Switching Spectroscopy PFM

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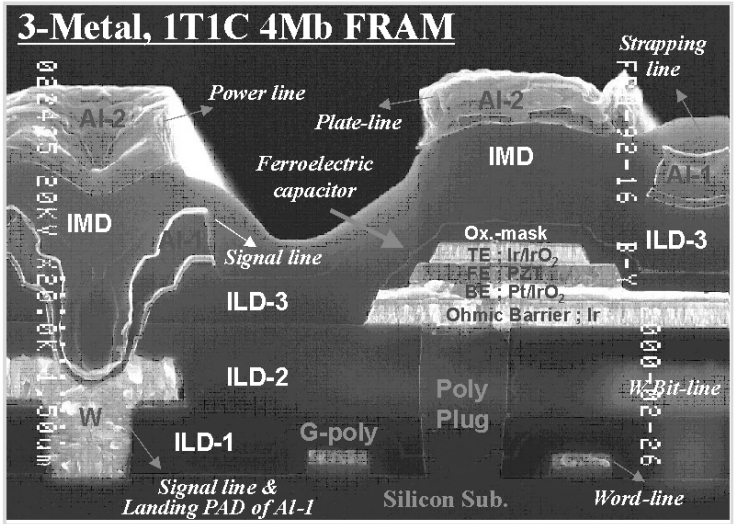
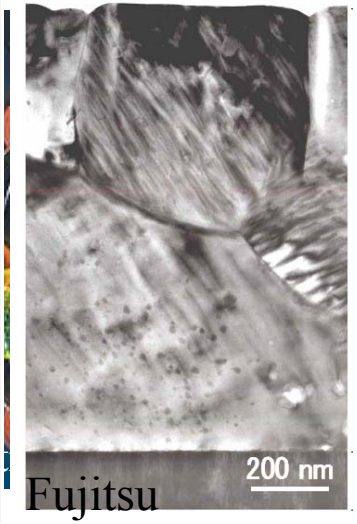
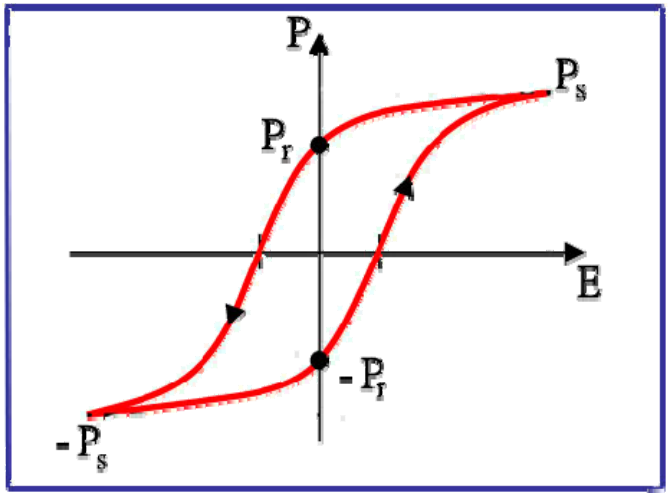
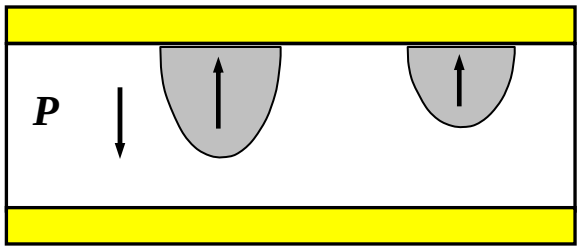
Polarization Dynamics: Real and Ideal







Top electrode



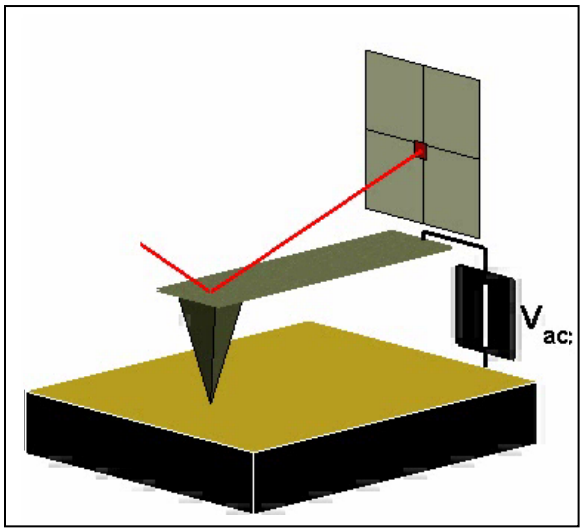
Bottom electrode

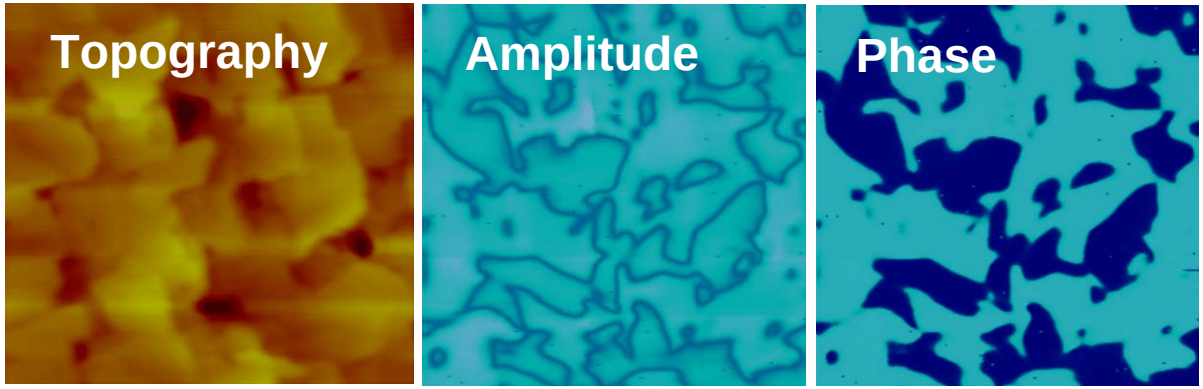
In macroscopic hysteresis measurements, measured is switchable polarization charge in a capacitor. This provides information (imprint, fatigue, etc) vital for ferroelectric devices. However, measurements are averaged over large area and this approach is inapplicable to nanoscale structures.

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

Piezoresponse Force Microscopy - PFM

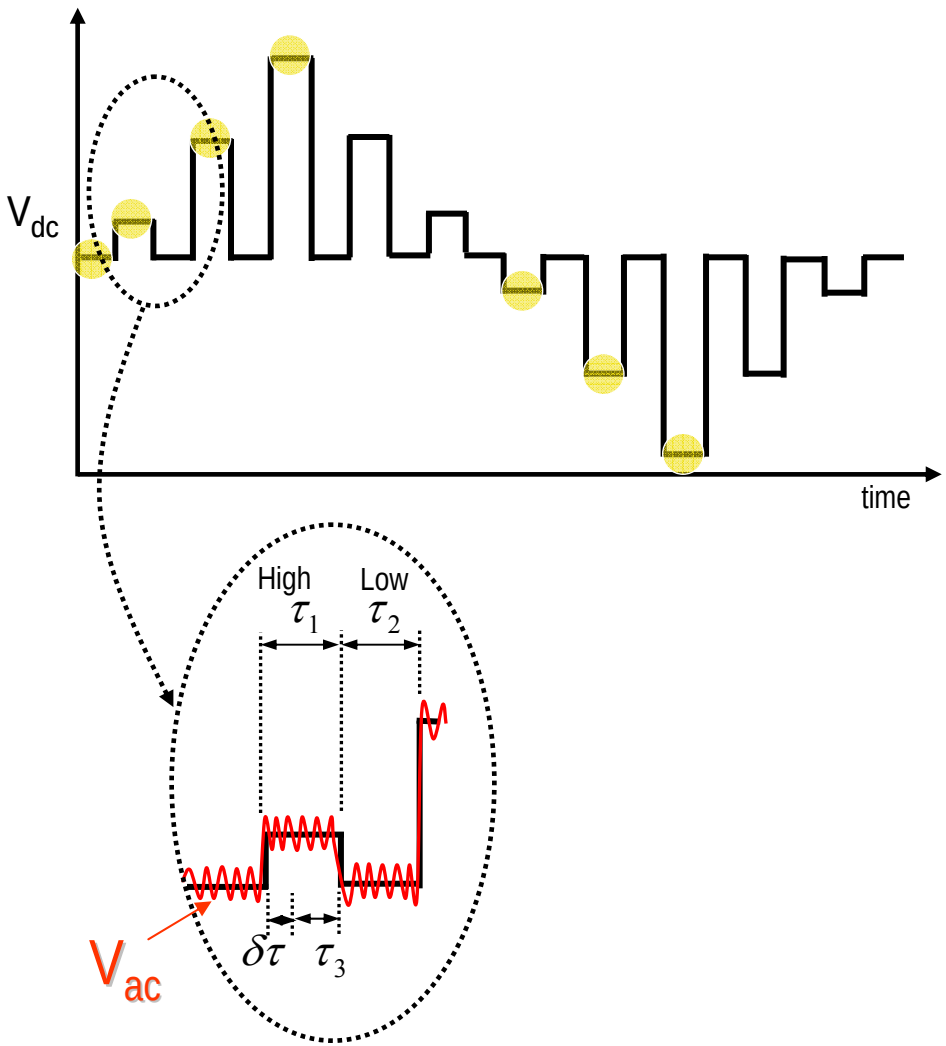
Polarization is strongly coupled to electromechanical response

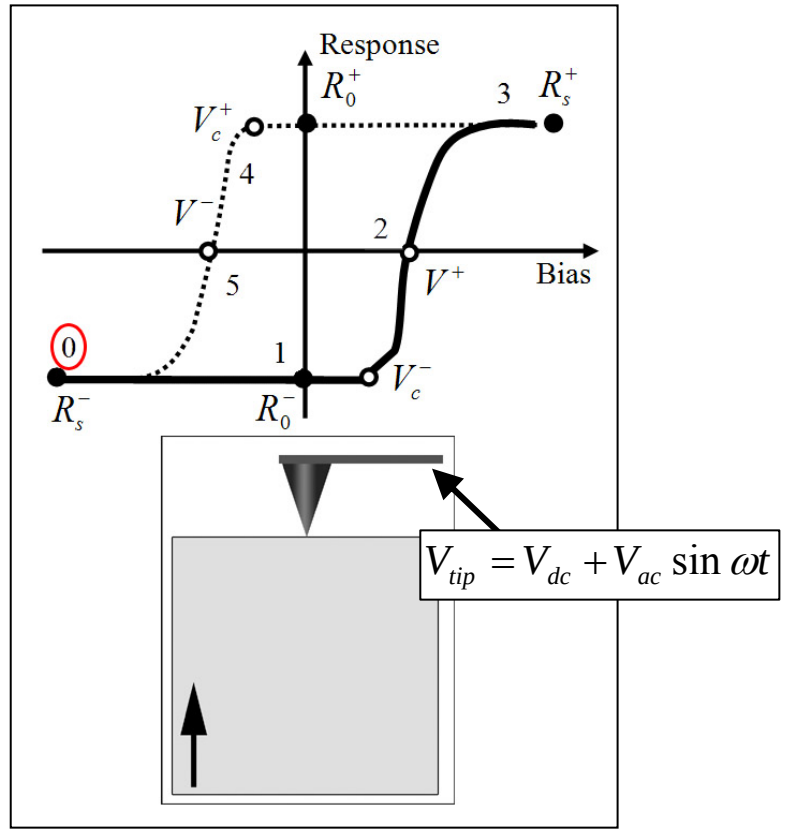




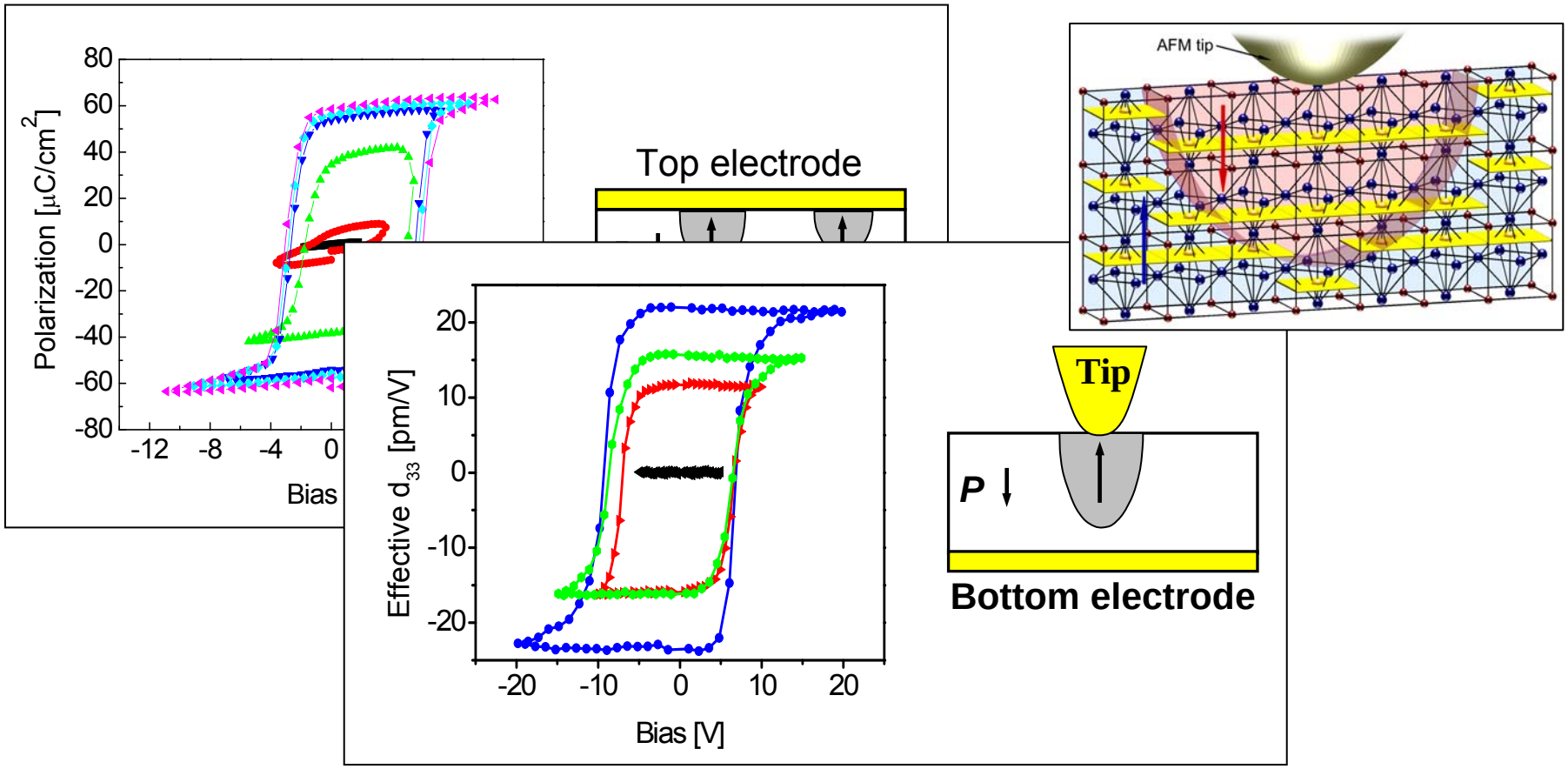
2D Piezoresponse Map

Piezoresponse Force Spectroscopy





Local Polarization Dynamics: Piezoresponse Force Spectroscopy



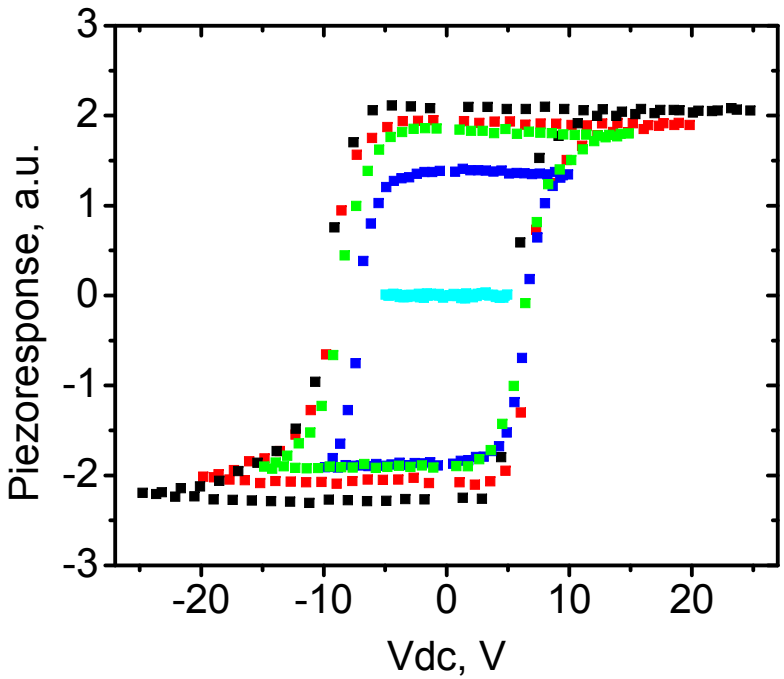
Mechanisms for local and macroscopic switching:

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?

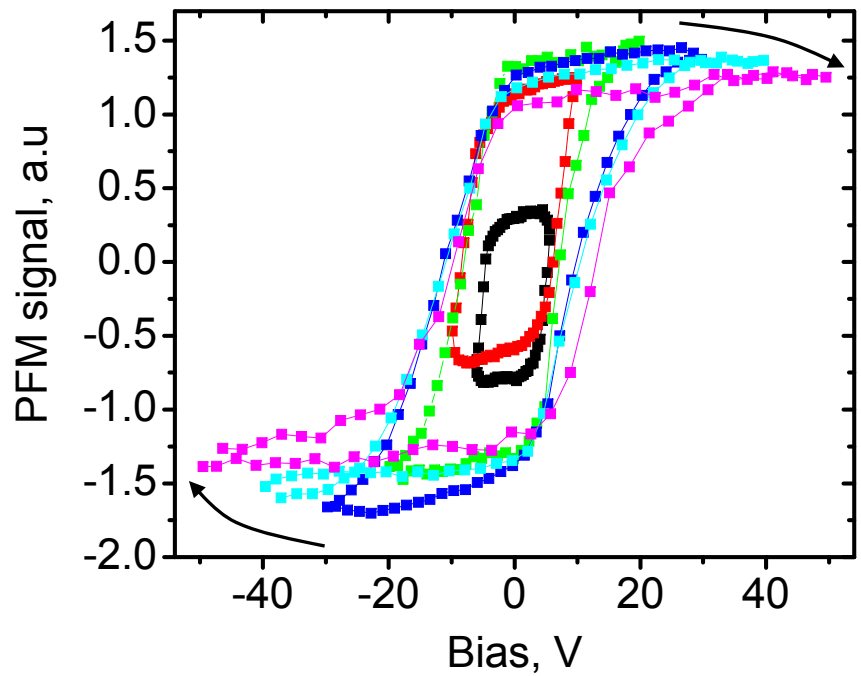
Challenge 1: Can we develop the theory describing hysteresis loop formation in PFM?
Challenge 2: Can we study spatial variability of switching behavior to link it to structure?

