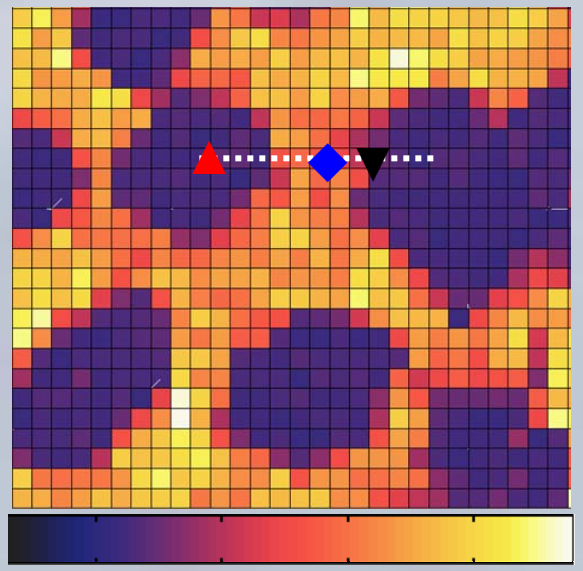
- The PFM, work of switching, and Loop width maps are different: data is statistically significant
- Grain boundary is associated with hindered switching (enhanced pinning).

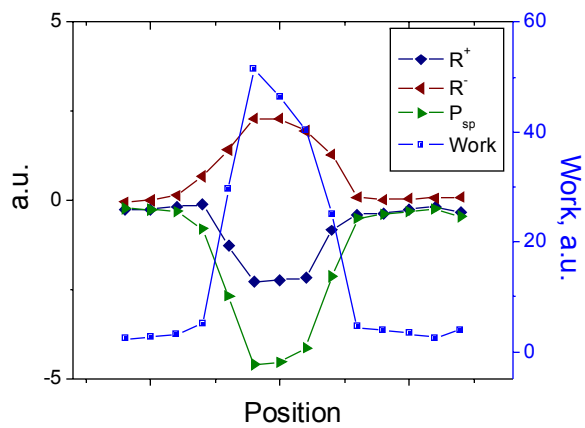
SSPFM of Multiferroic Nanostructure

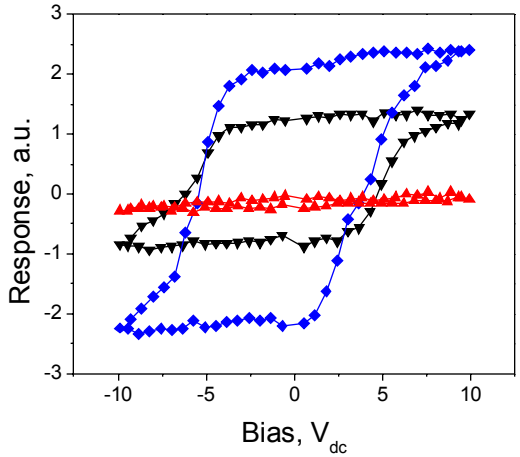








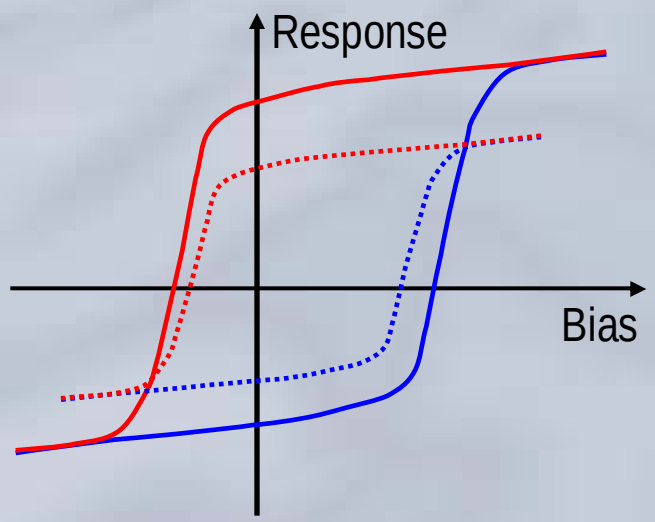




Each pixel ~50 nm x 50 nm

Switching Spectroscopy Piezoresponse Force Microscopy - SSPFM

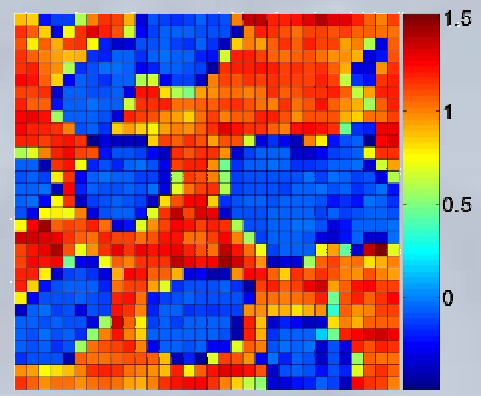
Now we have the data. What can we learn?



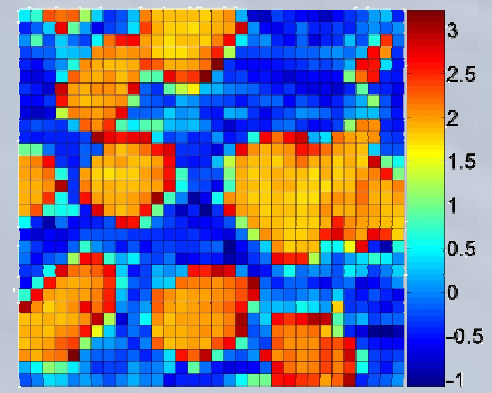
$$PR^{+}(V) = d_f + \alpha PR_0^{+}(\beta V + V_i)$$

- Image analysis reveals some features; however, interpretation is not straightforward
- Only imprint images show clear grain-grain variations
- We need analytical theory!