Hysteresis Loops in Epitaxial Ferroelectrics

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



Epitaxial PZT
(M. Alexe, MPI)

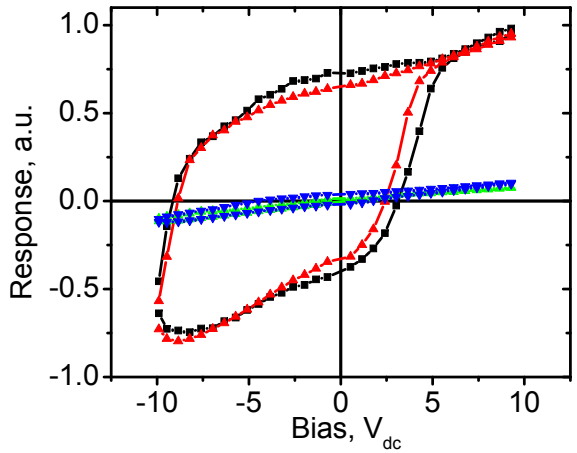


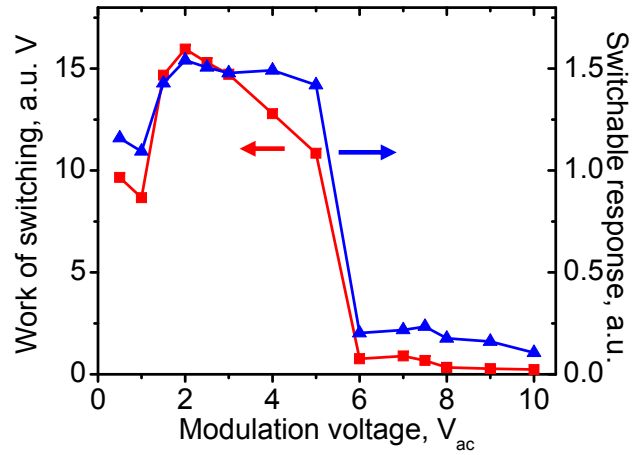
In ideal films, the behavior of hysteresis loop with bias suggests the mechanism:

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

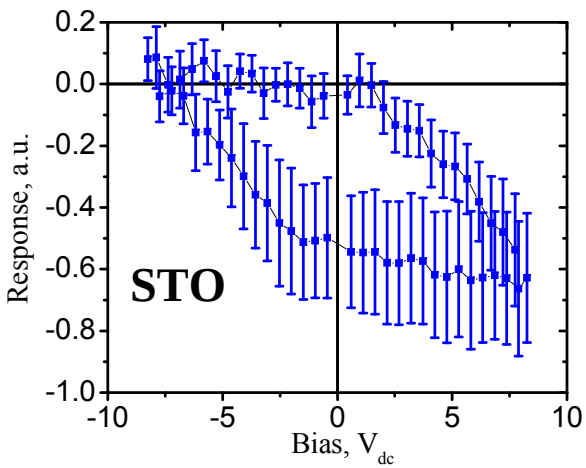
Effect of modulation bias

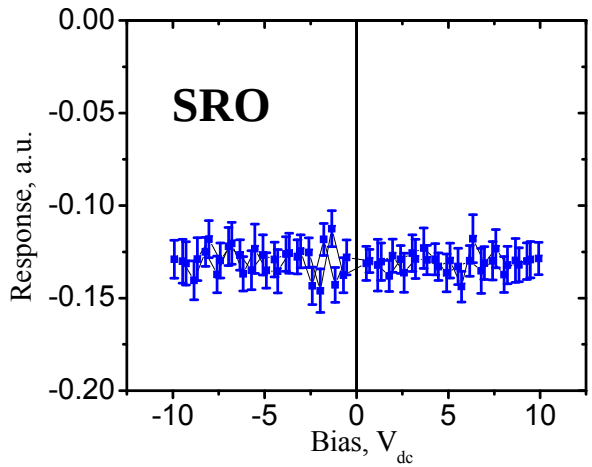




Loops are reproducible for driving voltages below coercive bias, and collapse above

Response on non-piezoelectric surface



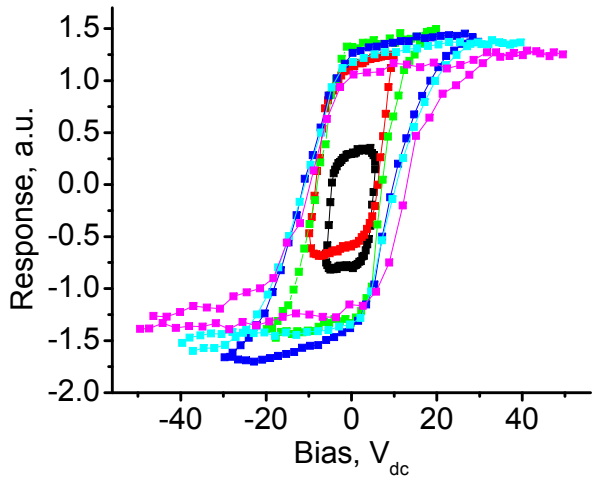


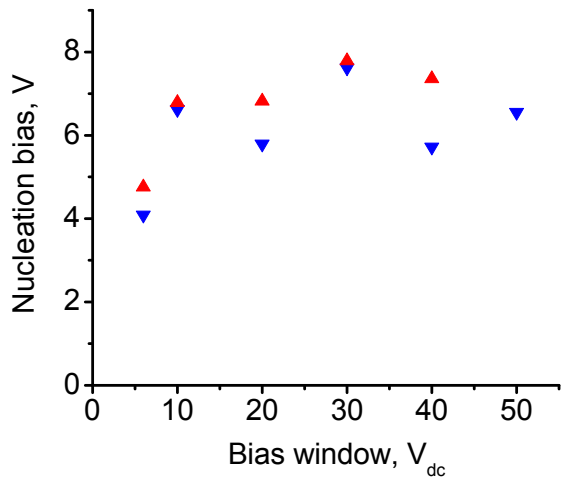
Sometimes, non-zero response is observed on non-ferroelectric surfaces.

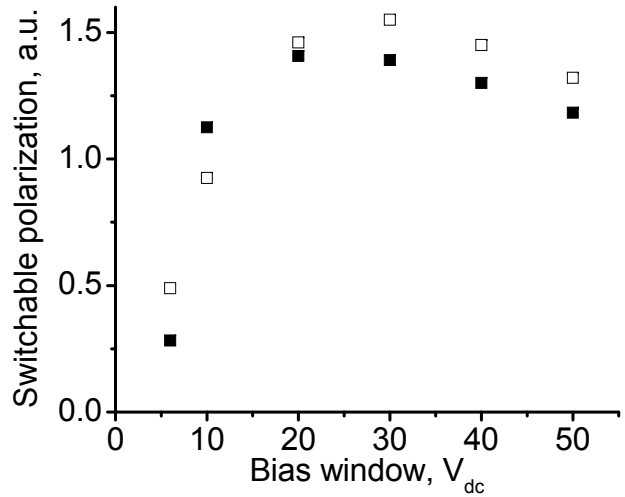
- Electrochemistry?
- Electrocapillary effects?
- Surface ferroelectricity?

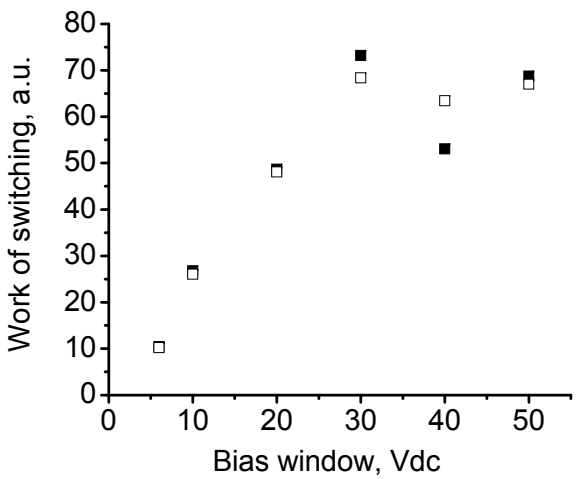
Effect of Imaging Conditions on Hysteresis Loops

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)

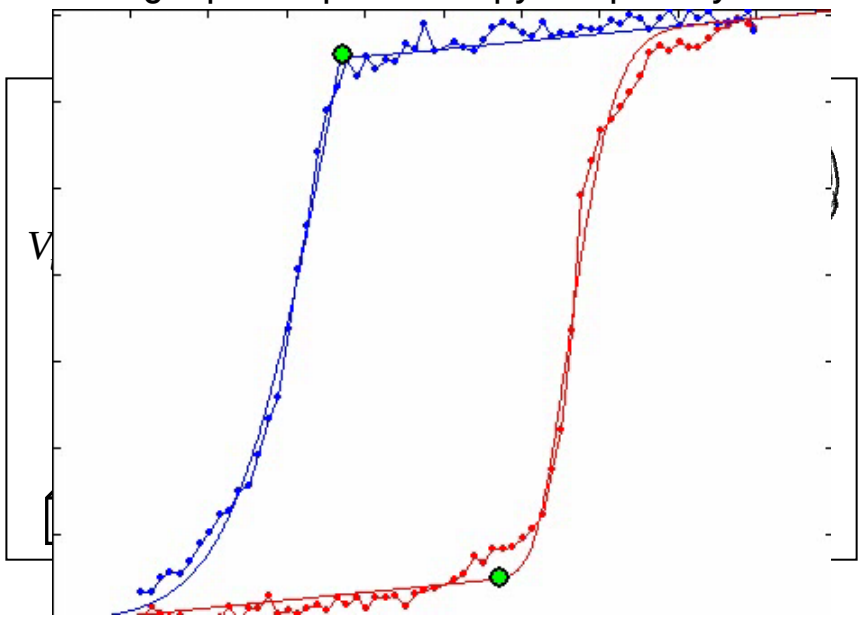
For some materials, “anomalous” behavior is observed at large biases

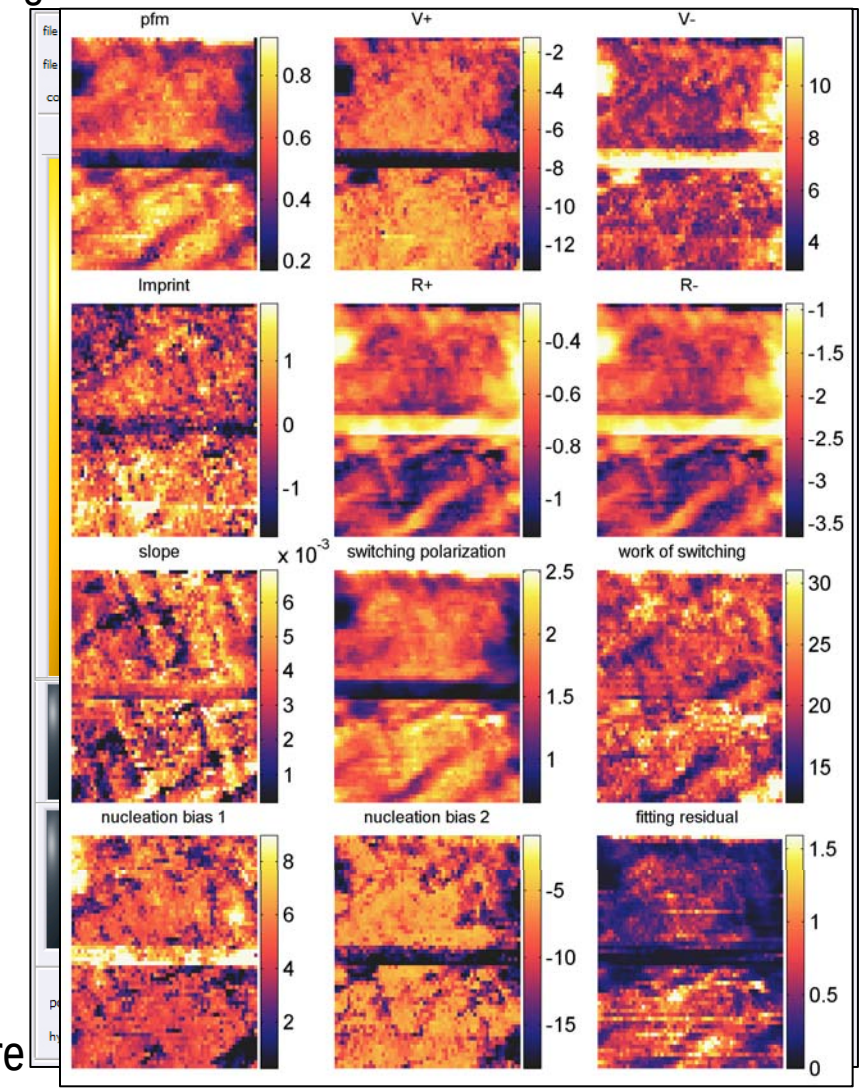
Loop parameters evolve as:

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

Switching Spectroscopy Piezoresponse Force Microscopy

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

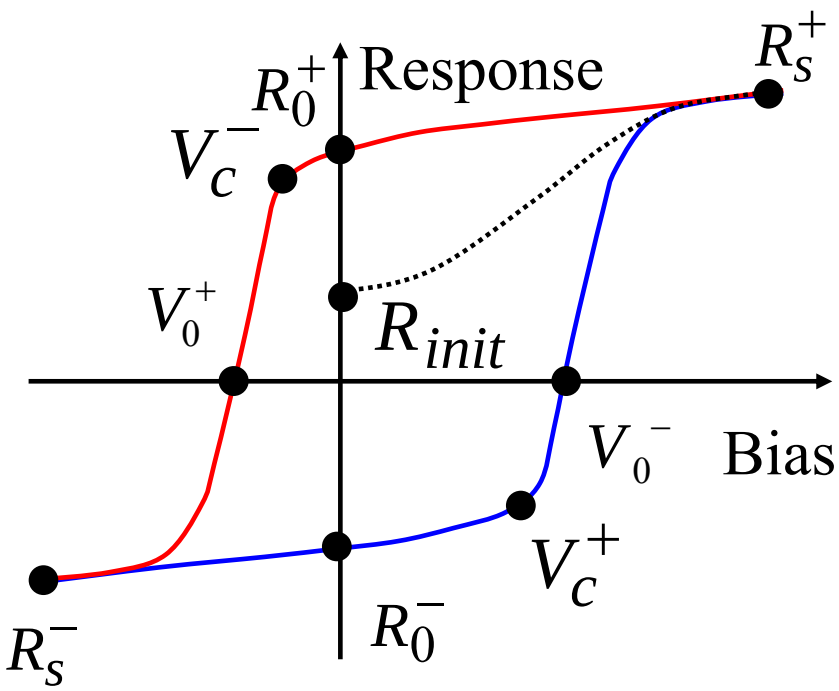




SS-PFM capabilities

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

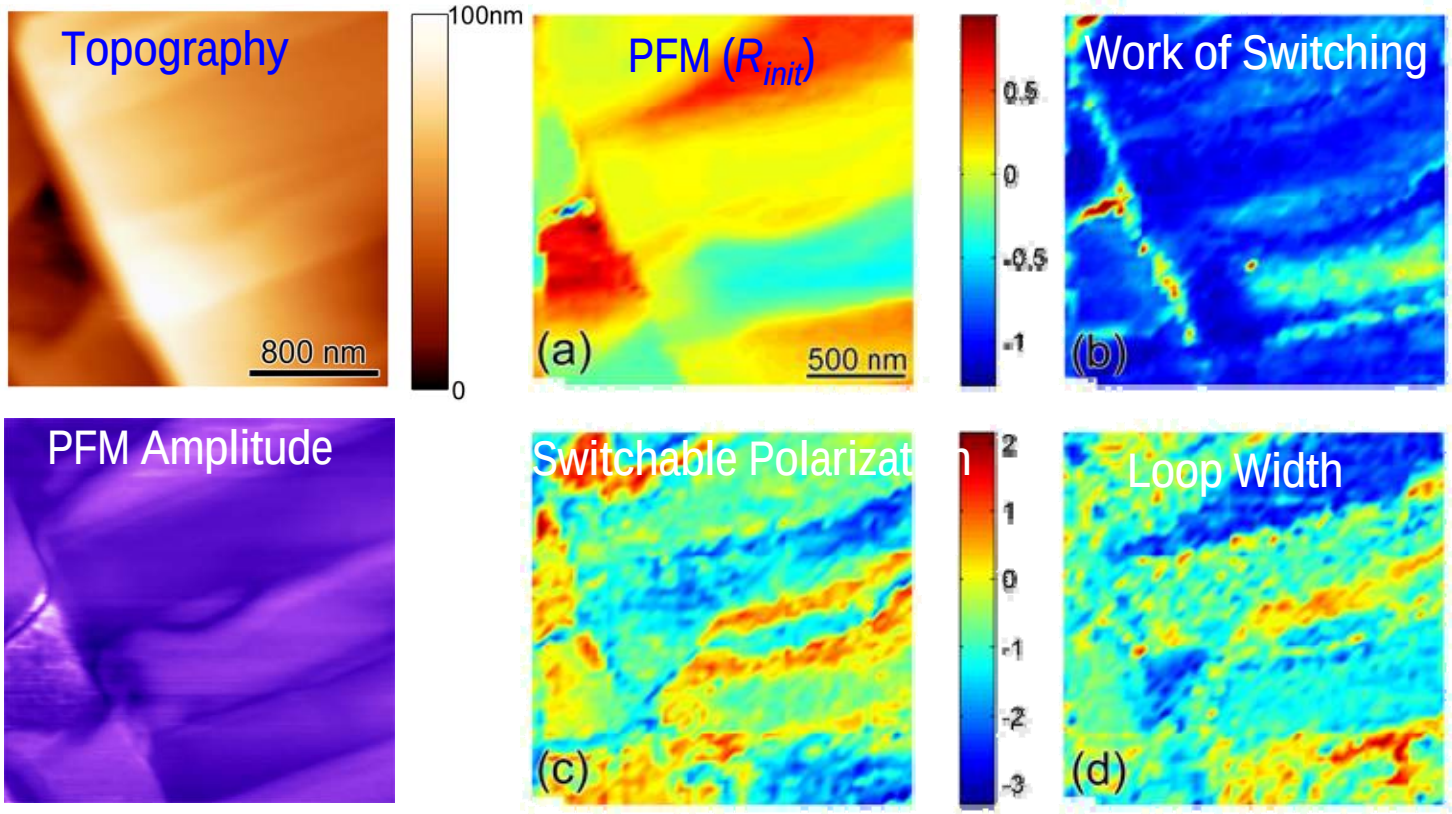
Data Analysis in SS-PFM



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

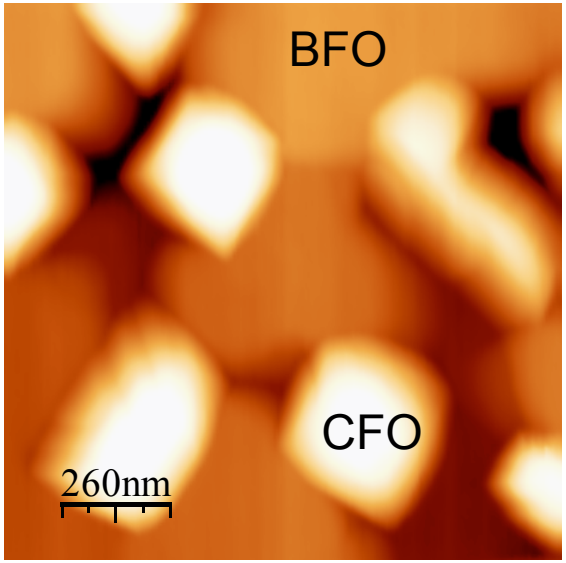
1. **Statistical analysis**
2. **Direct curve fitting**

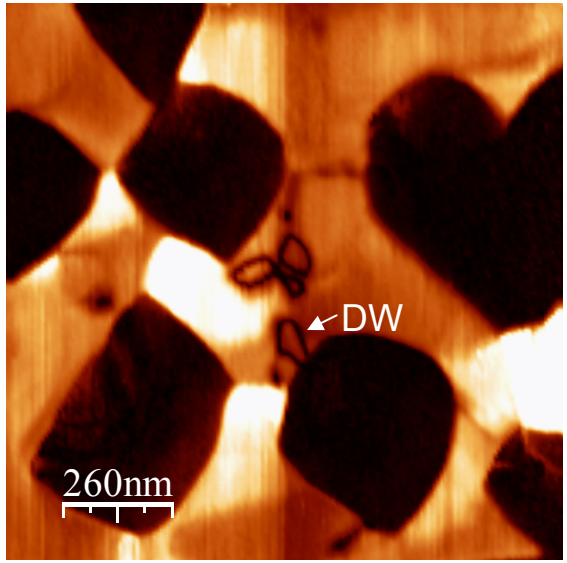
SS-PFM of Polycrystalline PZT

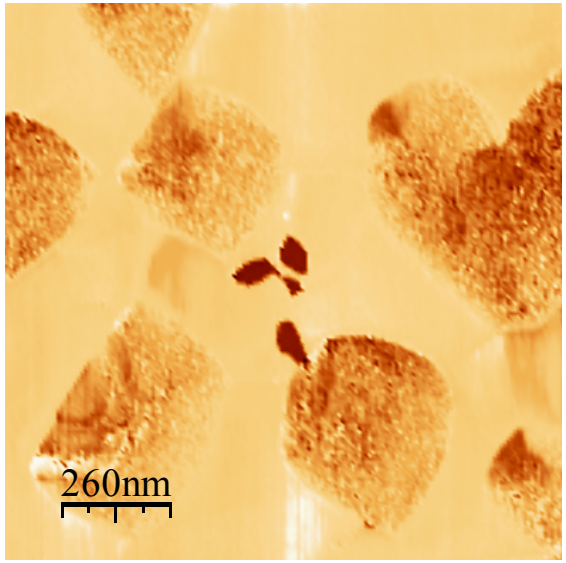


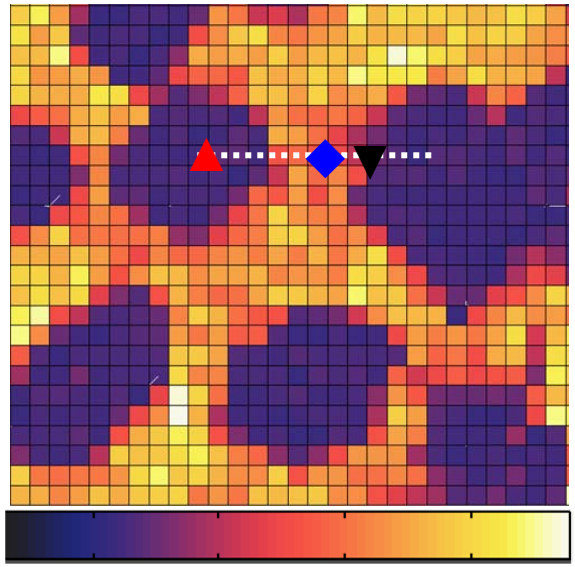
- The PFM, work of switching, and Loop width maps are different: data is statistically significant
- Grain boundary is associated with hindered switching (enhanced pinning).

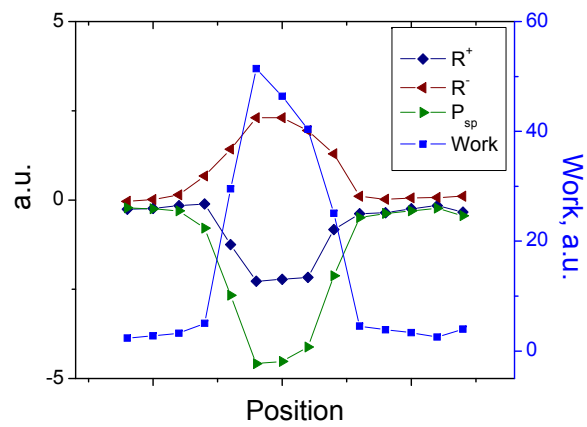
SSPFM of Multiferroic Nanostructure

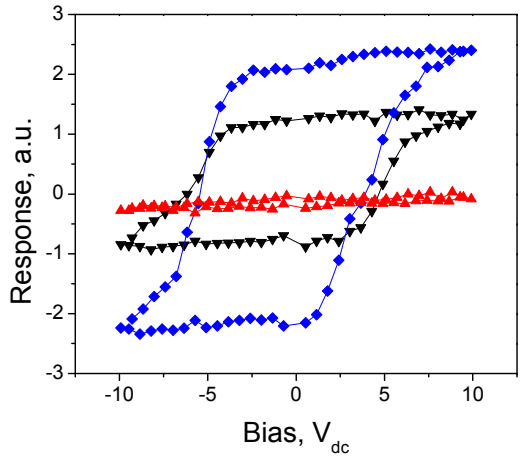








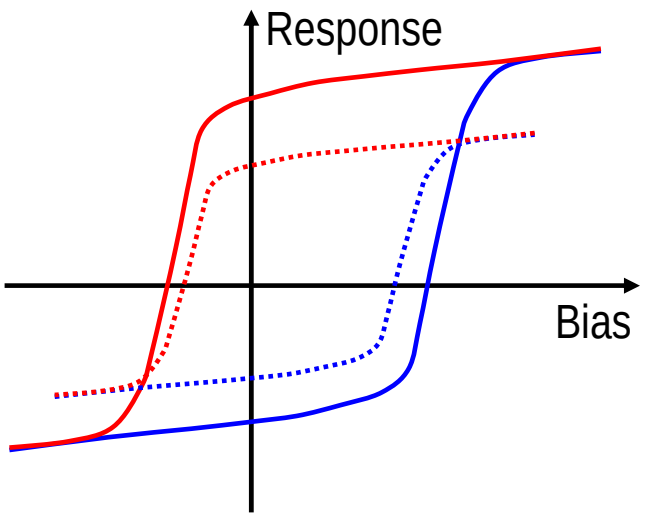




Each pixel ~50 nm x 50 nm

Switching Spectroscopy Piezoresponse Force Microscopy - SSPFM

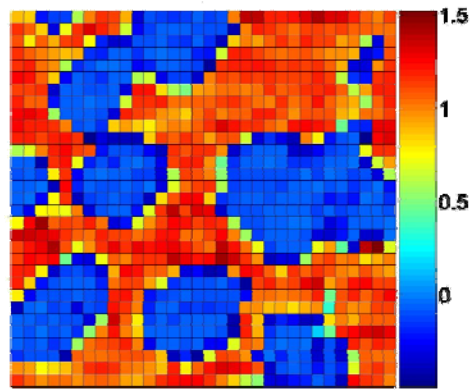
Now we have the data. What can we learn?



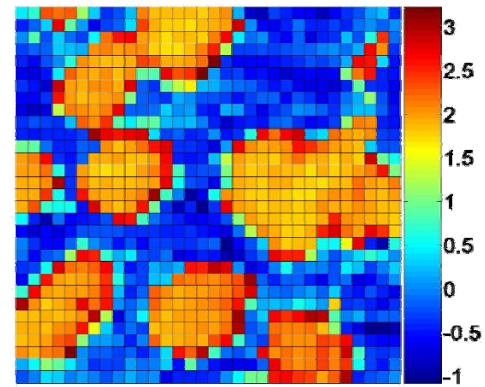
$$PR^{+}(V) = d_f + \alpha PR_0^{+}(\beta V + V_i)$$

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

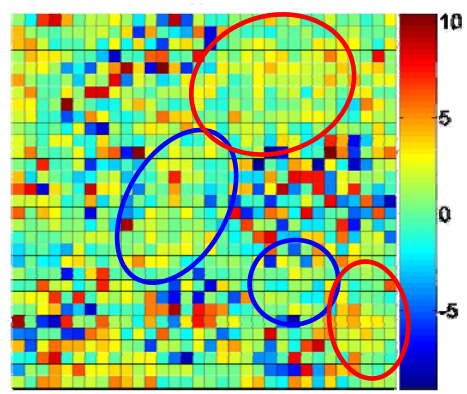
Switchable response, α



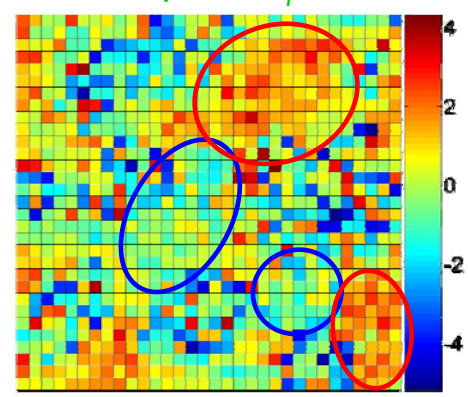
Vertical offset, d_f



Coercive bias, β



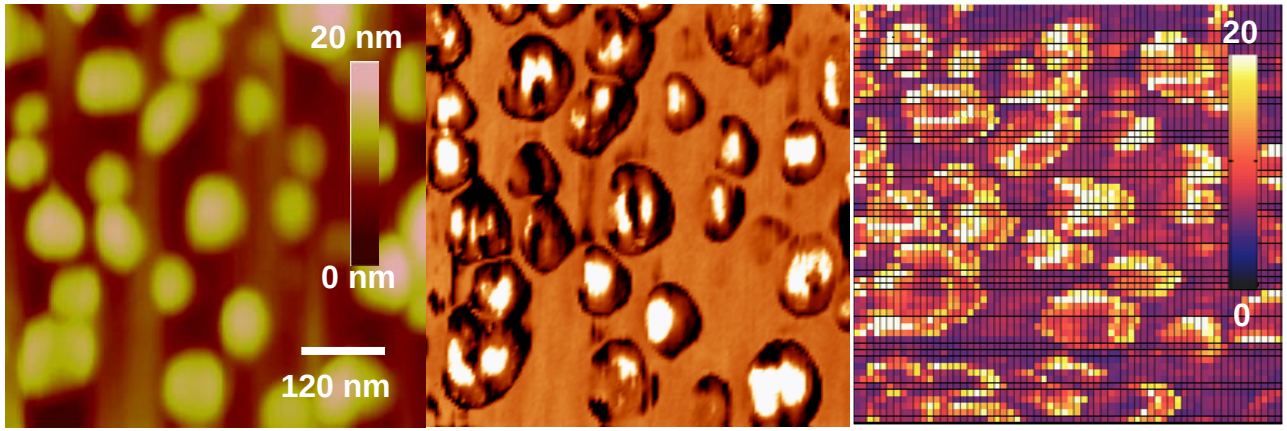
Imprint, V_i

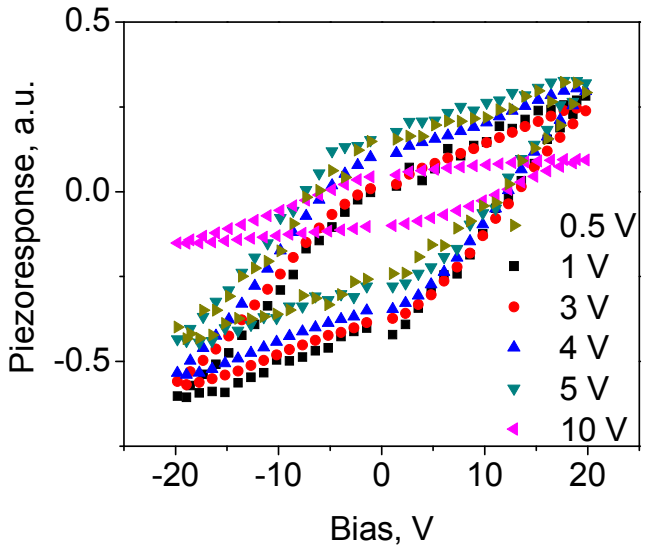


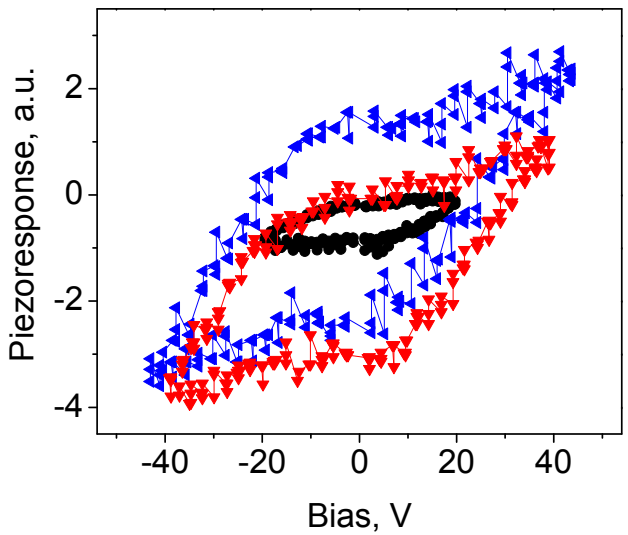
Perfect system: Interfaces do not affect switching

SS-PFM of Ferroelectric Nanodots

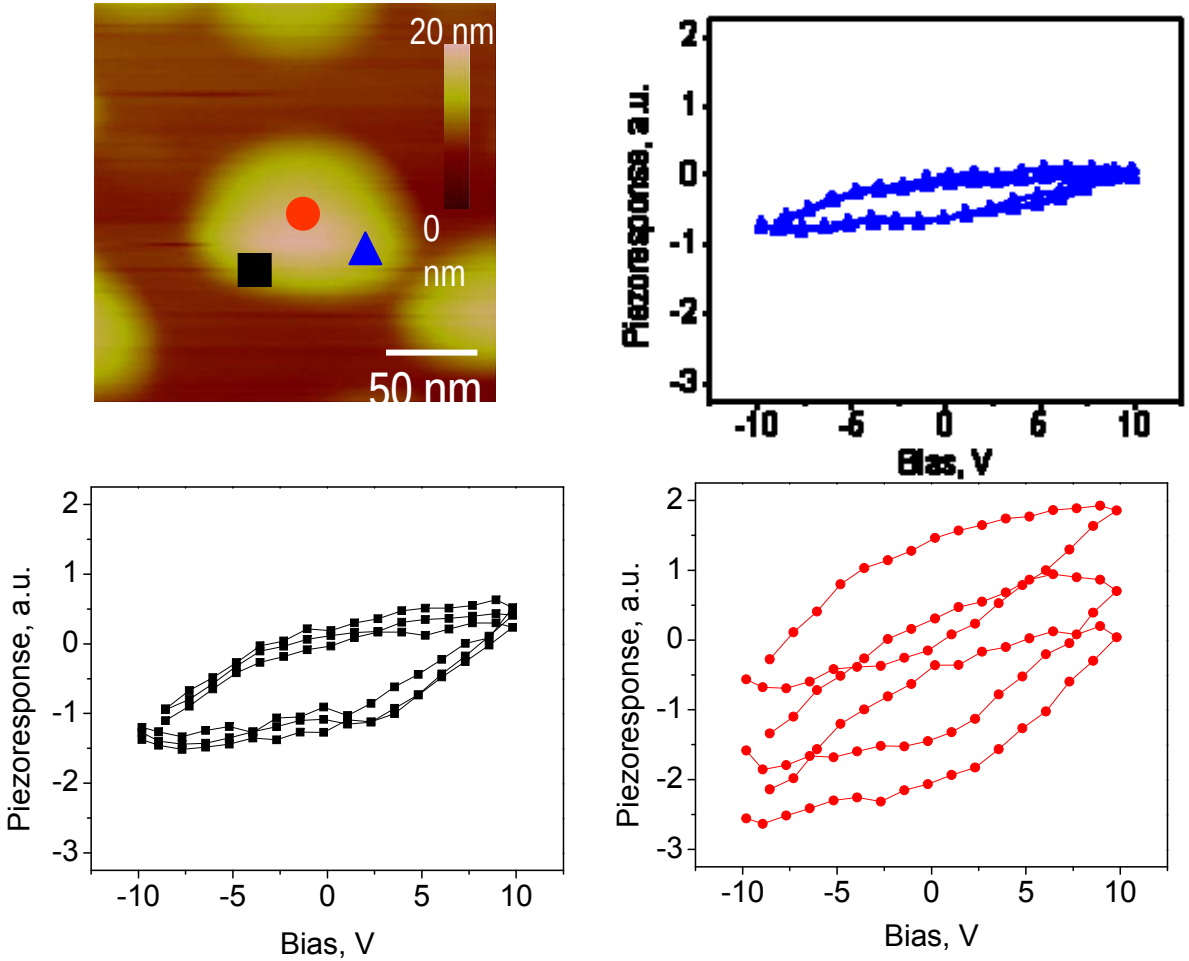
- What is the size limit of ferroelectricity?
- Are switching properties uniform within the nanoobject?