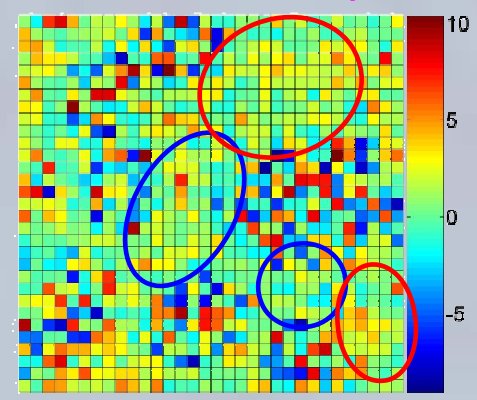
Switchable response, α



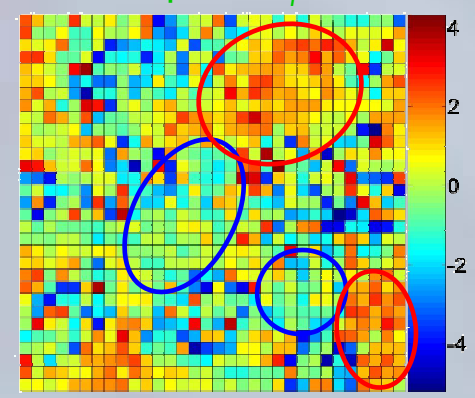
Vertical offset, d_f



Coercive bias, β



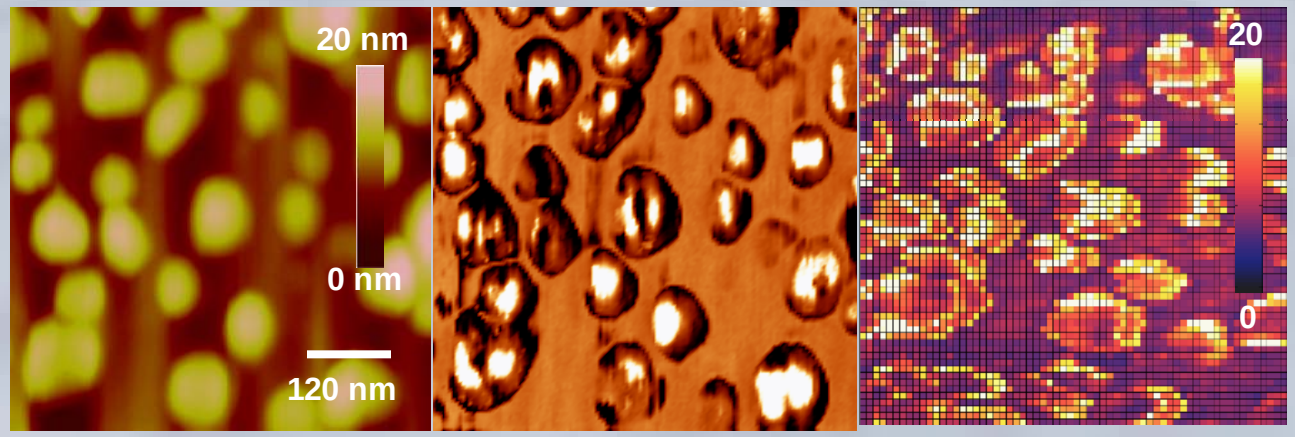
Imprint, V_i

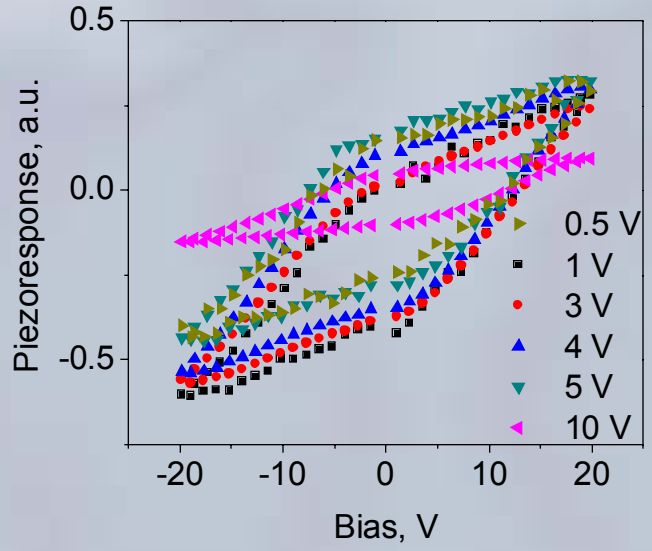


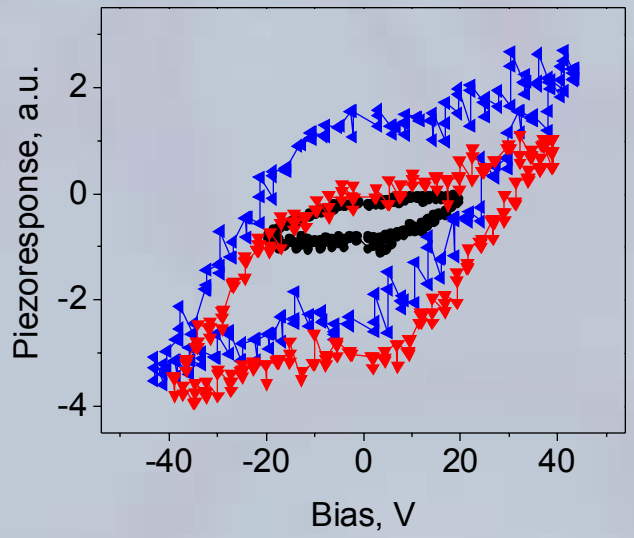
Perfect system: Interfaces do not affect switching

SS-PFM of Ferroelectric Nanodots

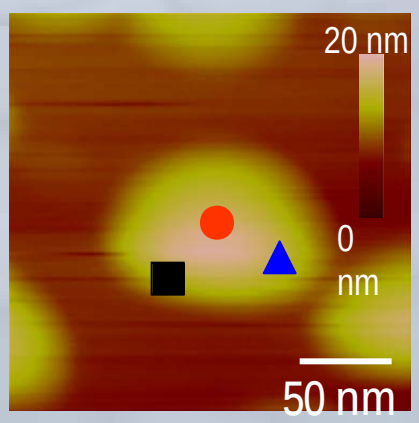
- What is the size limit of ferroelectricity?
- Are switching properties uniform within the nanoobject?

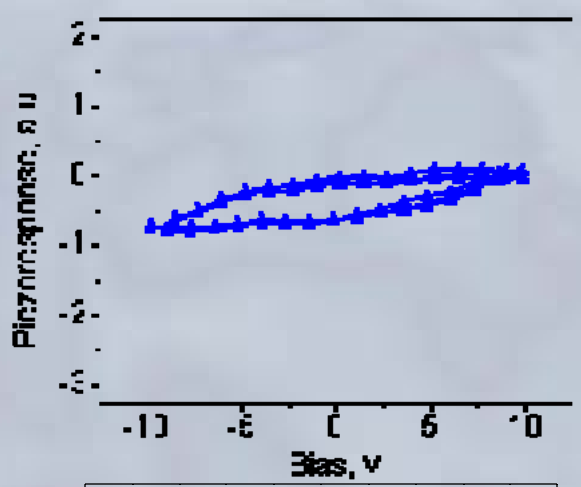


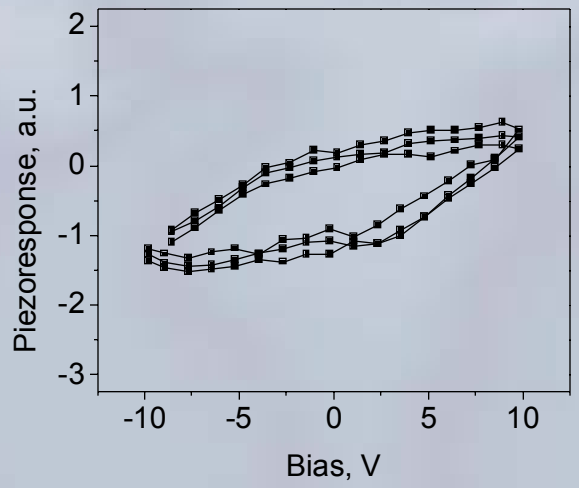


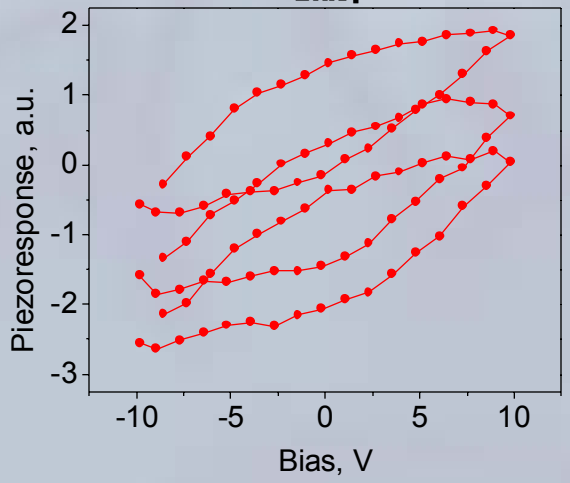


Switching Variability within a Single Nanodot





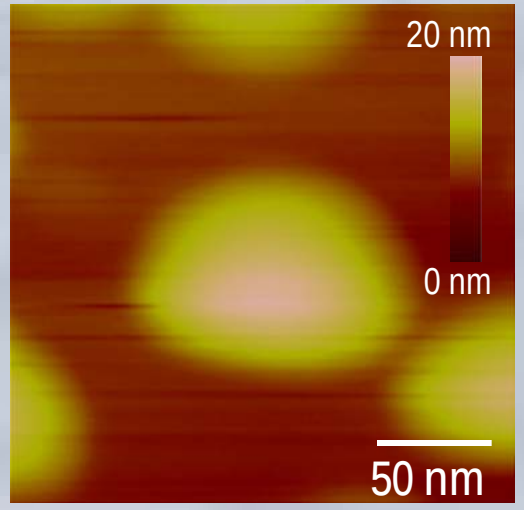




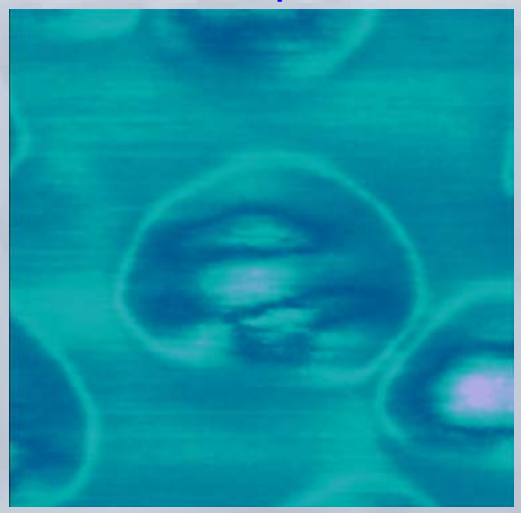
Different parts of a nanodot have different hysteresis loops