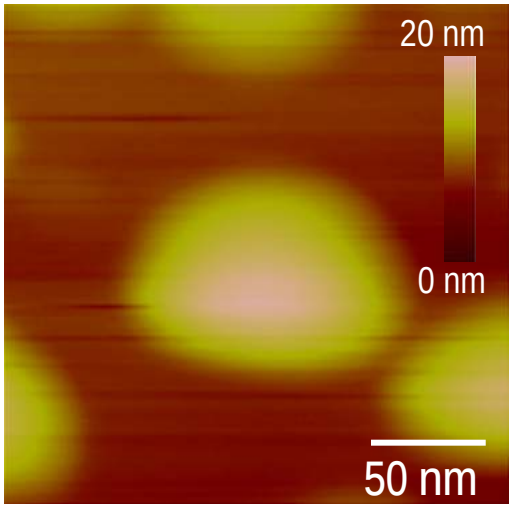
Switching Variability within a Single Nanodot



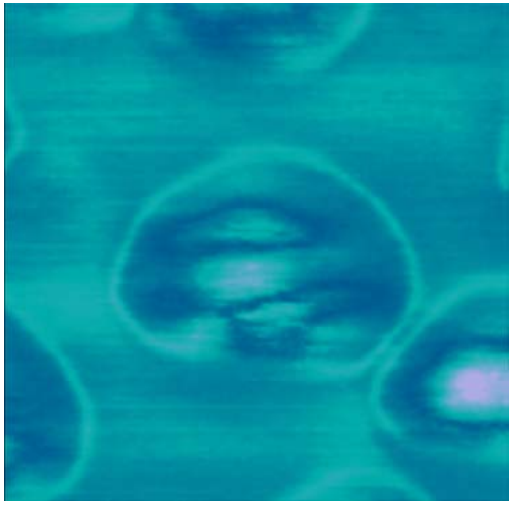
Different parts of a nanodot have different hysteresis loops

SS-PFM of Ferroelectric Nanoparticles

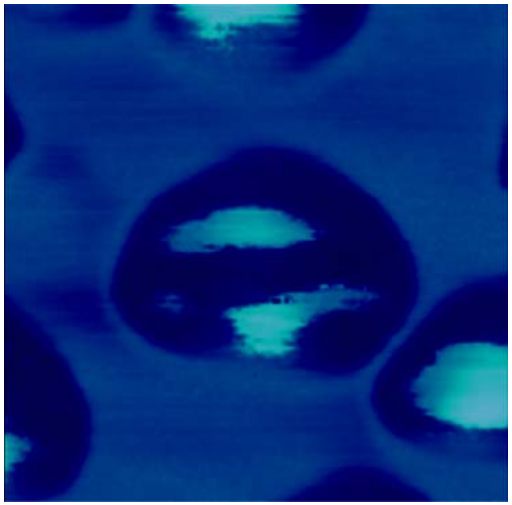
Topography



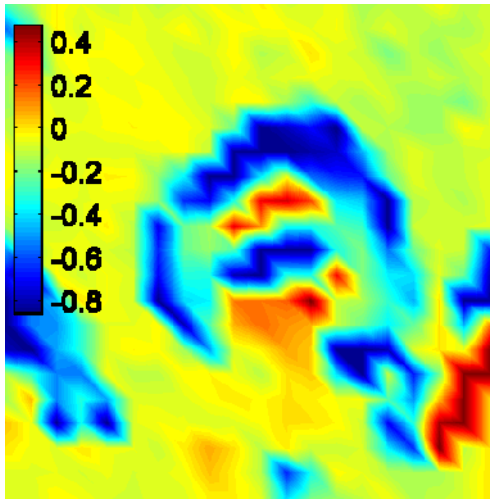
PFM Amplitude



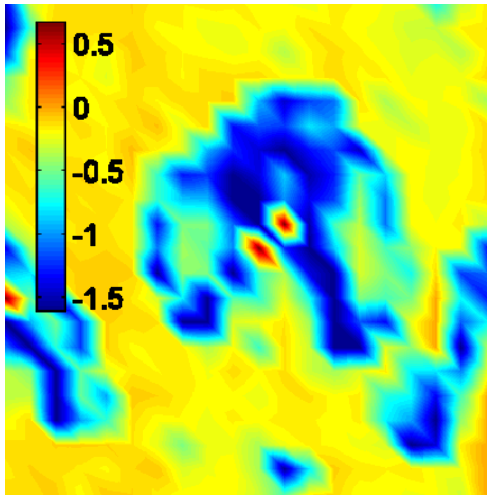
PFM Phase



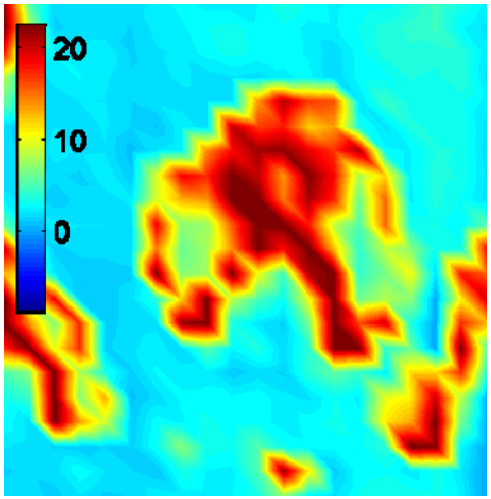
Initial response



Switchable Polarization

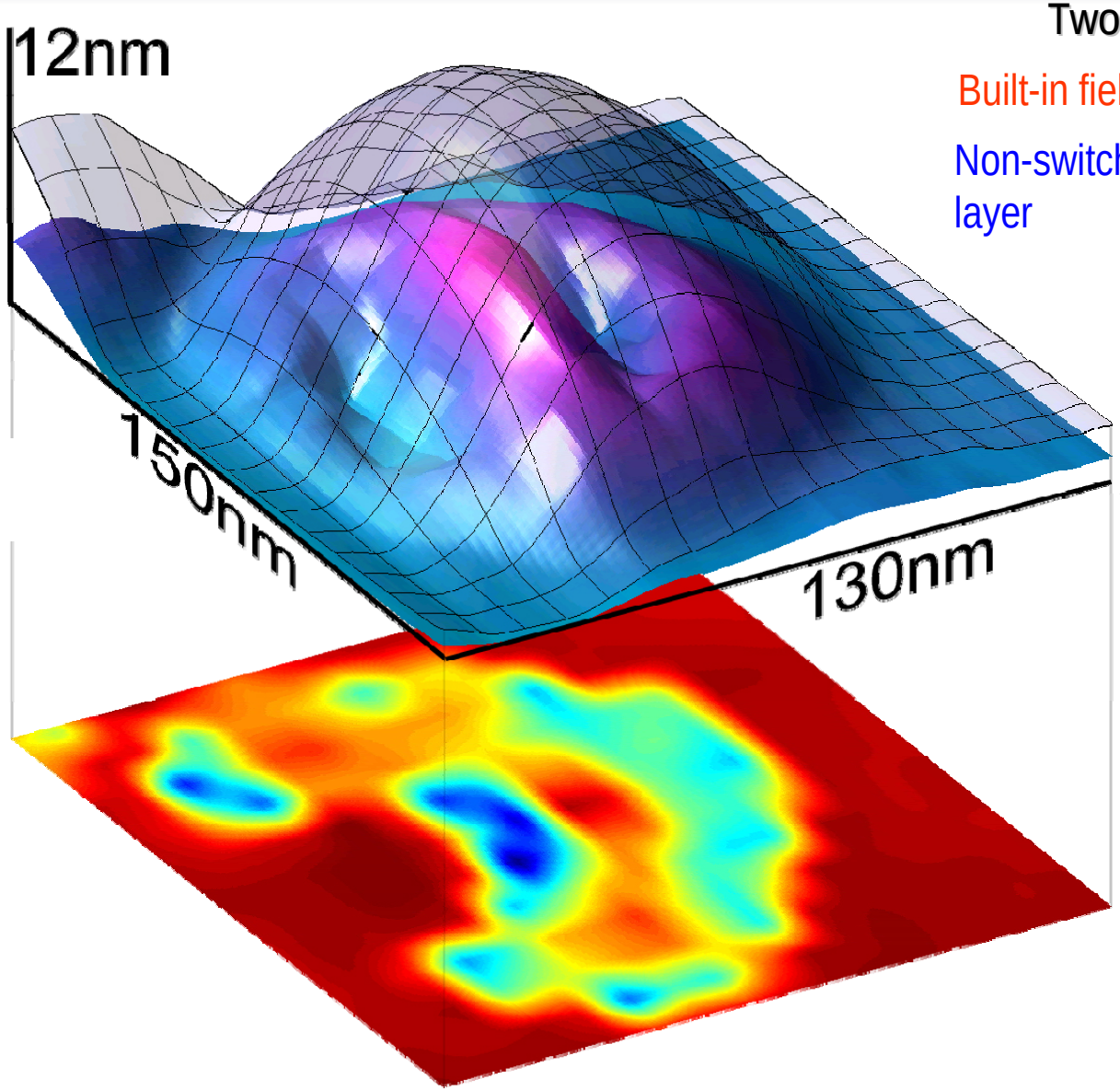


Work of Switching



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

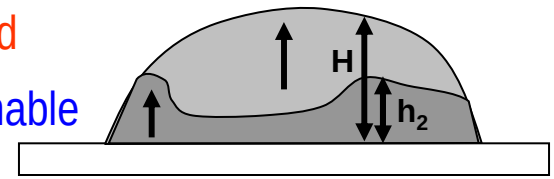
SS-PFM of Ferroelectric Nanoparticles

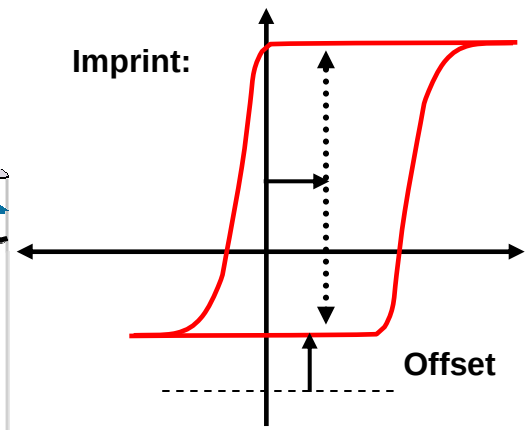


Two-layer model

Built-in field

Non-switchable layer



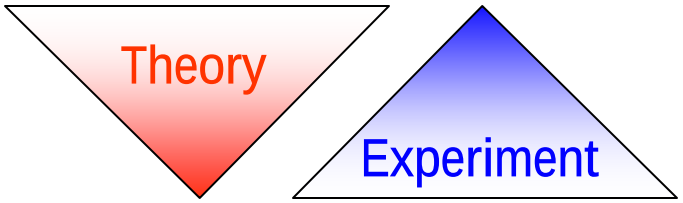


SS-PFM capabilities

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

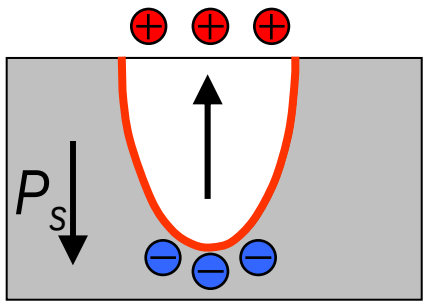
Analytical Theory for Piezoresponse Force Spectroscopy

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



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

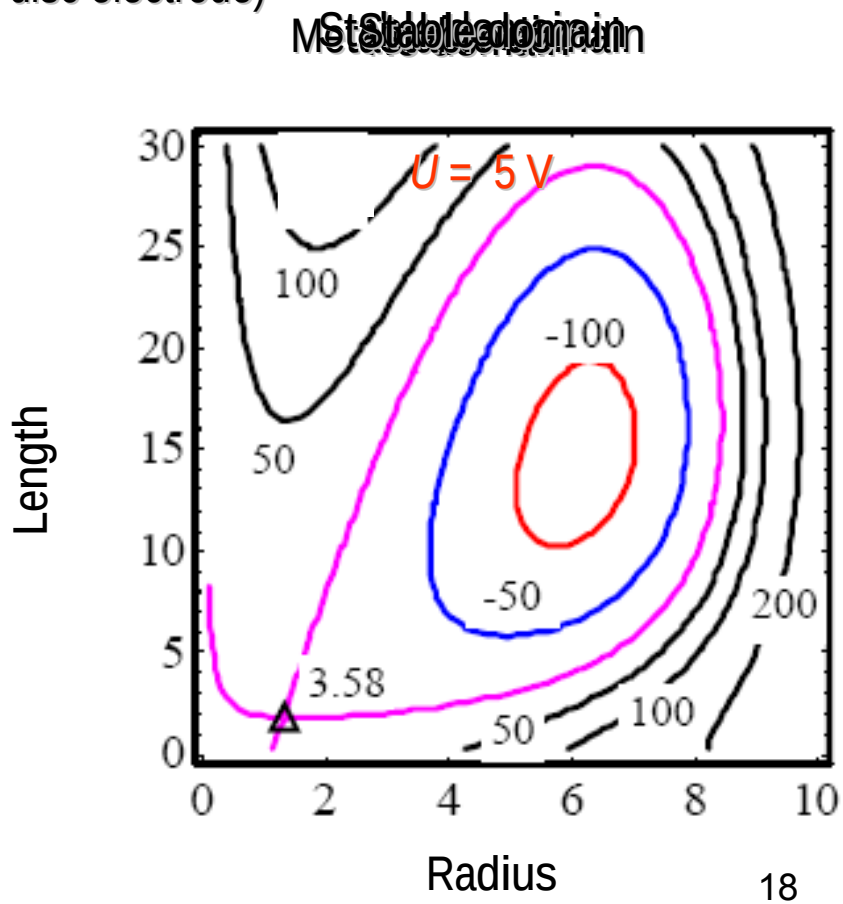


Landauer model:
r – domain radius
l – domain length

Domain energy:

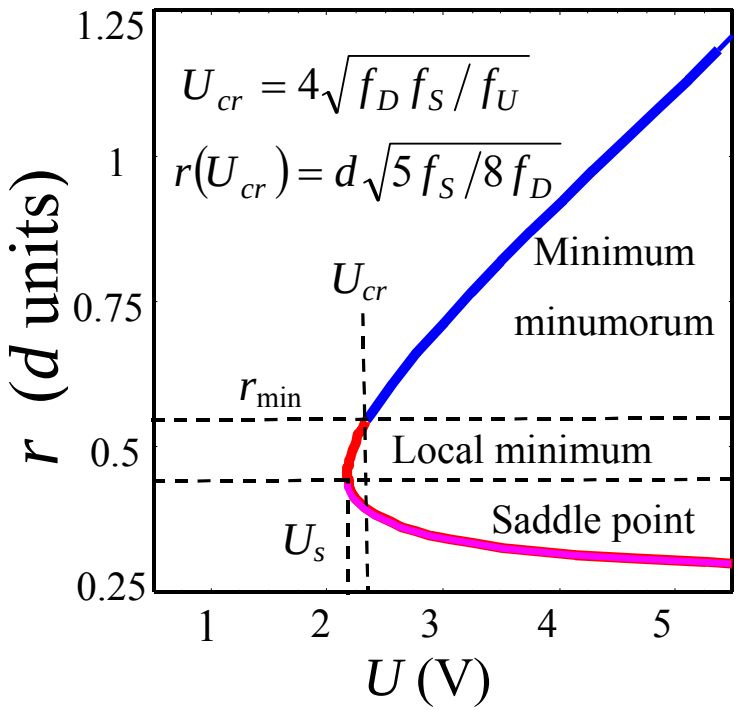
$$\Phi(r,l) = \Phi_S(r,l) + \Phi_D(r,l) - U\Phi_{UL}(r,l)$$

Domain wall energy
Depolarization energy
Interaction energy



Domain Dynamics in Thermodynamic Limit

Evolution of special points on free energy surface



Wall energy

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

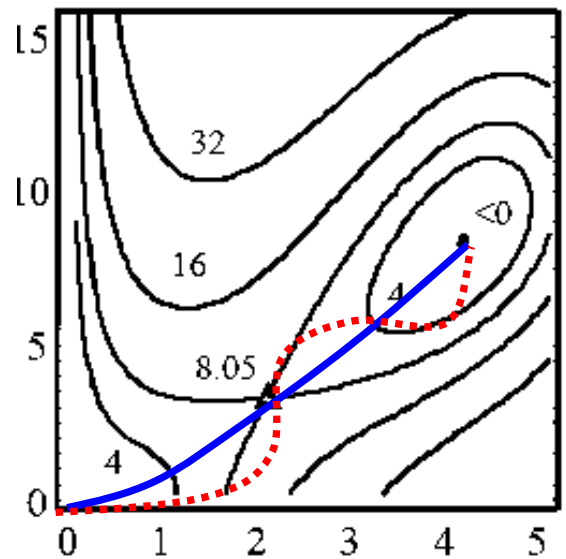
Polarization

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

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:

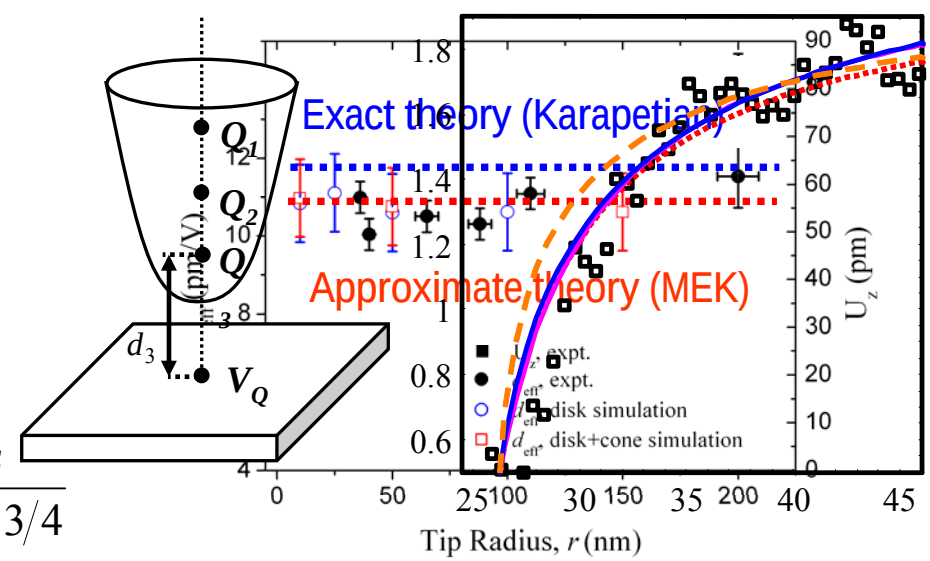
$$u_3(\rho) = V_Q(\rho)\frac{1+\nu}{Y}\left(e_{31} f_1(\gamma) + e_{15} f_2(\gamma) + e_{33} f_3(\gamma)\right)$$

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

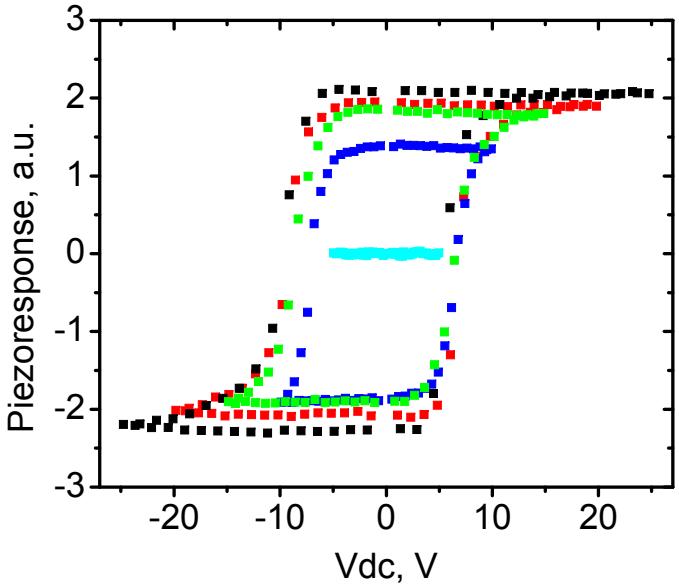
$$d_{33}^{eff} \approx \frac{3}{4}\left(d_{33} + \left(\frac{1}{3} + \frac{4}{3}\nu\right) d_{31}\right)\frac{s}{|s| + 1/4} + \frac{1}{4} d_{15} \frac{s}{|s| + 3/4}$$

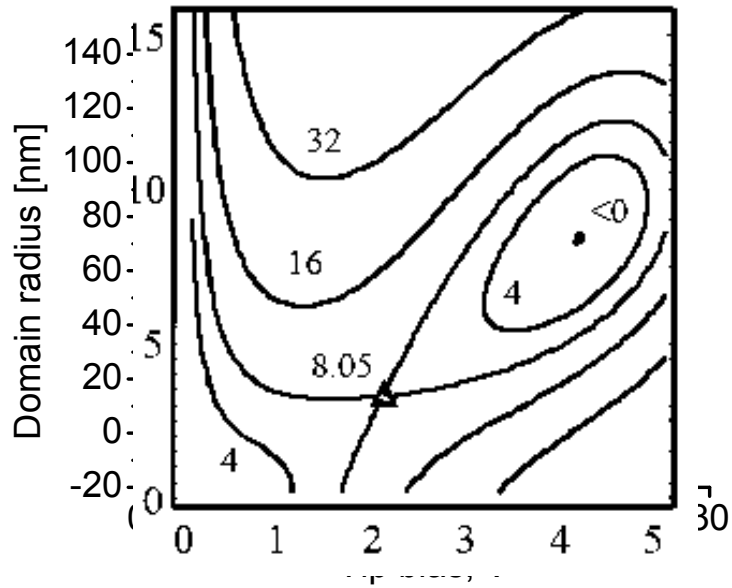


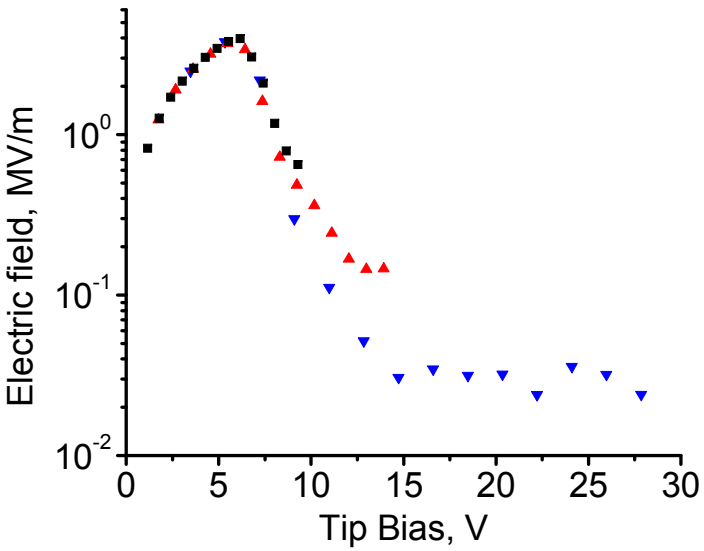
Tip parameters can be calibrated!

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

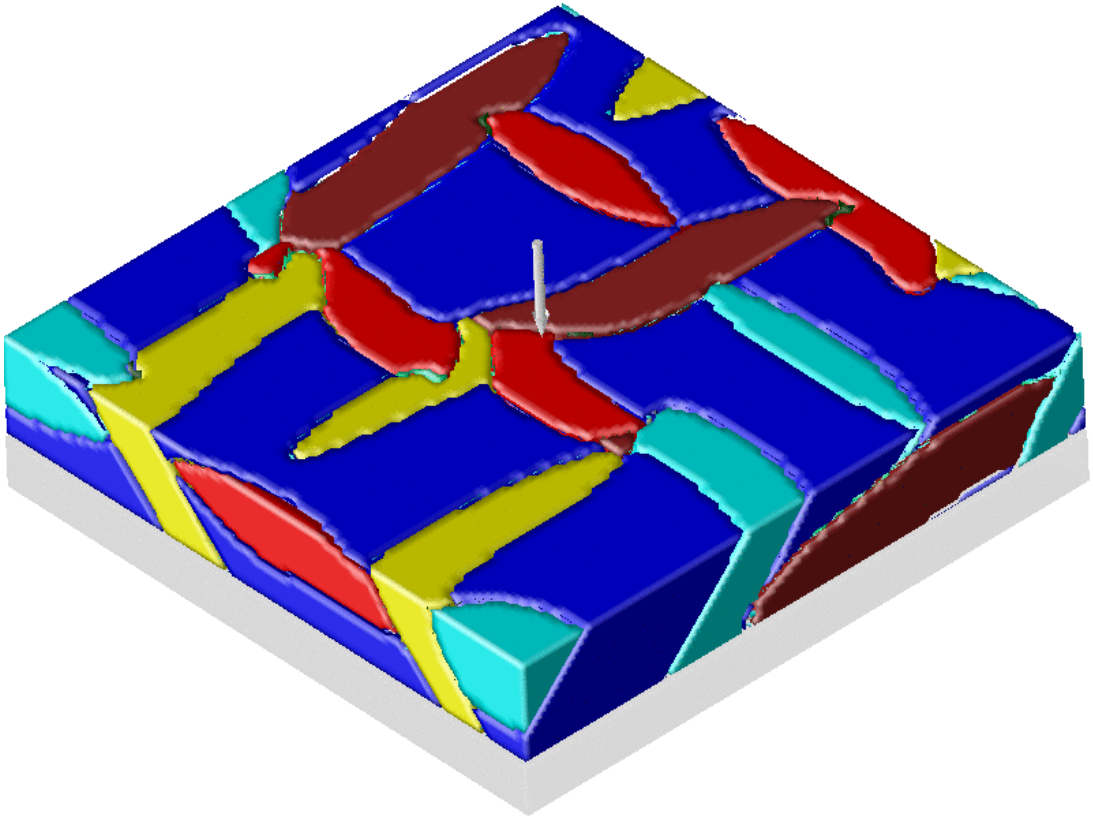
Is the process thermally activated?

Or is it intrinsic switching?

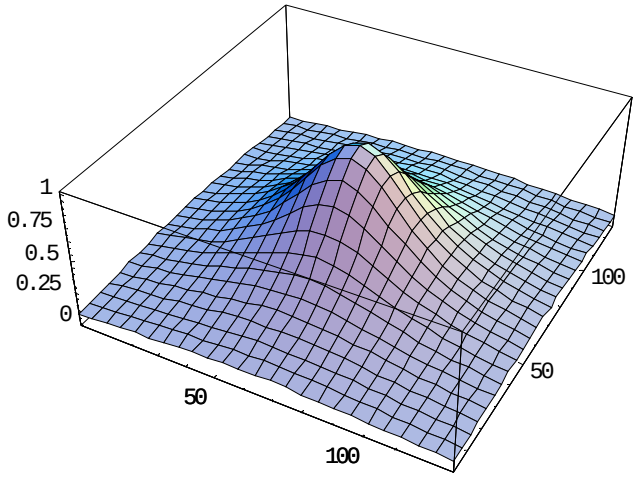
Phase-Field Modeling of Switching Phenomena

Long Qing Chen and Samrat Choudhury, Penn State

I. Generate domain structure using PFM



II. Apply tip potential on the top surface

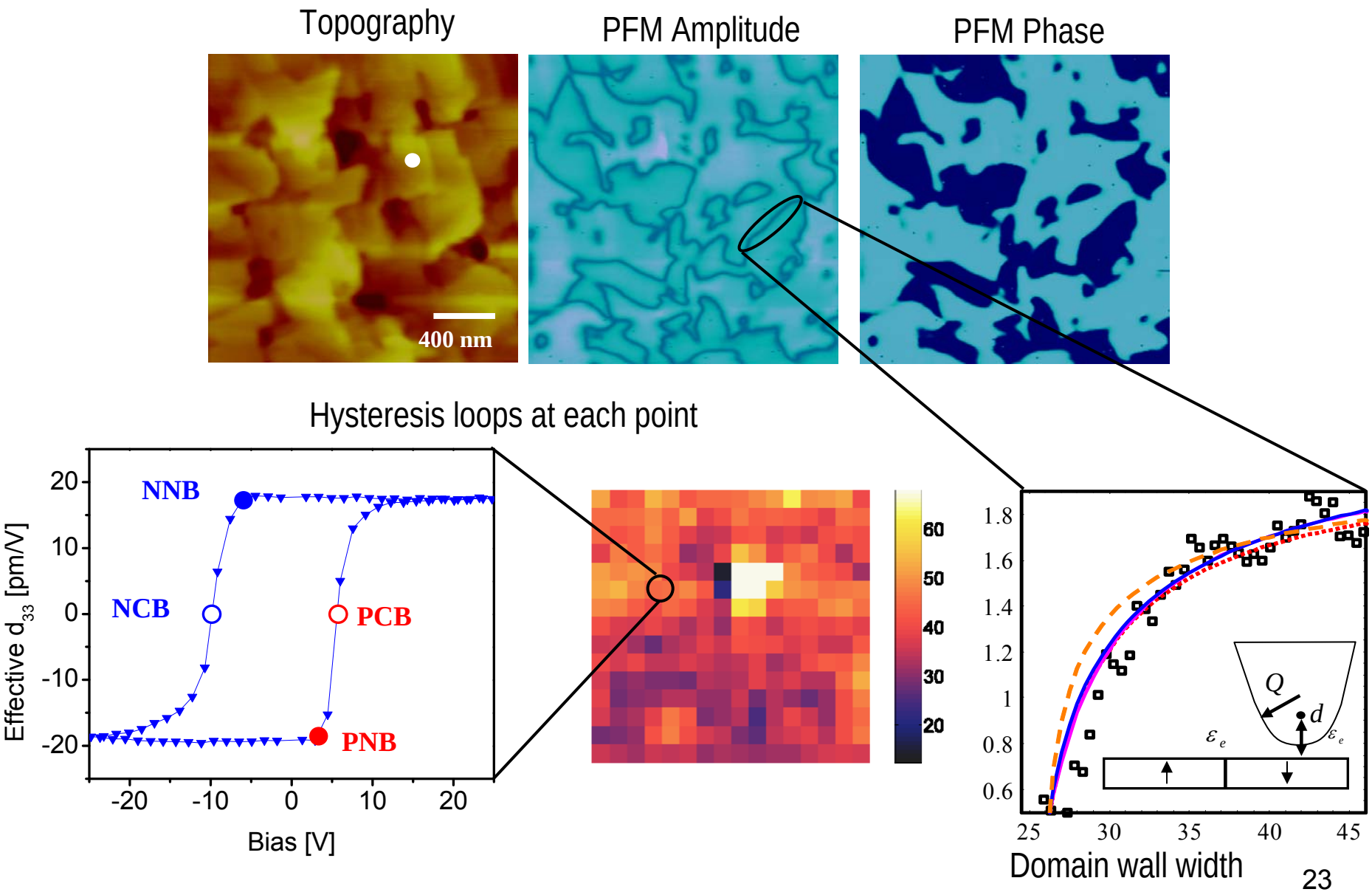


2-D Lorentz distribution

III. Increase potential and observe domain evolution

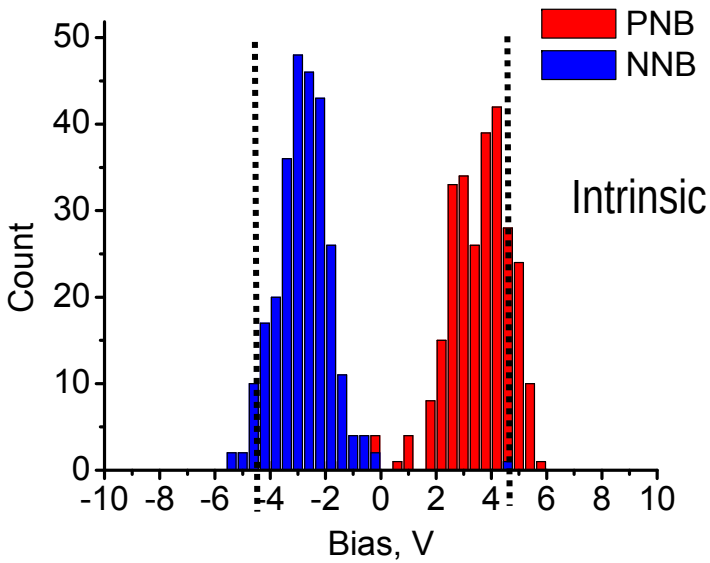
Switching in phase field theory is intrinsic (no temperature, no defects, no lattice).

Statistics of Nucleation Biases

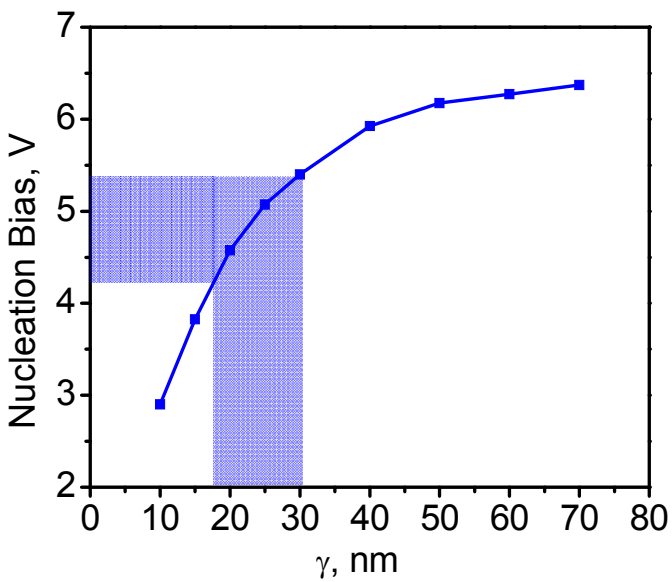


Phase-Field Modeling of Switching Phenomena

Switching in phase field theory is intrinsic (no temperature, no defects, no lattice).



Threshold	PNB	NNB	NVav
0.5%	3.2 ± 2.4	-1.2 ± 1.9	2.2 ± 2.1
3%	**3.7 ± 2.2**	**-2.8 ± 1.7**	**3.3 ± 2.0**
10%	4.1± 2.3	-3.6 ± 1.1	3.9 ± 1.7
Intrinsic	**4.6 ± 0.5**	**- 4.6 ± 0.5**	**4.6 ± 0.5**



- Tip size is determined self-consistently from measured domain wall width
- Phase field modeling is used to determine nucleation bias as a function of tip size
- The measured nucleation biases are ~70% of intrinsic (comp. to 10-100 smaller in capacitors)

In the absence of defects, nucleation in PFM is close to intrinsic!

Ferroelectrics are never perfect

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

Can we learn how they affect switching?