SS-PFM of Ferroelectric Nanoparticles

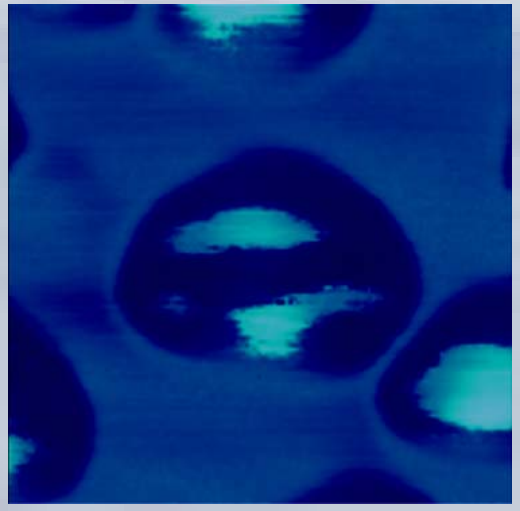
Topography



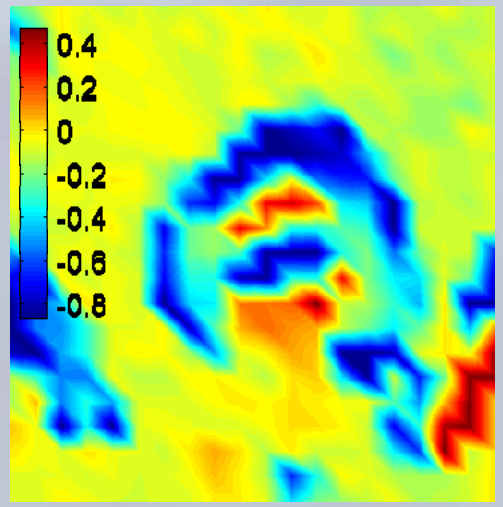
PFM Amplitude



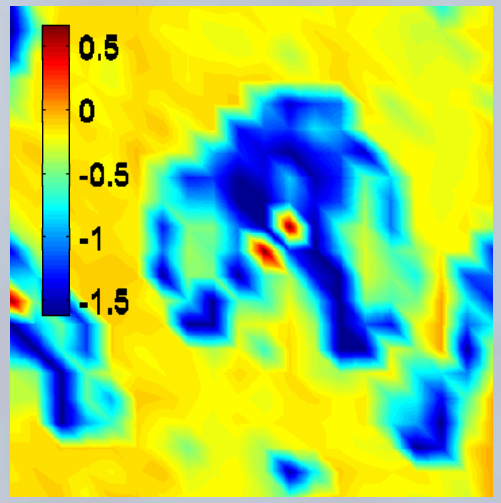
PFM Phase



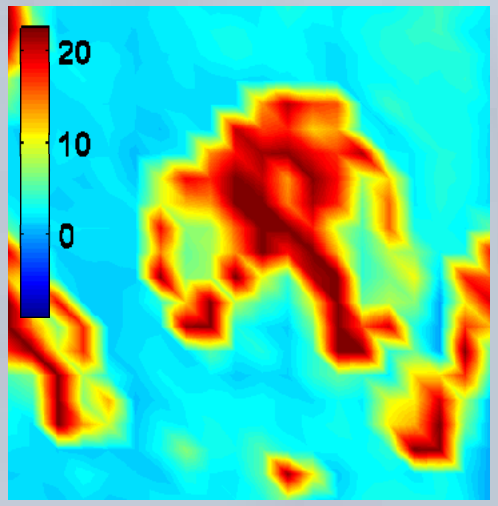
Initial response



Switchable Polarization

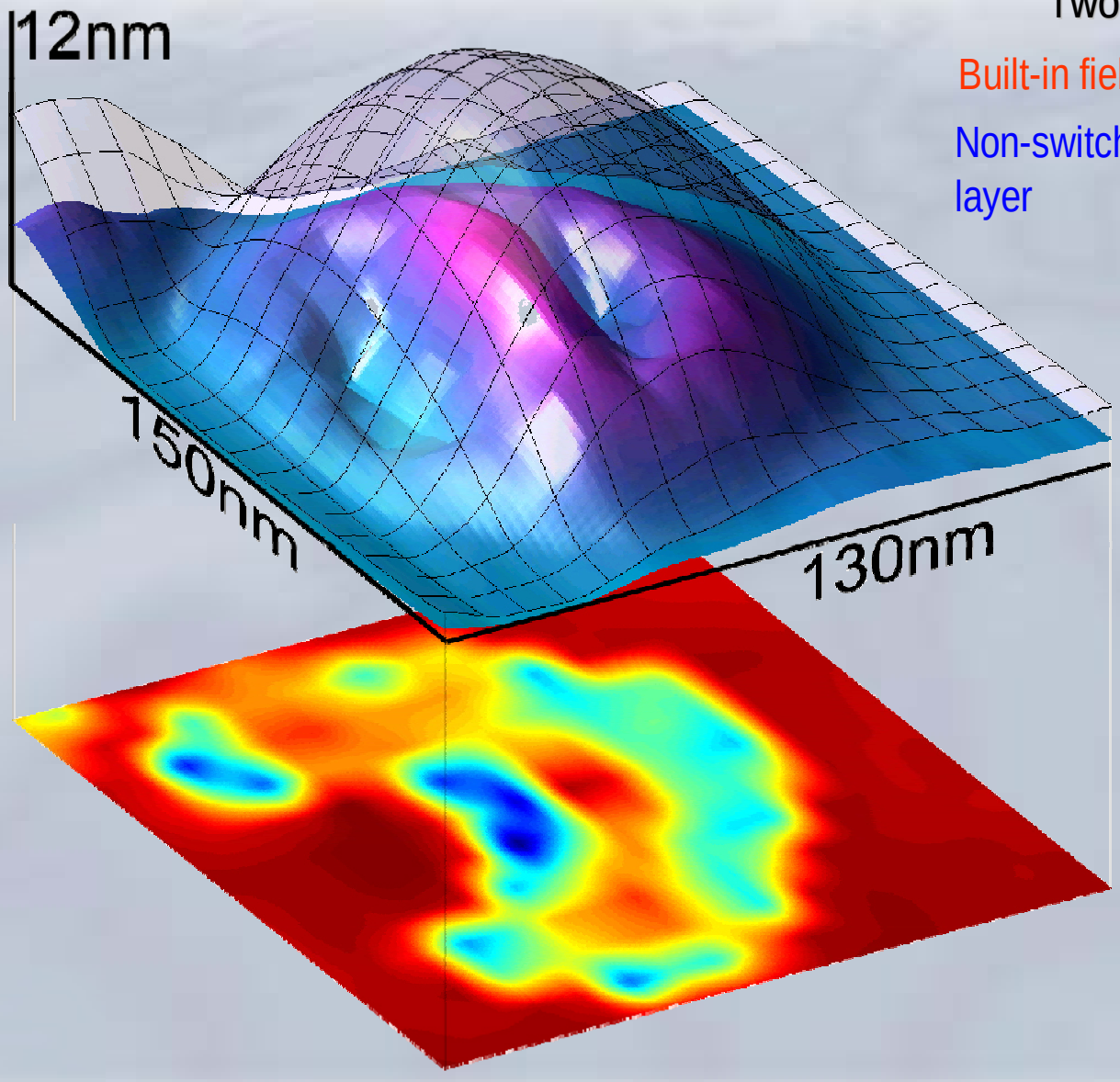


Work of Switching



SS-PFM allows to study switching processes inside single 70 nm nanoparticle.