Landauer Paradox

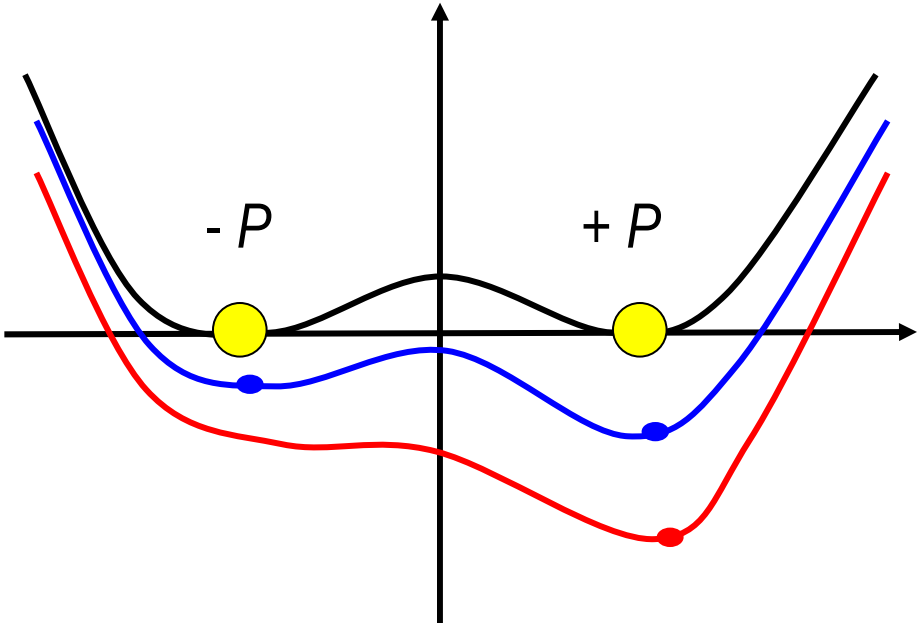
JOURNAL OF APPLIED PHYSICS VOLUME 28, NUMBER 2 FEBRUARY, 1957

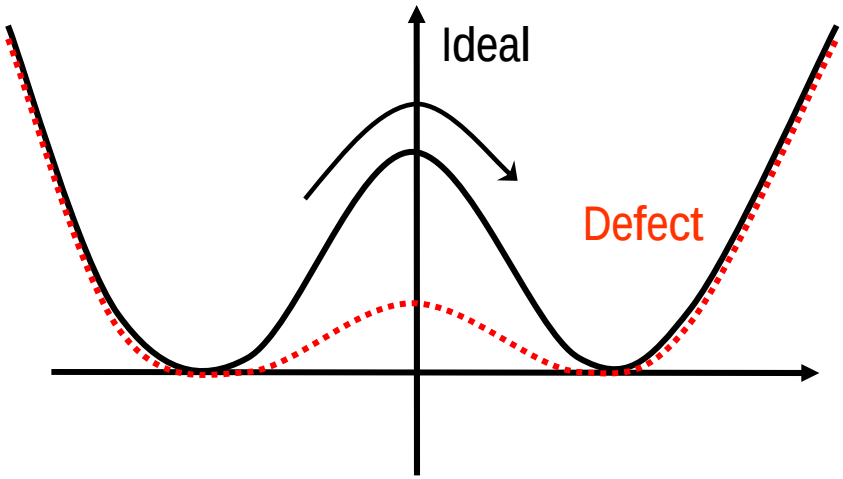
The results of this treatment combined with previous estimates of a domain wall energy of 7 ergs/cm^2 lead to a variation of nucleus energy with domain size which would permit only implausibly large domains to expand in the presence of a typical coercive field.

- 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

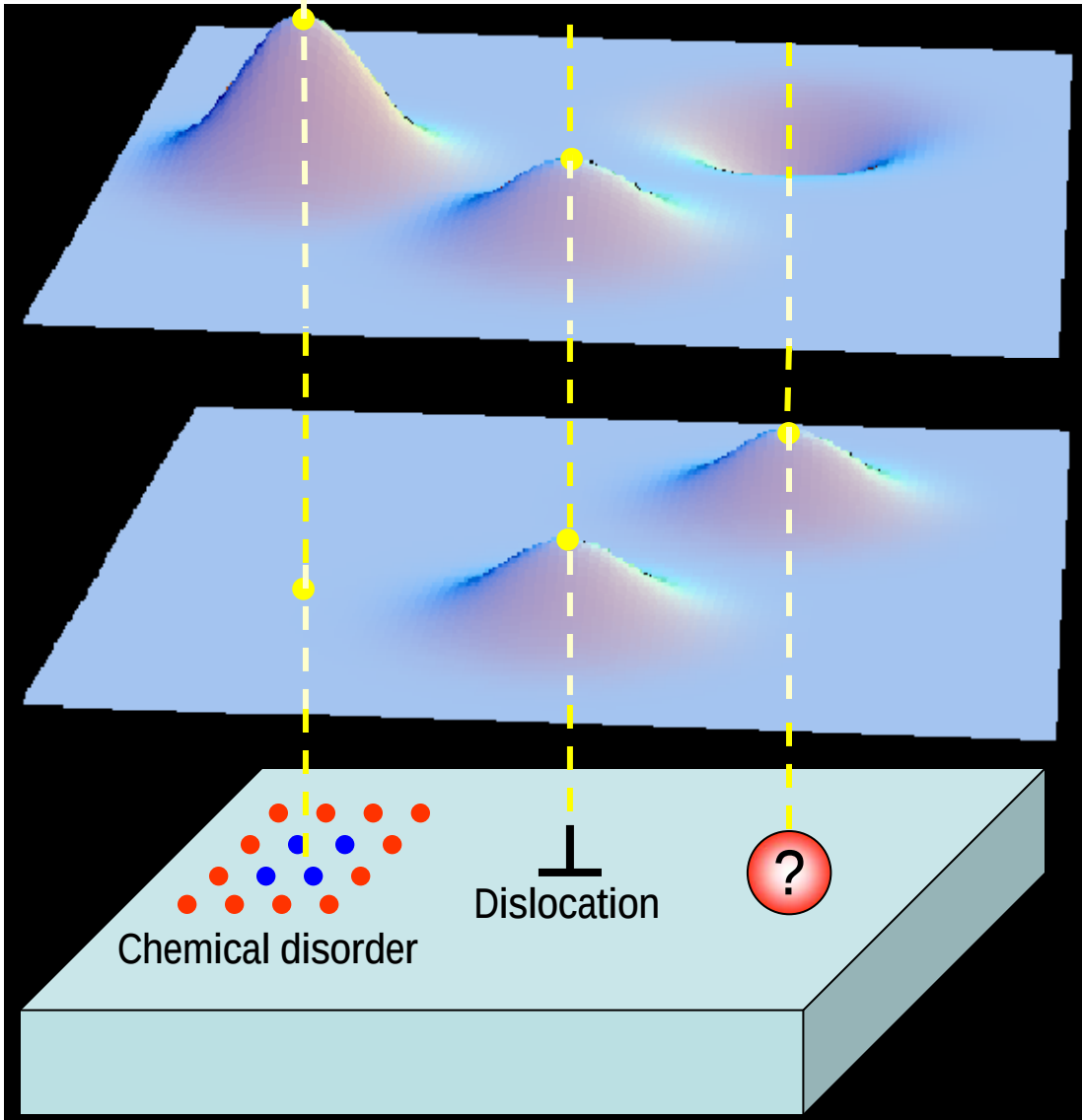
Bond disorder

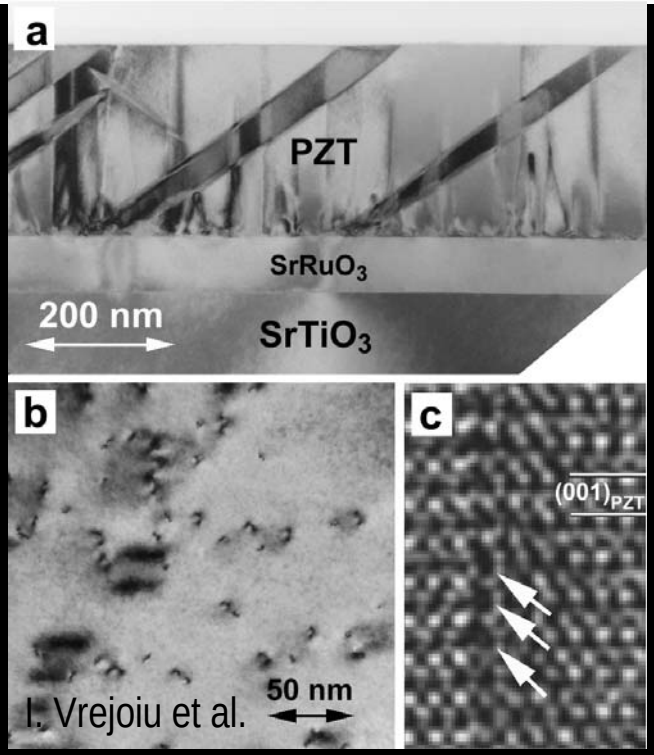
Preserves symmetry between equivalent states

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:

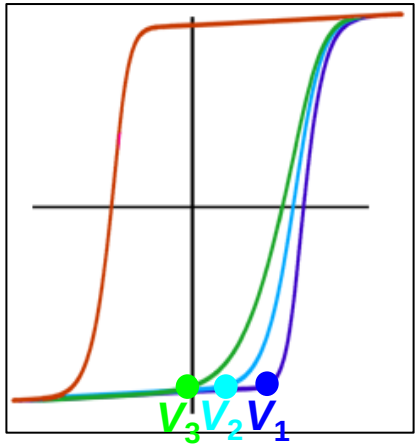
- Interfaces, and grain boundaries
- Dislocations
- Vacancies and vacancy clusters
- Dopant segregation

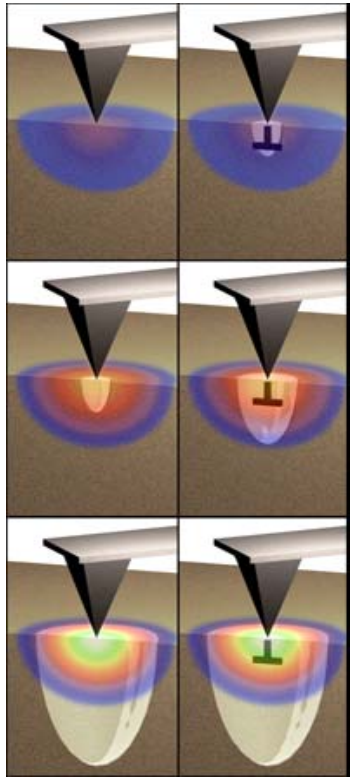
How can we study the role of defects on switching behavior?

Answer: one at a time!

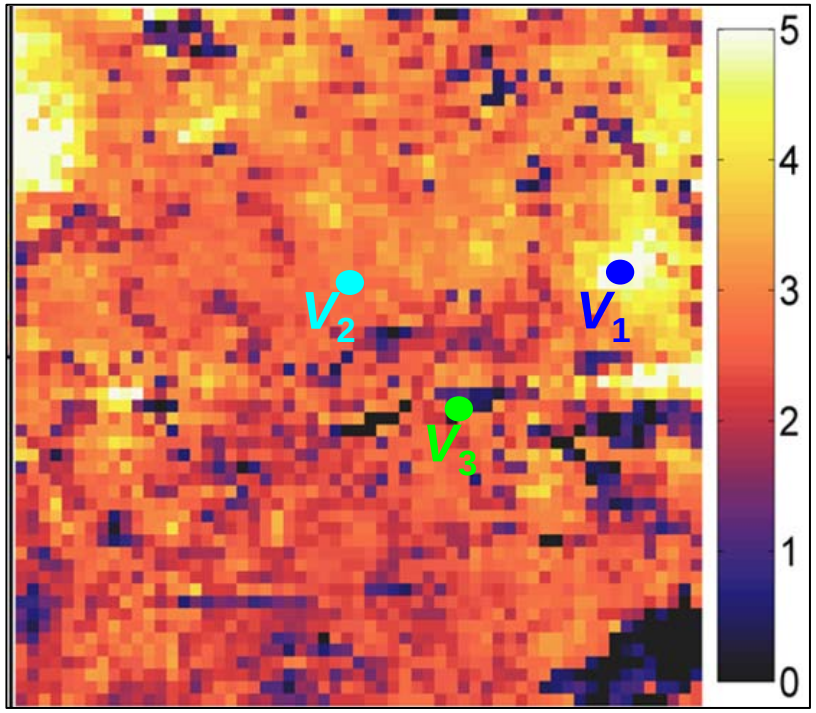
The hunt for the Snark: Imaging Nucleation Centers

- 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





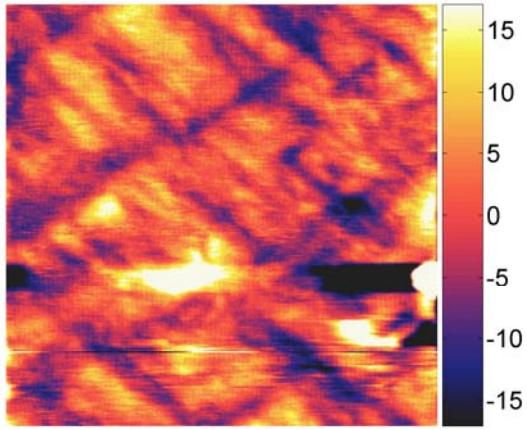
Map of Nucleation Bias



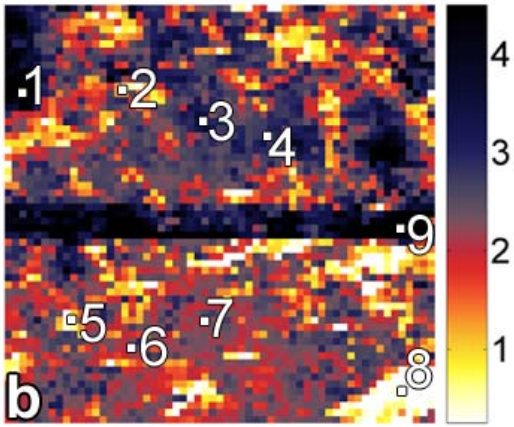
Local PFM nucleation bias maps yield information on spatial and energy distribution of switching centers

Nucleation Analysis in Epitaxial PZT Film

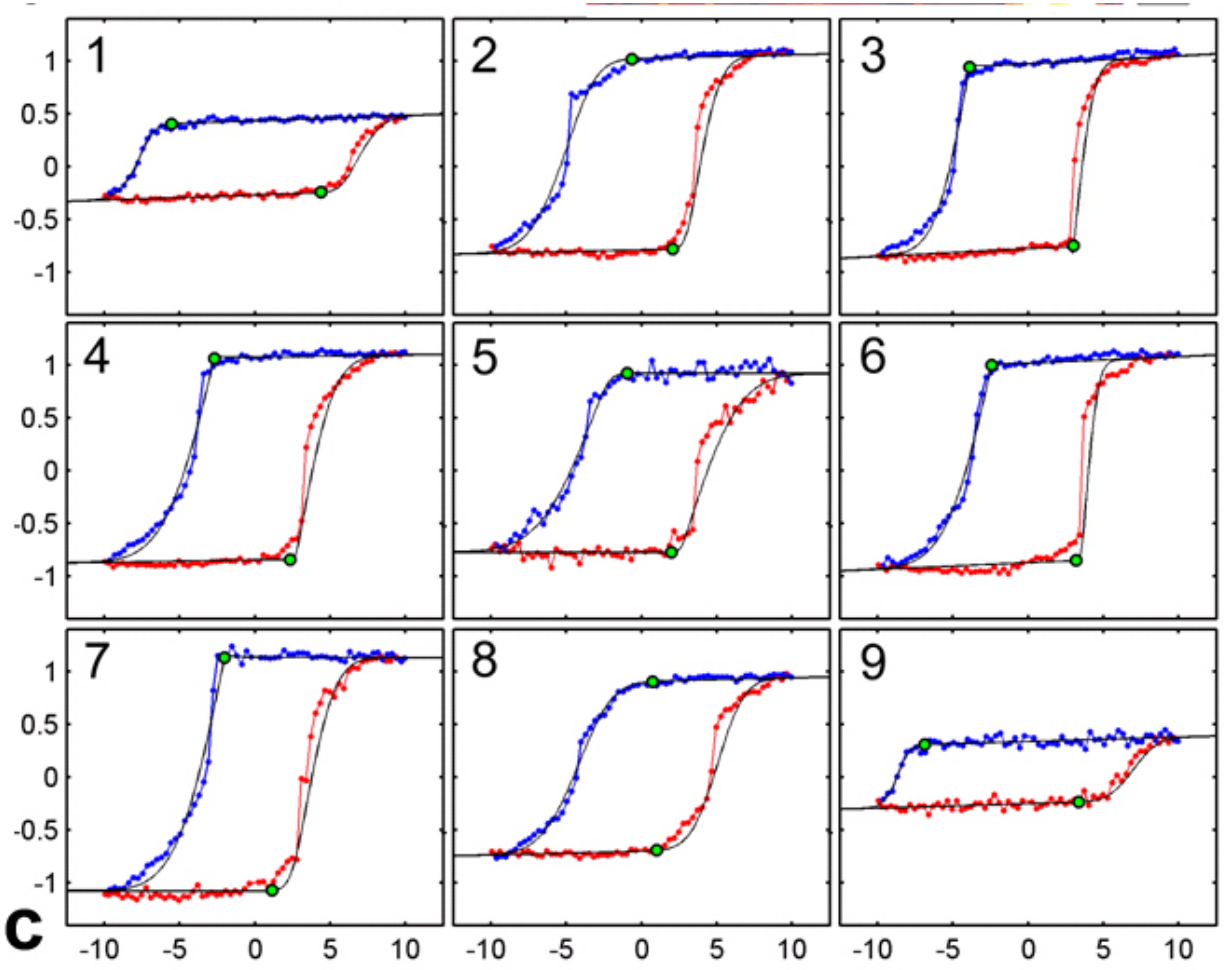
Topography



Nucleation bias map



Spatial Variability of Switching Behavior

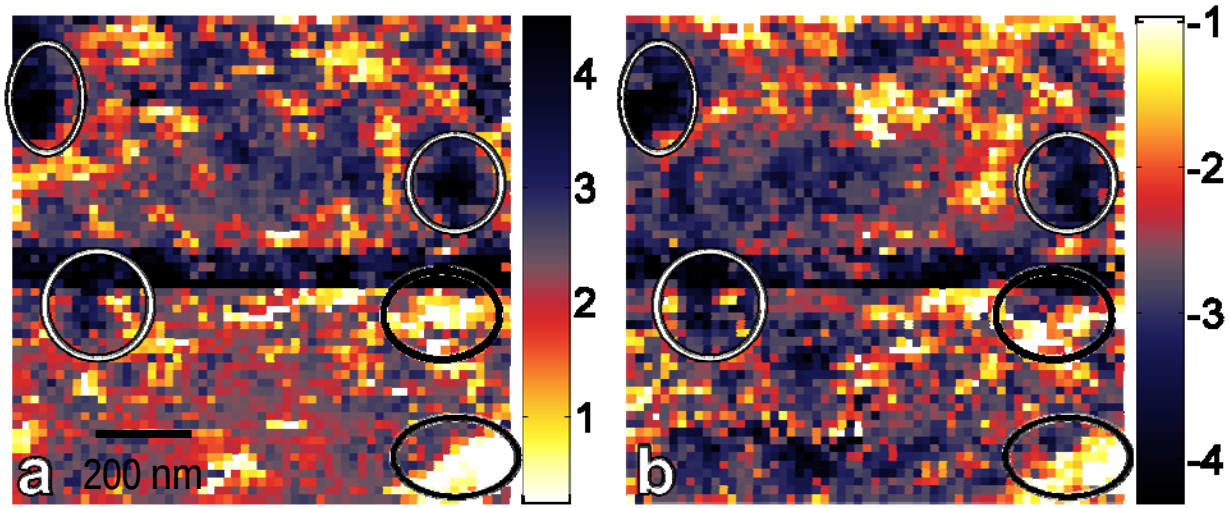


- SS-PFM yields 64x64x256 data array (4-6 hour acquisition), 10,000 hysteresis loops
- Strong variability of switching behavior between different points