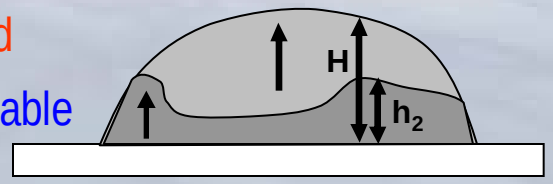
SS-PFM of Ferroelectric Nanoparticles

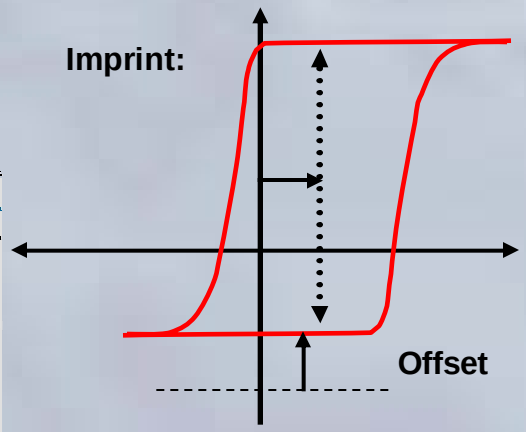


Two-layer model

Built-in field

Non-switchable layer





SS-PFM capabilities

- Real-space mapping
  - Frozen polarization layer
  - Built-in field in ferroelectric layer
  - Electromechanical response
- Future applications
  - Heterostructures
  - Tunneling barriers

Analytical Theory for Piezoresponse Force Spectroscopy

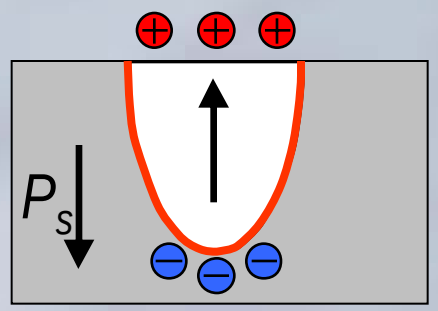
Task 1. Model for domain growth – size vs. voltage on the tip
Task 2. Relationship between domain parameters and PFM signal
Task 3. Determination of tip parameters in experiment

Theory

Experiment

1. Domain nucleation and growth in the tip-induced field

- Tip is modeled as a finite source (point charge, sphere, disc electrode)
- Domain geometry is approximated as semiellipsoid



Landauer model:
r – domain radius
l – domain length

Domain energy:

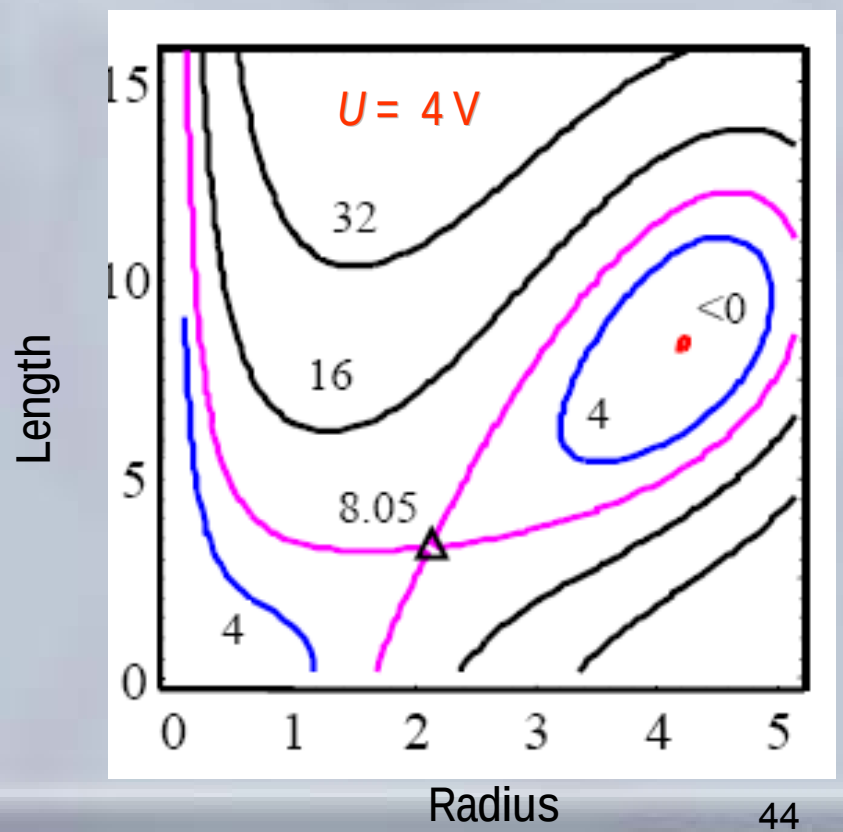
$$\Phi(r,l) = \Phi_S(r,l) + \Phi_D(r,l) - U\Phi_{UL}(r,l)$$

Domain wall energy

Depolarization energy

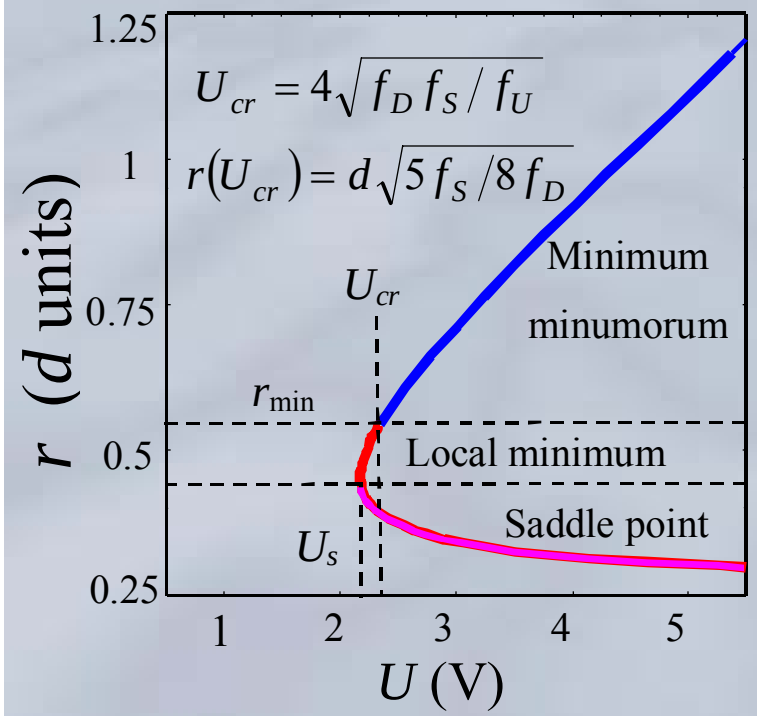
Interaction energy

Stable domain



Domain Dynamics in Thermodynamic Limit

Evolution of special points on free energy surface



Wall energy

$$f_S = \pi^2 \psi_S d^2 \gamma$$

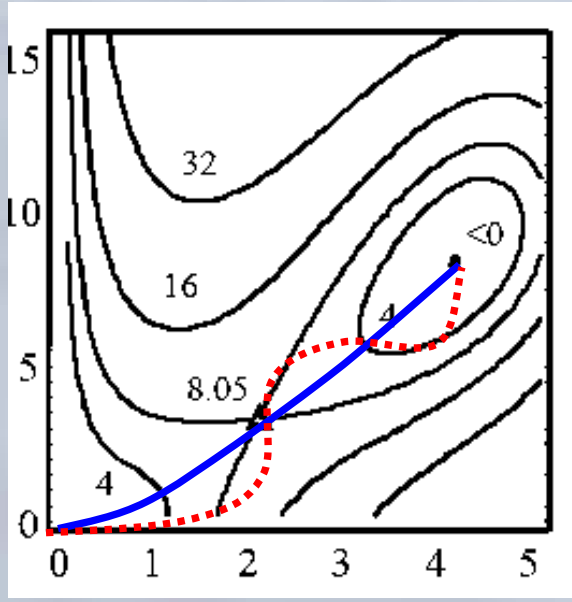
Polarization

$$f_D = \frac{4P_S^2 d^3}{3\varepsilon_0(\kappa + \varepsilon_e)}$$

Screening

$$f_U = \frac{(C_t/\varepsilon_0)P_S d}{2(\kappa + \varepsilon_e)}$$

Nucleation dynamics



- In thermodynamic case, there is no hysteresis
- Geometric and energy parameters of critical points
- Activation energy for nucleation (saddle point)
- Parameters of equilibrium domain (minimim)

If energy landscape is steep:

- Only one path, measurements are reproducible
- Thermally activated nucleation

$$\tau(U) \sim \tau_0 \exp(E_a / kT)$$

If energy landscape is shallow:

- Multiple paths are possible
- Sample energy space (Jarozinsky equality)

How does nucleation process proceed?