Nucleation Center Mapping in High-Defect Density PZT film

Positive nucleation bias

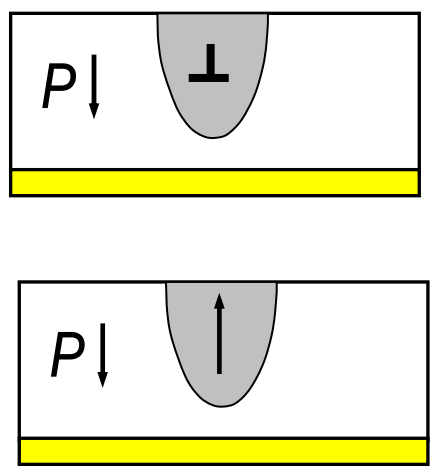
Negative nucleation bias

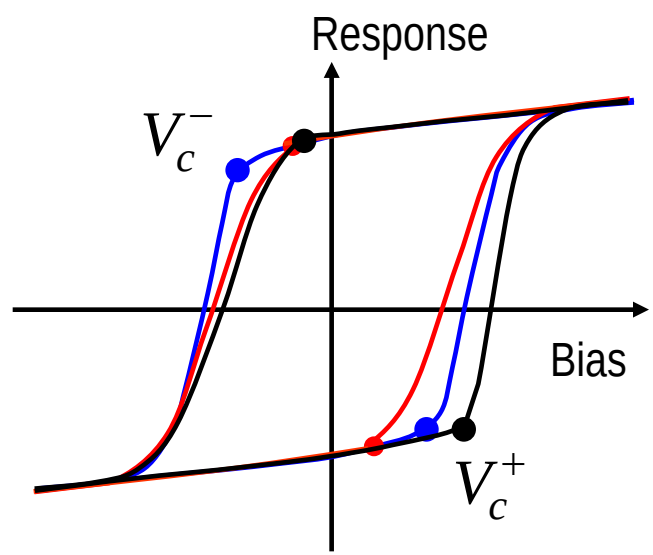


Defect classification based on free energy:

Defect Type I (symmetric)
- lowered wall energy
- lowered depolarization energy
- dead layer/poor contact

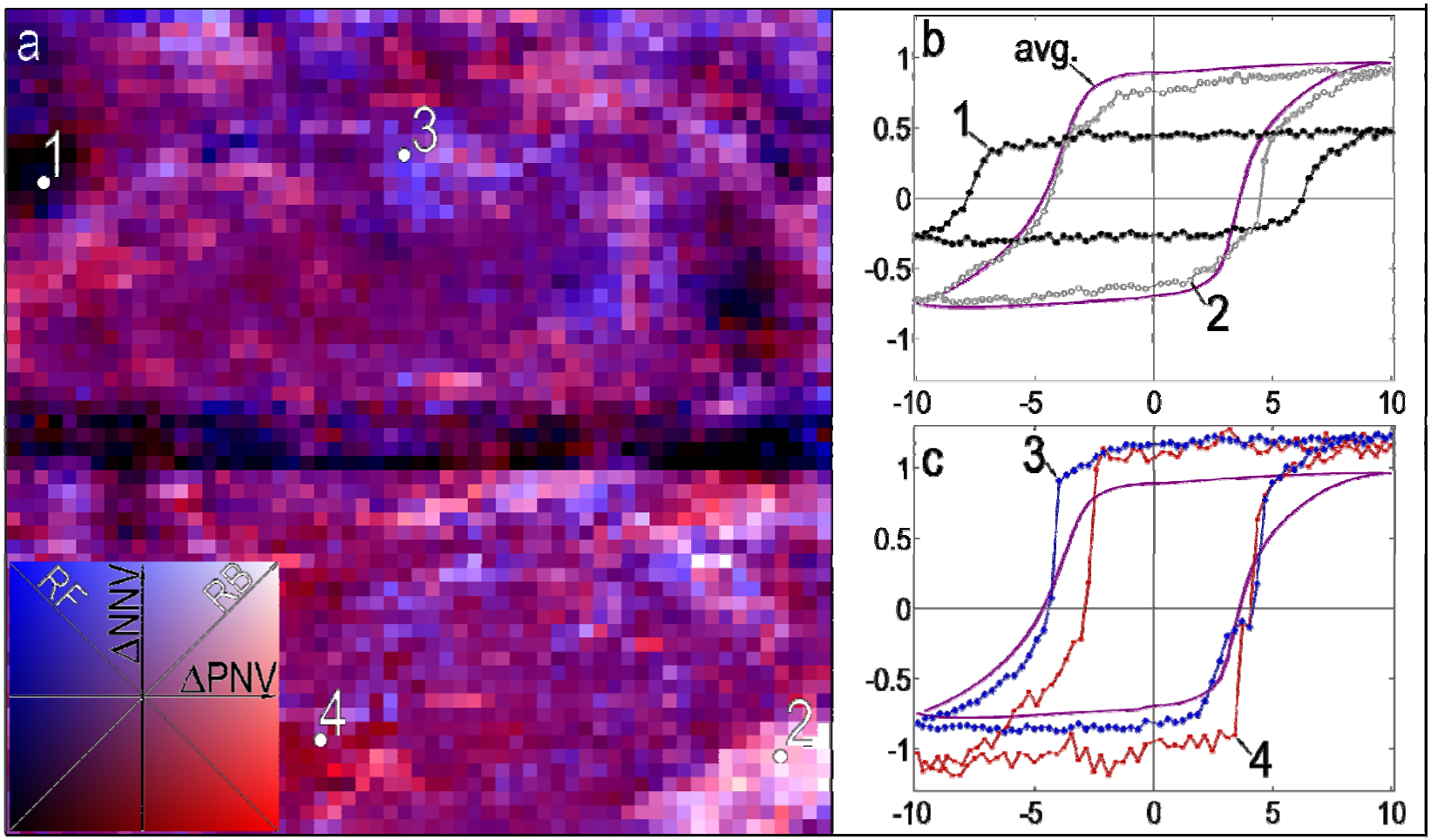
Defect Type II (antisymmetric)
- local charge
- "frozen polarization"





I. Vrejoiu, G. Le Rhun, N. D. Zakharov, D. Hesse, L. Pintilie and M. Alexe, Phil. Mag. 28, 4477 (2006).
I.Vrejoiu, G. Le Rhun, L. Pintilie, D. Hesse, M. Alexe and U. Gösele Adv. Mater. 18,1657 (2006).

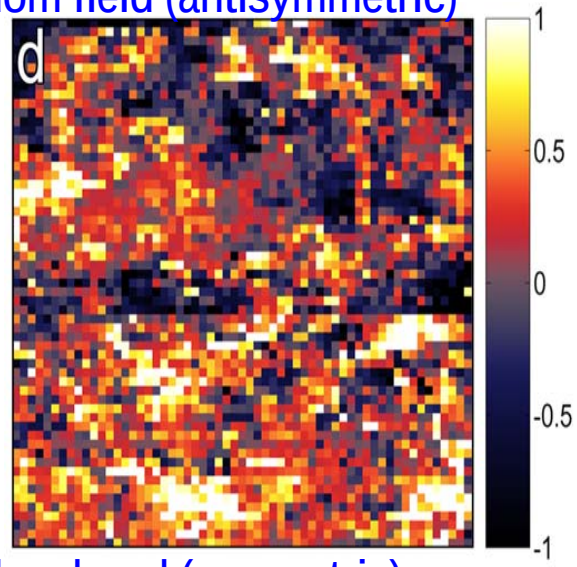
Mapping Disorder Potential Components



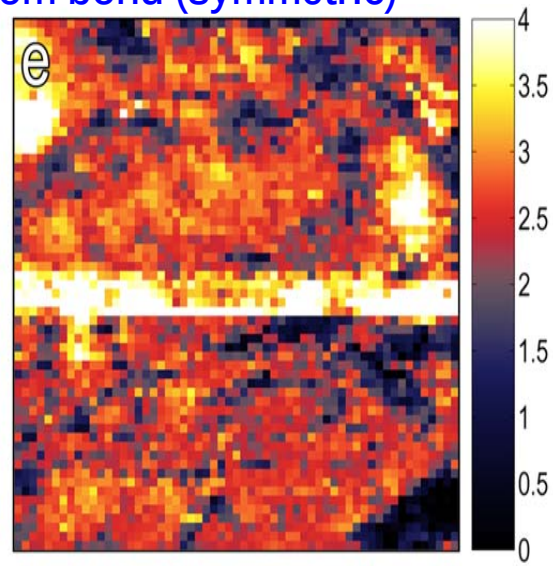
Random bond and random field disorder potential components are mapped independently

Mapping Switching Dynamics

Random field (antisymmetric)

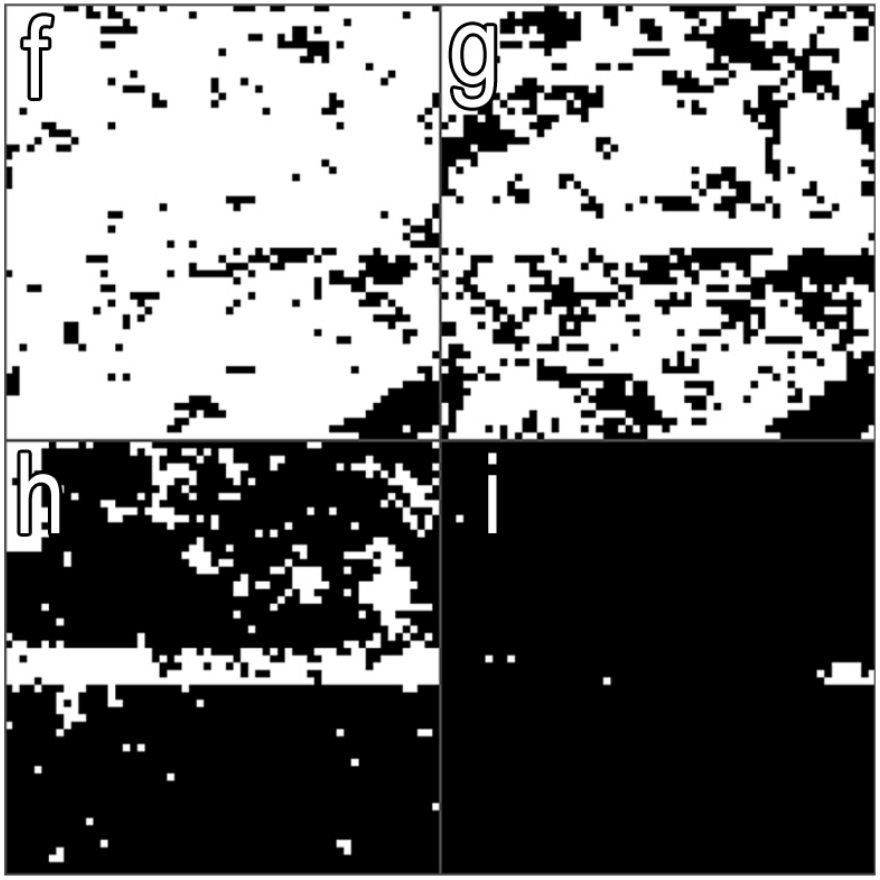


Random bond (symmetric)



Bias = 1 V

Bias = 3 V

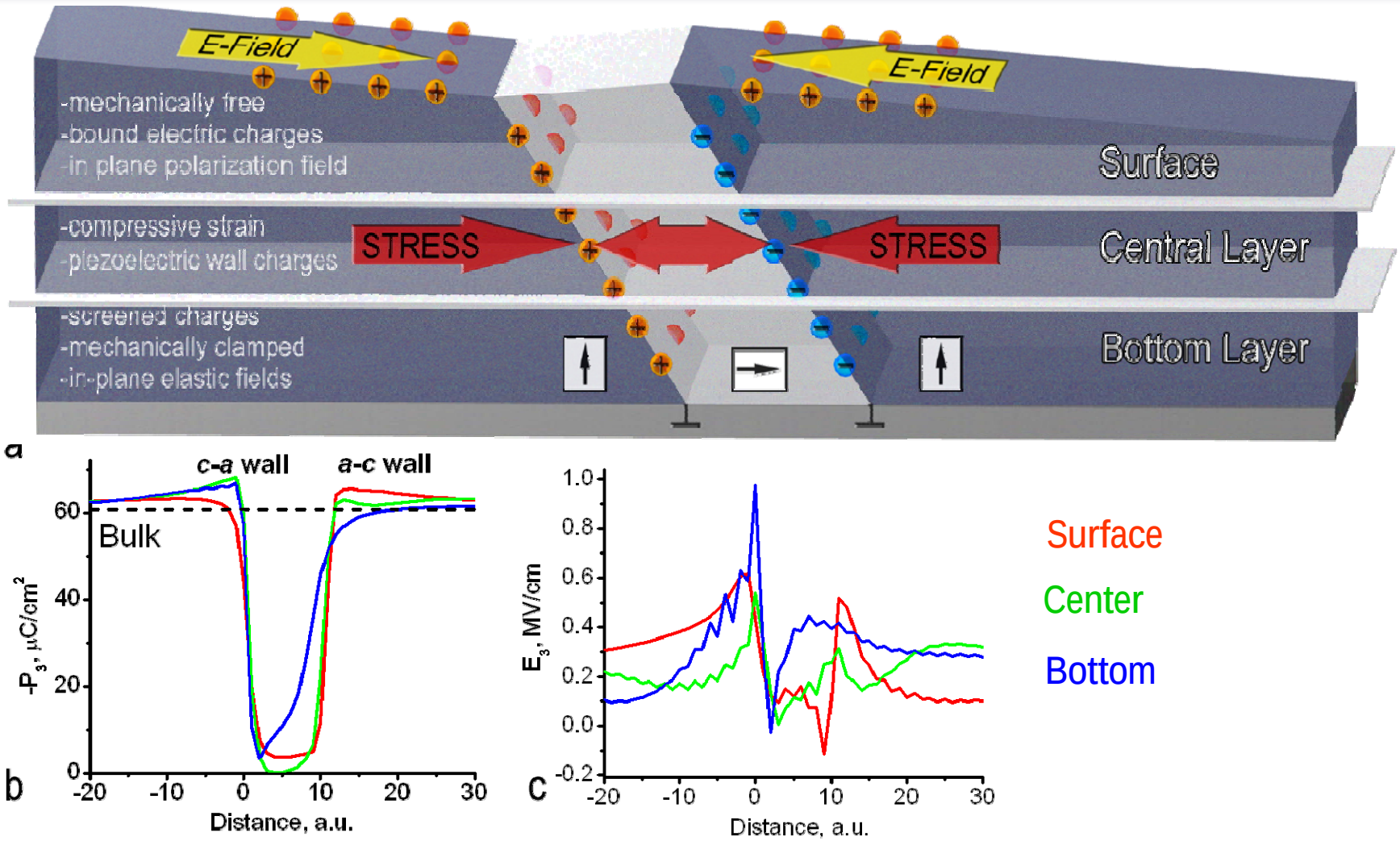


Bias = 7 V

Bias = 10 V

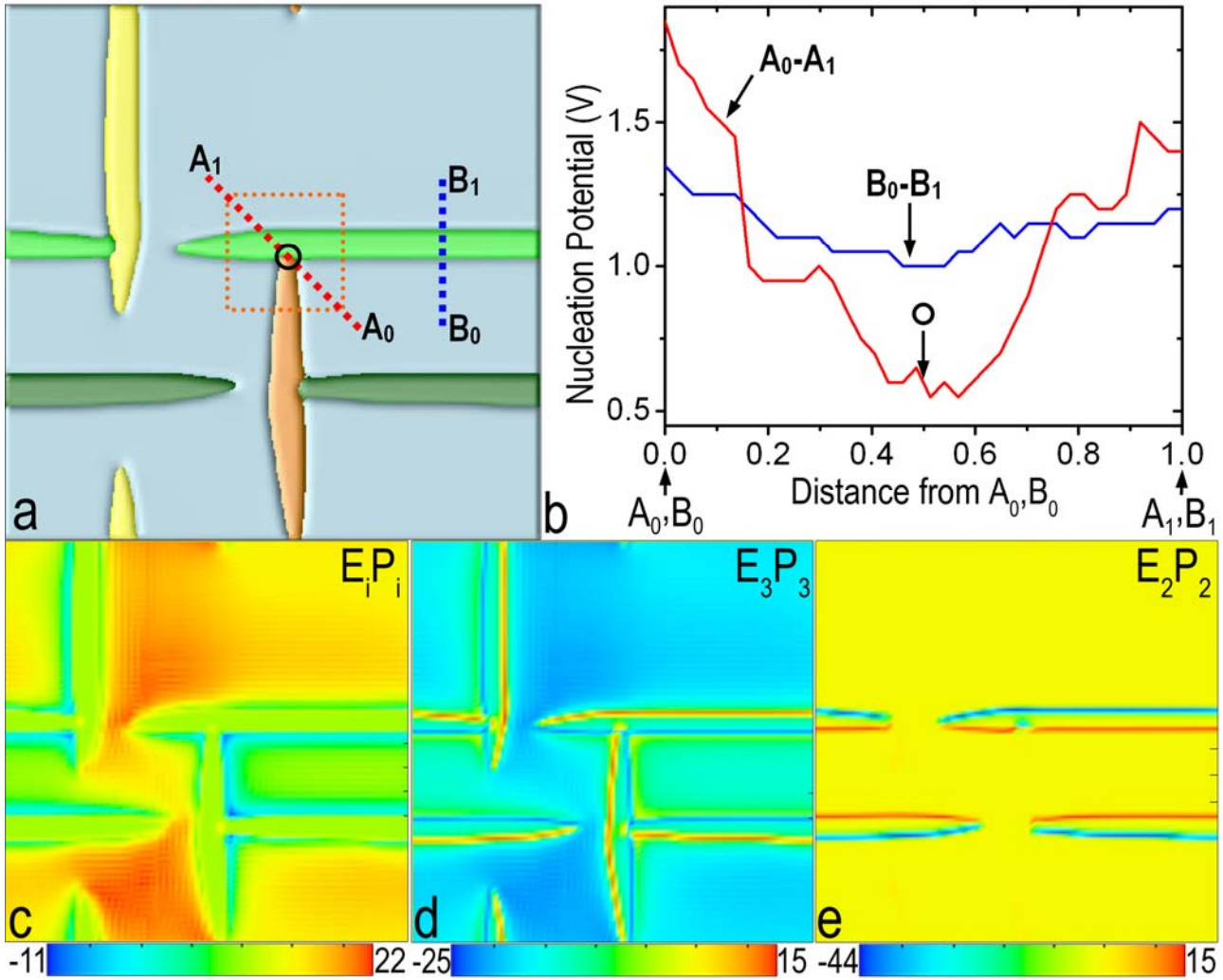
- Capacitor experiment shows preferential sites
- SS-PFM probes propensity for switching at each site

Mapping Switching Dynamics



- Phase field modeling provides the information on the electrostatic field structure and polarization distribution within the field: strain, interface, and surface effects at once.
- Area with highest E_3 act as a nucleation site in a uniform field.