Analytical Theory for PFM Signal Formation

Decoupled approximation (Schneider, Gopalan, Morozovska-Eliseev-Kalinin)

- Calculate electric field for rigid dielectric, $d_{ijk} = e_{ijk} = 0$
- Calculate strain field using piezoelectric constitutive equations, $X_{ij} = E_k e_{kij}$
- Calculate displacement field using Green's function for non-piezoelectric elastic solid

$$u_i(\mathbf{x}) = \int_0^{\infty} d\xi_3 \int_{-\infty}^{\infty} d\xi_2 \int_{-\infty}^{\infty} d\xi_1 \frac{\partial G_{ij}(\mathbf{x},\xi)}{\partial \xi_l} E_k(\xi) e_{kjl}$$

For most materials, error < 10%

Analytical results for weak elastic isotropy

1. PFM on transversely isotropic materials:

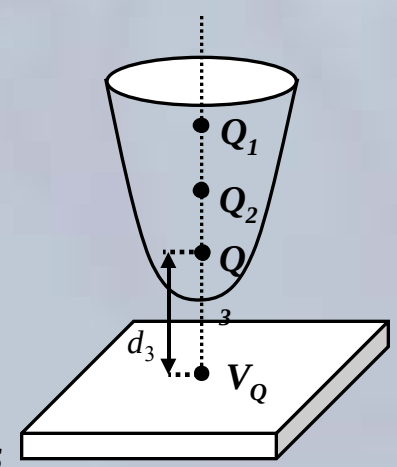
$$u_3(\rho) = V_Q(\rho)\frac{1+\nu}{Y}\left(e_{31} f_1(\gamma) + e_{15} f_2(\gamma) + e_{33} f_3(\gamma)\right)$$

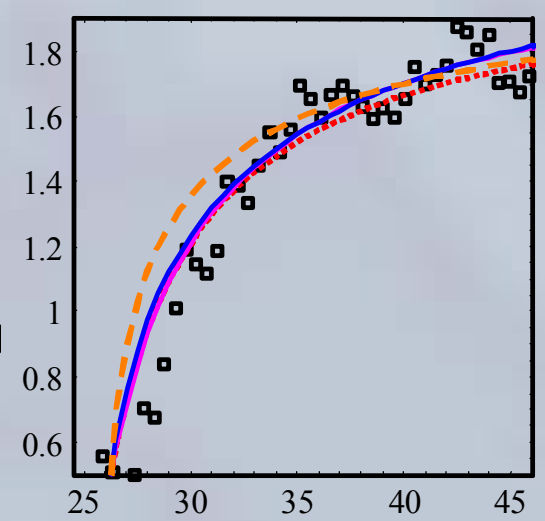
2. PFM on anisotropic materials:

$$u_i(0) = V_Q(0) W_{i\alpha k} d_{k\alpha}$$

3. Domain wall profile in the point charge model

$$d_{33}^{eff} \approx \frac{3}{4}\left(d_{33} + \left(\frac{1}{3} + \frac{4}{3}\nu\right) d_{31}\right)\frac{s}{|s| + 1/4} + \frac{1}{4} d_{15} \frac{s}{|s| + 3/4}$$

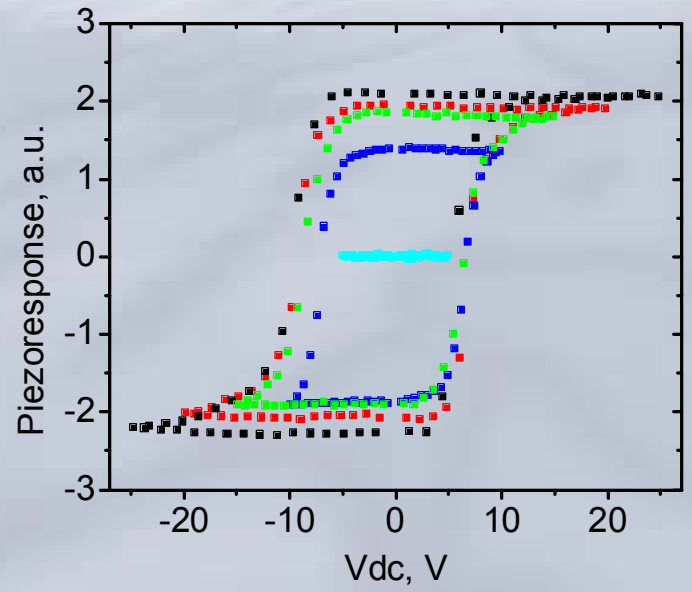


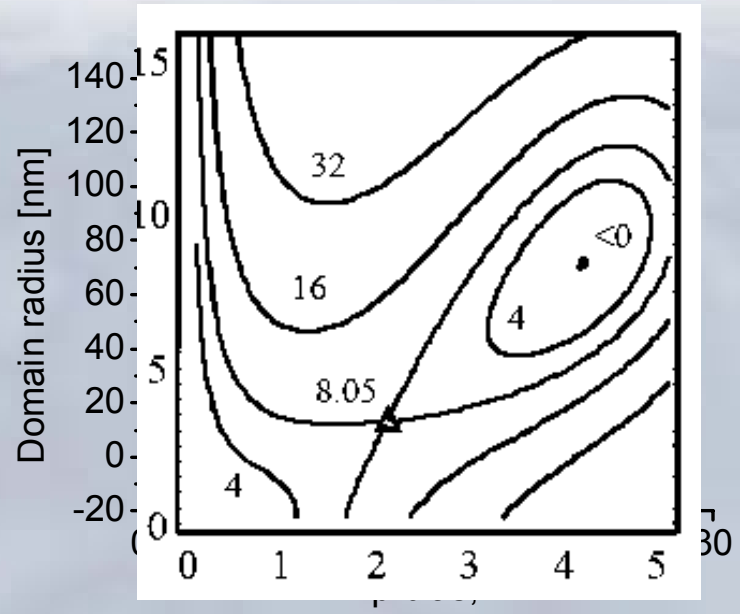


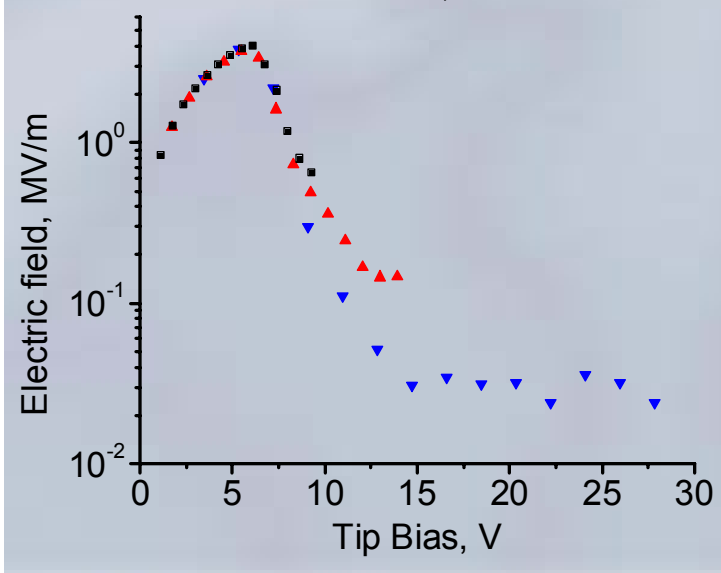
Tip parameters can be calibrated!

Data by L. Tian and V. Gopalan (Penn State)

Deconvolution of Domain Parameters from Hysteresis Data







Switching in epitaxial $BiFeO_3$

- Critical domain is r = 2 nm, l = 10 nm
- Estimated activation energy for nucleation is ~ 0.5 eV

Is the process thermally activated?

Or is it intrinsic switching?

Ferroelectrics are never perfect

- Defects: dislocations, precipitates, step edges
- Surfaces and interfaces

Can we learn how they affect switching?

Landauer Paradox

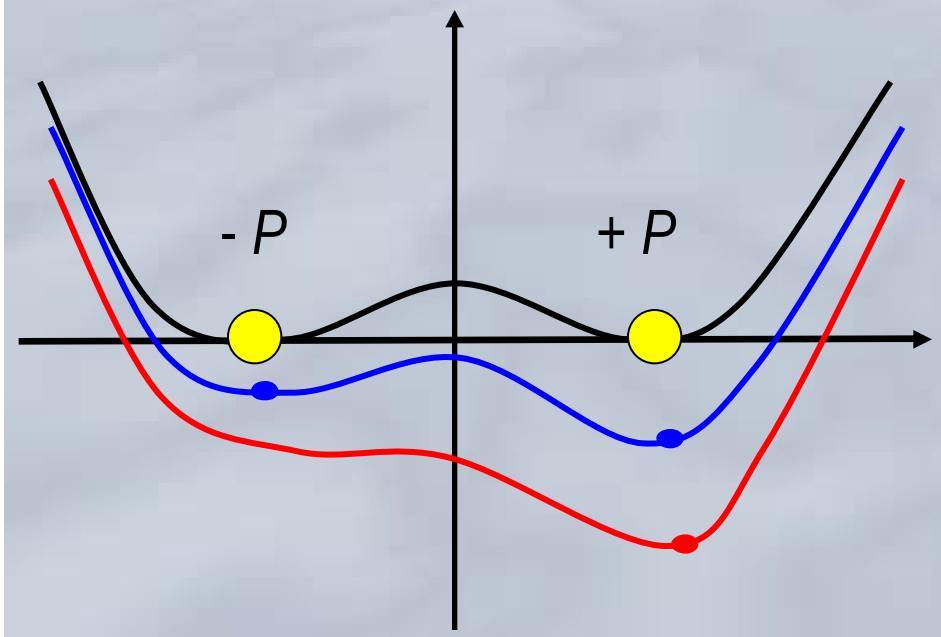
JOURNAL OF APPLIED PHYSICS VOLUME 28, NUMBER 2 FEBRUARY, 1957

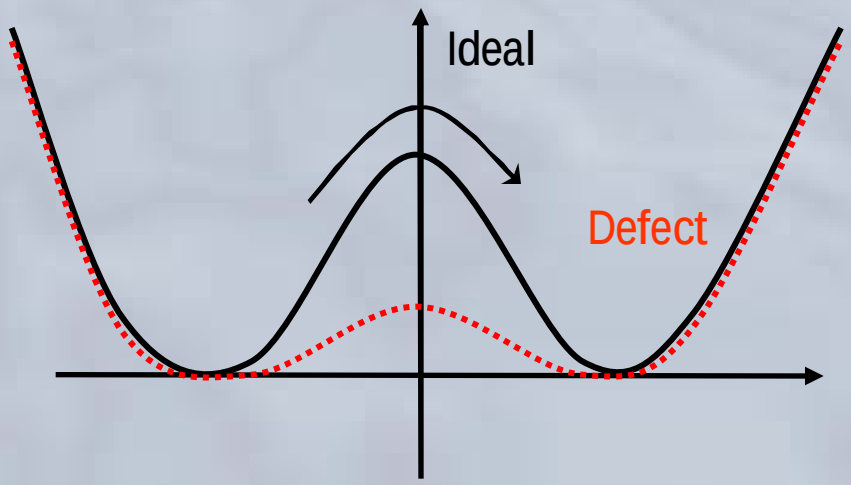
The results of this treatment combined with previous estimates of a domain wall energy of 7 ergs/cm^2 lead to a variation of nucleus energy with domain size which would permit only implausibly large domains to expand in the presence of a typical coercive field.

- Landauer paradox
  - In 1957, Landauer analyzed ferroelectric switching in uniform fields and have shown that nuclei size and activation energies are extremely large (Landauer paradox)
  - A lot of effort to explain intrinsic origins of Landauer paradox (Tagantsev, Rosenman, Bratkovskii)
  - Extrinsic switching controlled by defects: typical behavior for 1st order phase transitions
  - Spatial and energy distribution is an integral part of theory (Kolmogorov-Avrami-Ishibashi)

What are the nucleation centers?

Defects in a Nutshell





Field disorder

Broken symmetry between equivalent states

Small: Ferroelectric imprint

Large: Polar non-ferroelectric phase

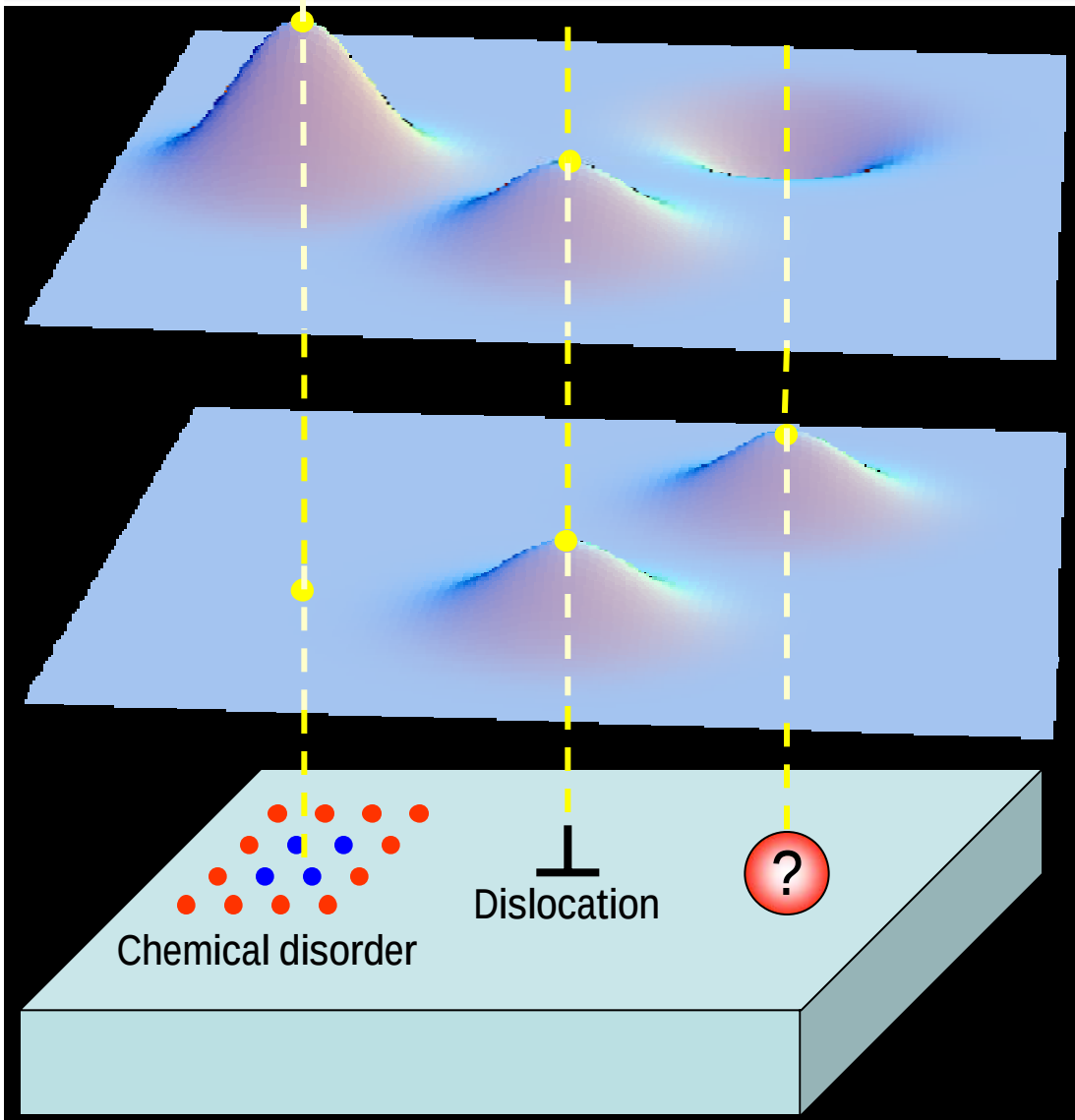
Bond disorder

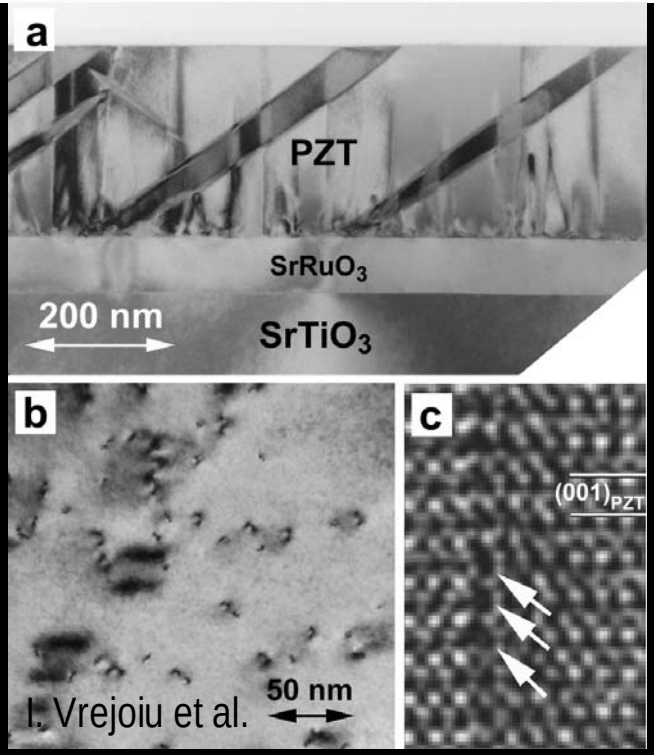
Preserves symmetry between equivalent states

Small: Lowers potential barrier between minima

Large: Non-polar phase

Life is More Interesting in > 0 Dimensions!





I. Vrejoiu et al.

Disorder components are linked to nanostructure:

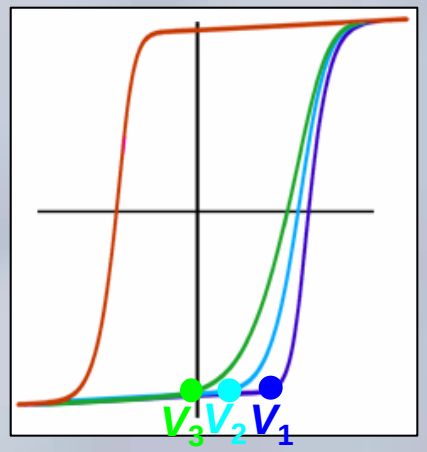
- Interfaces, and grain boundaries
- Dislocations
- Vacancies and vacancy clusters
- Dopant segregation

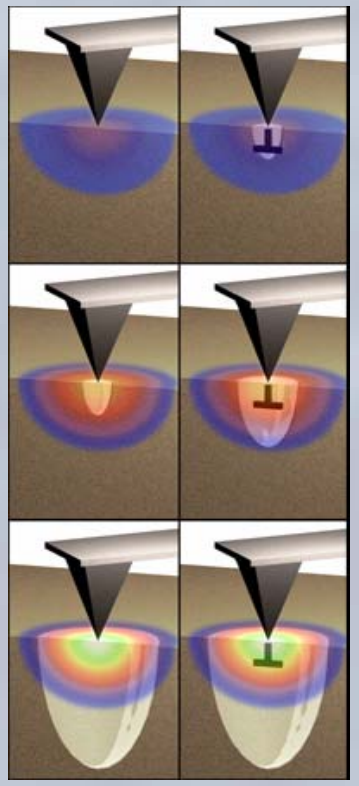
How can we study the role of defects on switching behavior?

Answer: one at a time!

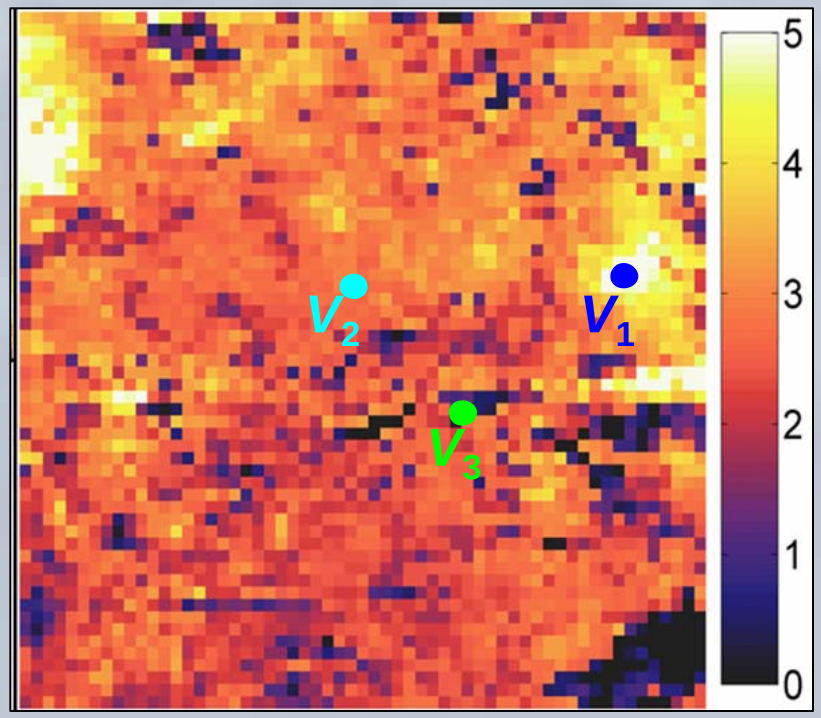
The hunt for the Snark: Imaging Nucleation Centers

- Macroscopic switching is determined by local switching centers (Landauer)
- From activation energies, centers should be well below 10 nm in size
- Centers will also affect local hysteresis loops and can be detected from local nucleation voltage





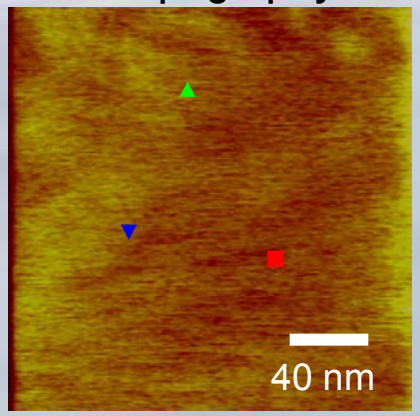
Map of Nucleation Bias



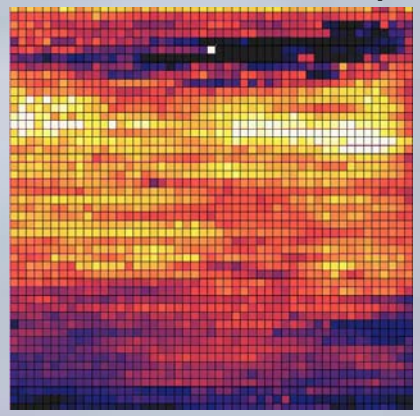
Local PFM nucleation bias maps yield information on spatial and energy distribution of switching centers

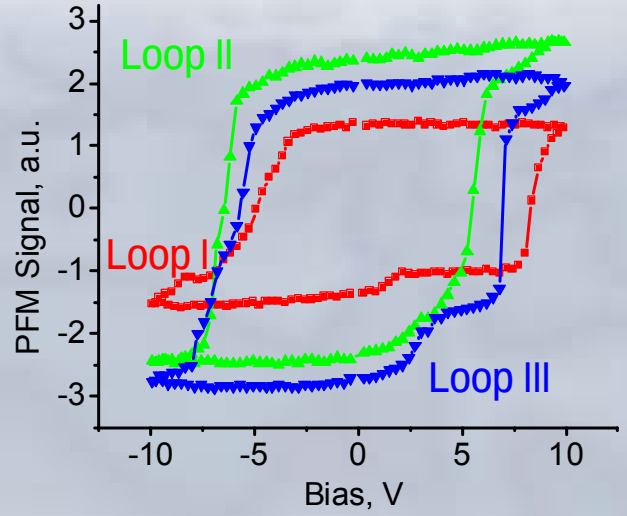
Hysteresis Loop Fine Structure

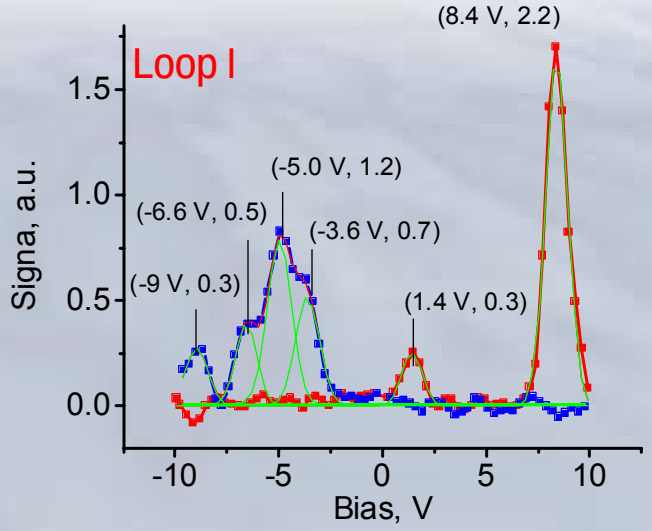
Topography

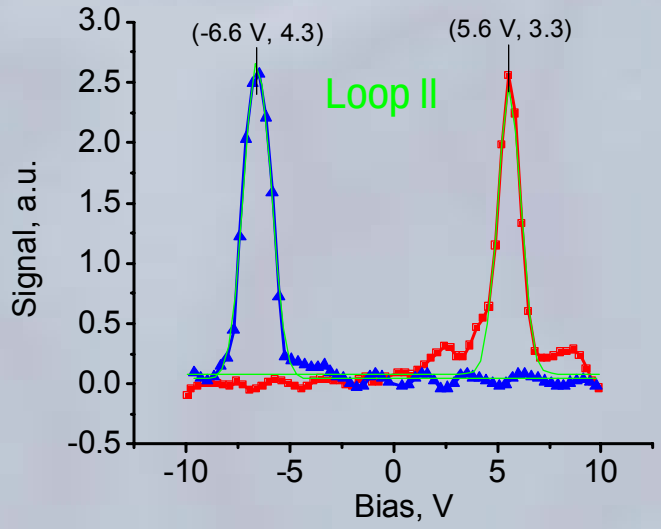


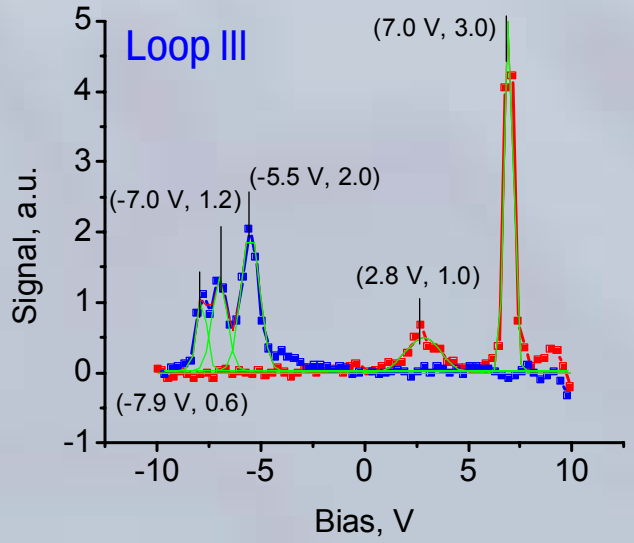
Nucleation bias map









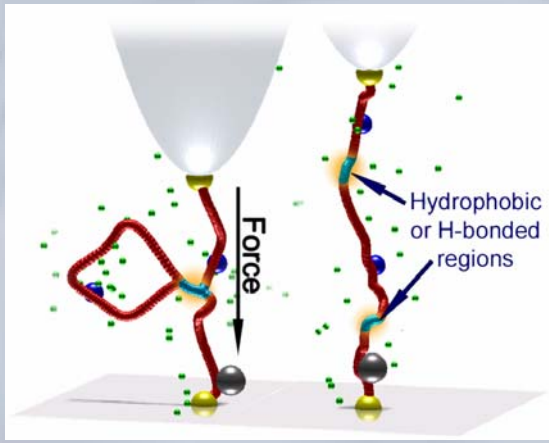


- Hysteresis loops have pronounced fine structure: discrete number of discernible events!
- Are these signatures of domain-defect interactions?

Future: Defect Effect on Local Phase Transitions

Force-Induced Transitions

Unfolding spectroscopy

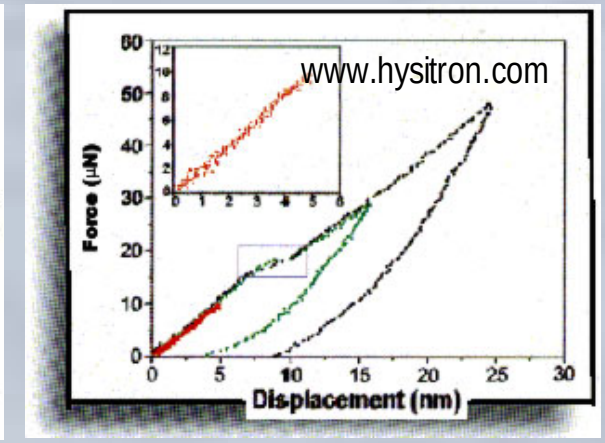


- Energies ~ kT: stochastic
- Reversible
- Only one parameter measured
- Need molecule hunting

Single-molecule reactions

- Thermodynamics
- Kinetics
- Statistical physics

Nanoindentation

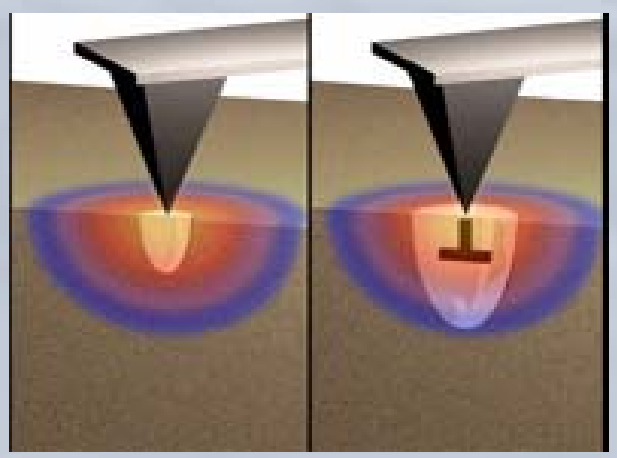


- Energies >> kT: deterministic
- (partially) Irreversible
- Only one parameter measured
- Strongly invasive

Nanomechanics

- Dislocation dynamics
- Pressure-induced transitions
- Cracking, etc

Bias-induced transitions



- Energies either >> kT or ~kT
- Can be reversible
- Many parameters can be measured

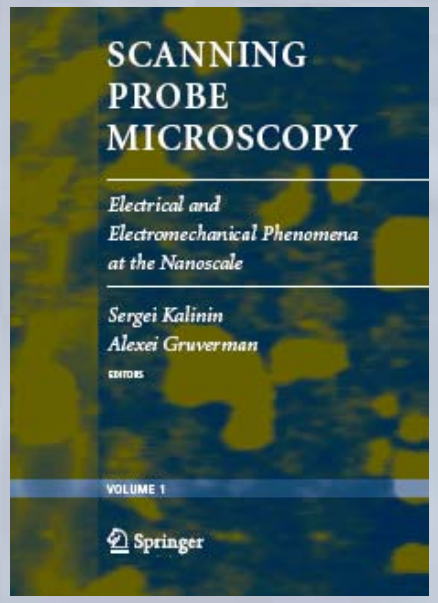
Nanoelectromechanics

- Polarization switching
- Electrochemical reactions
- Soft condensed matter
  - polyelectrolytes
  - biosystems
  - liquid crystals

Enabling tools in nanobiology and nanomechanics

Availability of SS-PFM and Liquid PFM

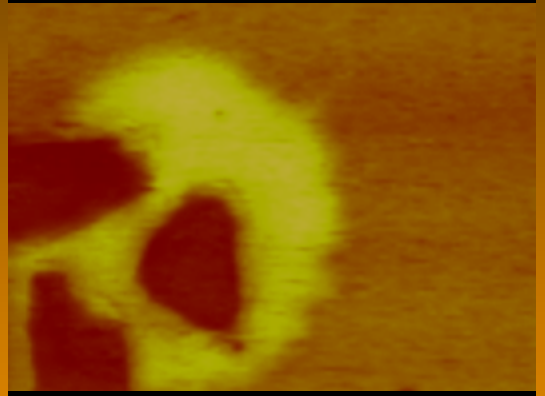
Center for Nanophase Materials Sciences at ORNL



- SSPFM is available as a part of NanoPhysics Program
- Call for proposals open (2 page)
- Planned instrument-specific short course
- Initial point of contact: sergei2@ornl.gov

Scanning Probe Microscopy: Electrical and Electromechanical Phenomena at the Nanoscale (Hardcover) by Sergei V. Kalinin, Alexei Gruverman (Eds), Springer.

Happy Halloween



From a domain
in bismuth ferrite