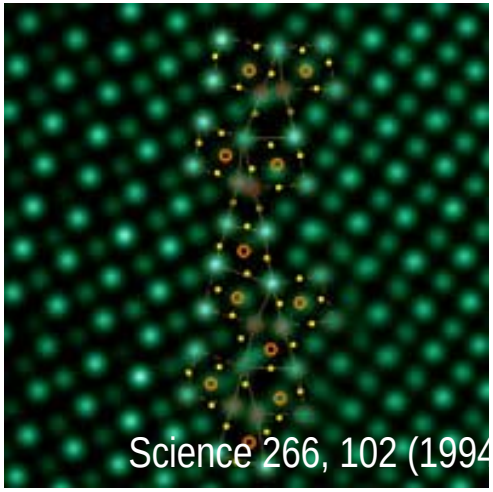
Mapping Switching Dynamics

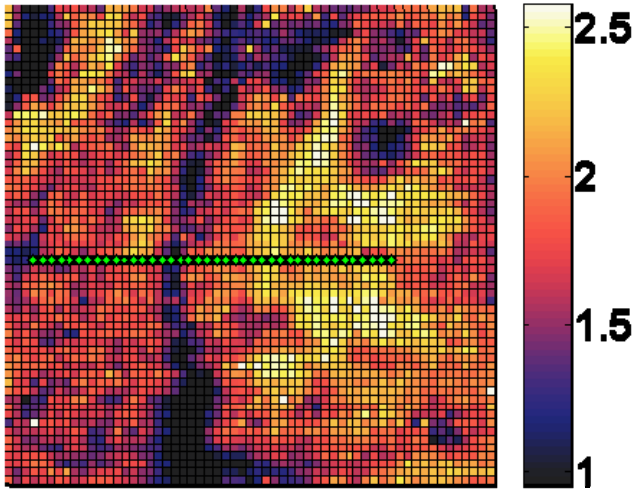


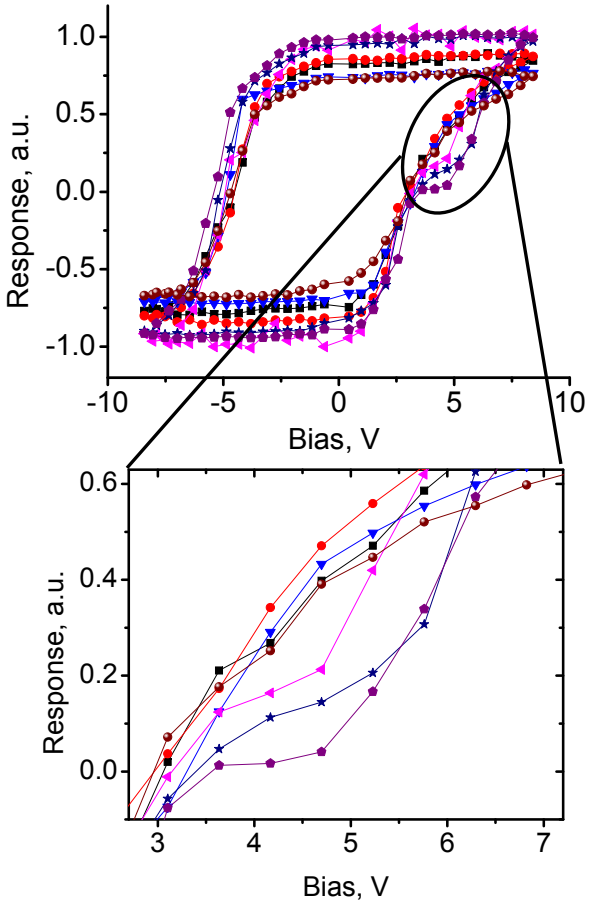
- Domain structure affects nucleation bias
- Realistic model yields 2 V for defect free place (comp. 3 V experimentally)
- And ~ 0.5 V for a1-a2 domain junction

Engineered Defect Structures: First Results

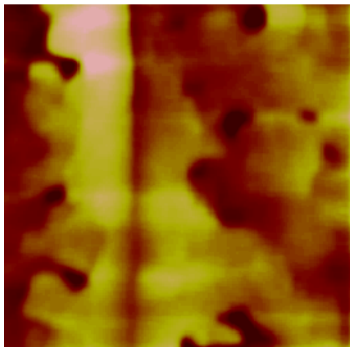
Model systems: ferroelectric thin films grown on grain boundaries in bicrystals



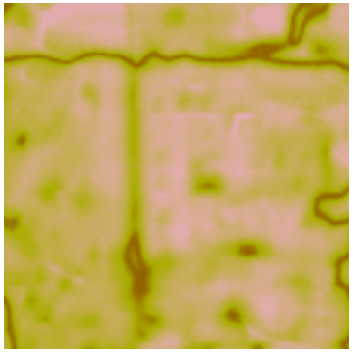




Topography



Amplitude



Phase

Towards atomistic understanding of polarization switching mechanisms

Hysteresis Loop Fine Structure

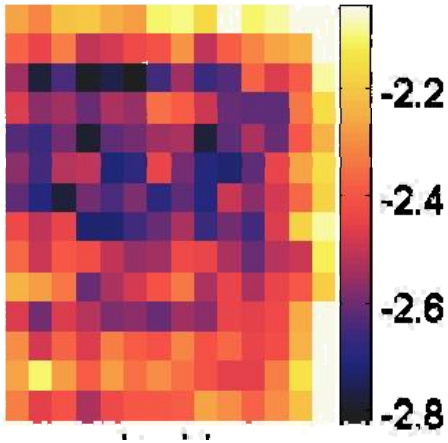
Anomalies are good things.

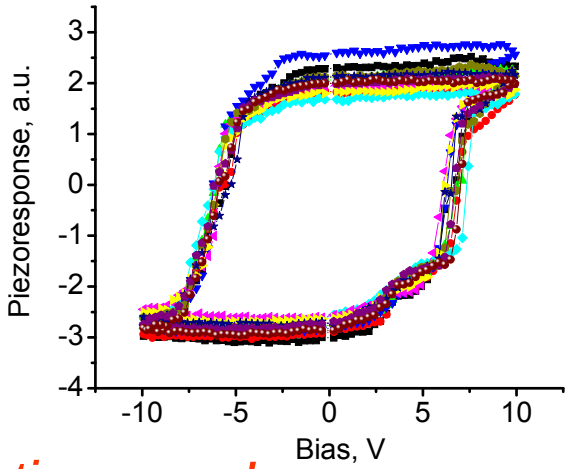
We like anomalies.

Anomalies always tell us something new about the patient!

(hit TV show)

Anomalies are reproducible (256 loops at 1 nm step)

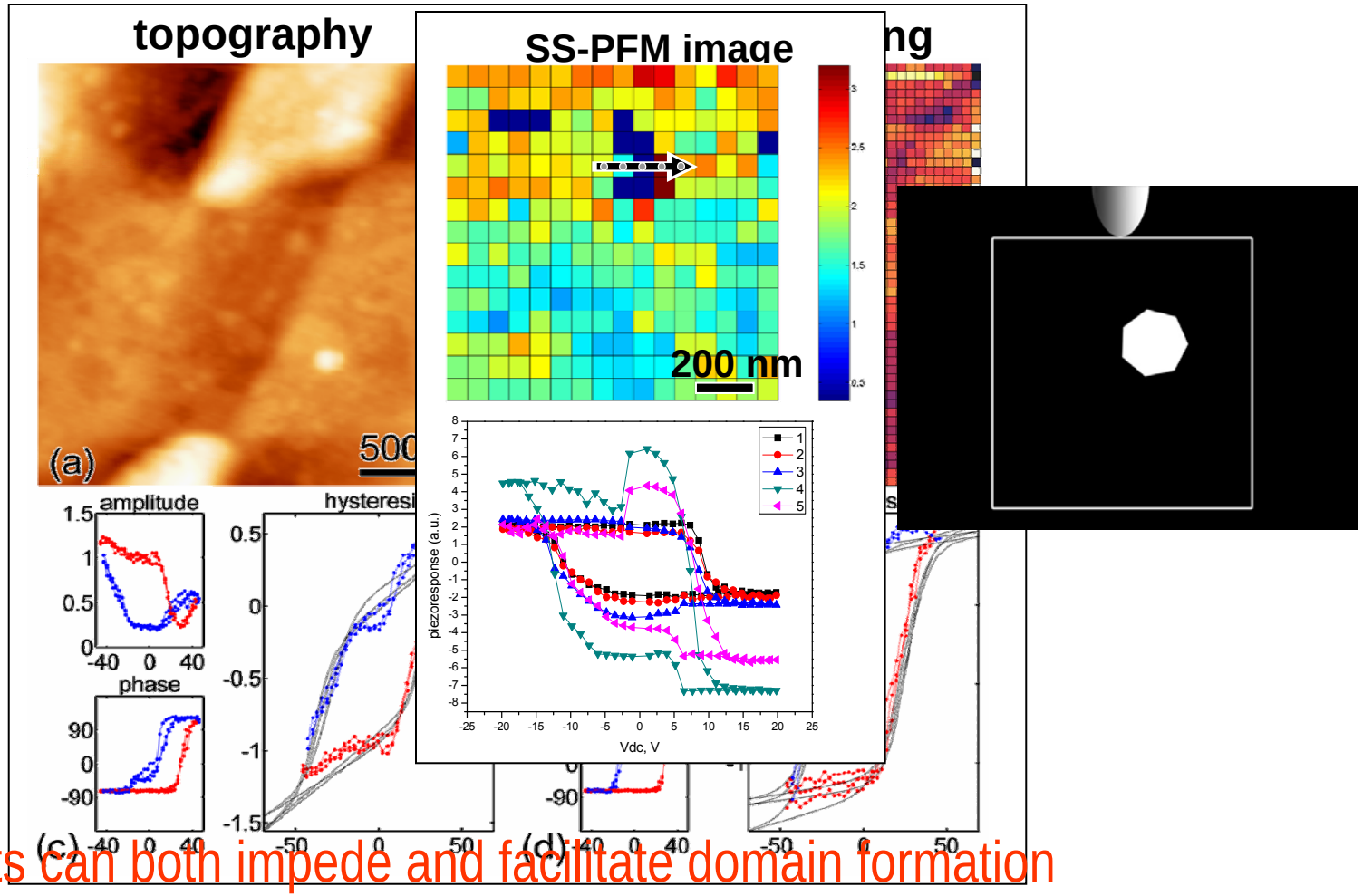




Local polarization switching is deterministic process!

Hysteresis Loop Fine Structure

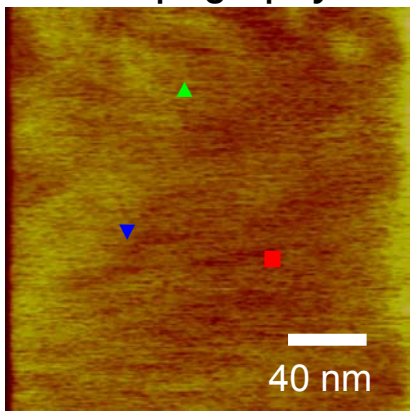
- Hysteresis loop shape is normal until the tip is near a defect
- Work of switching and loop shape near a defect reveals interactions between the growing domain and the defect



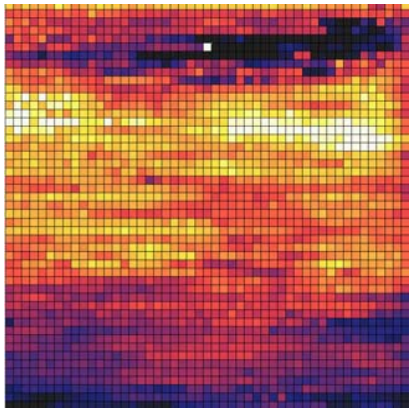
Defects can both impede and facilitate domain formation

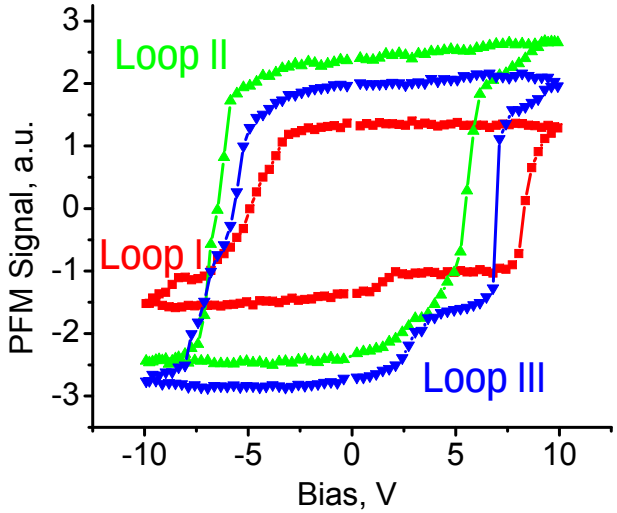
Hysteresis Loop Fine Structure

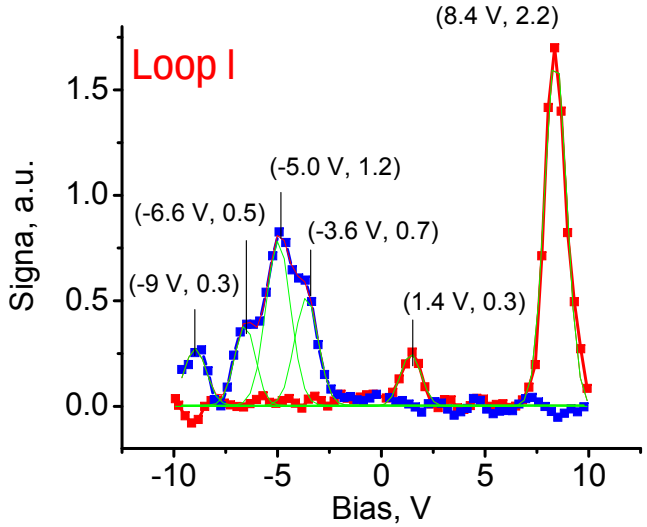
Topography

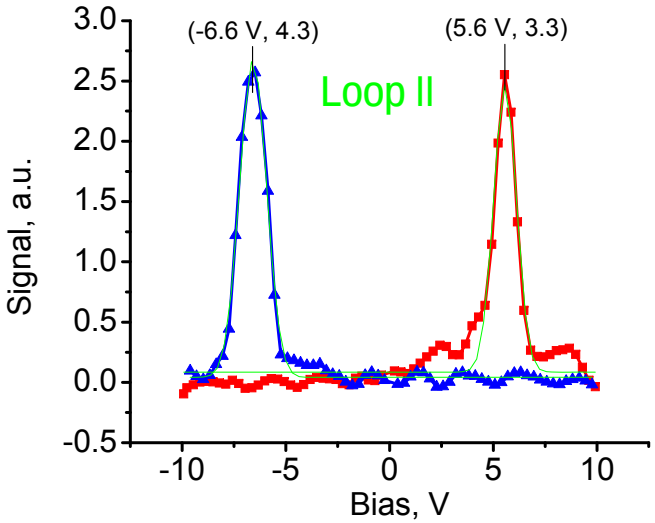


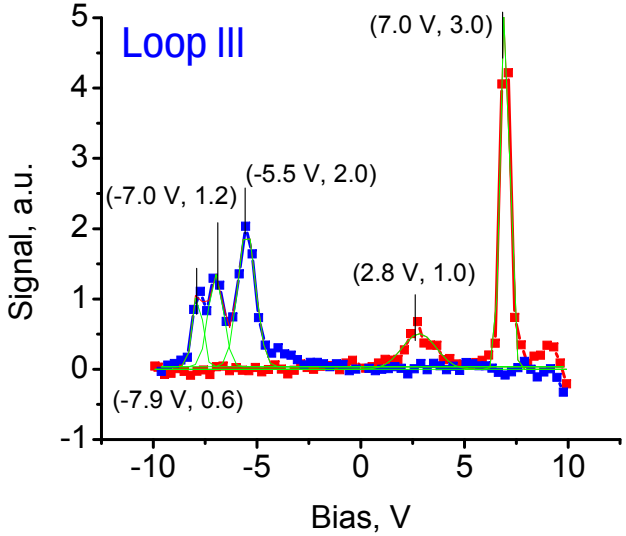
Nucleation bias map







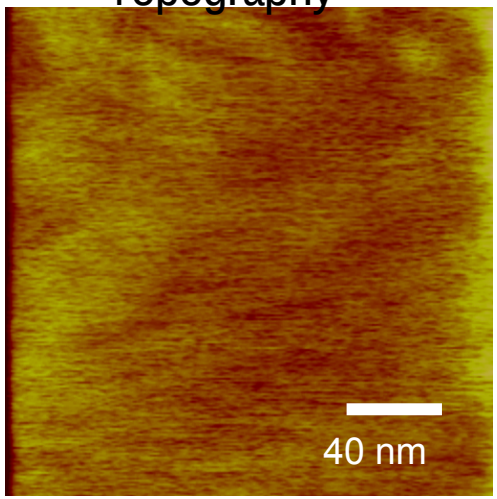




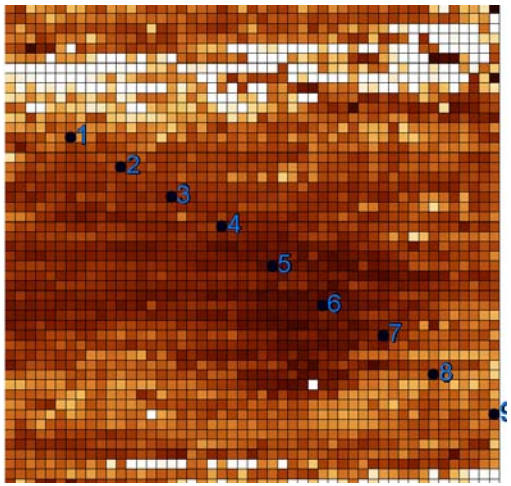
- Hysteresis loops have pronounced fine structure: discrete number of discernible events!
- Are these signatures of domain-defect interactions?

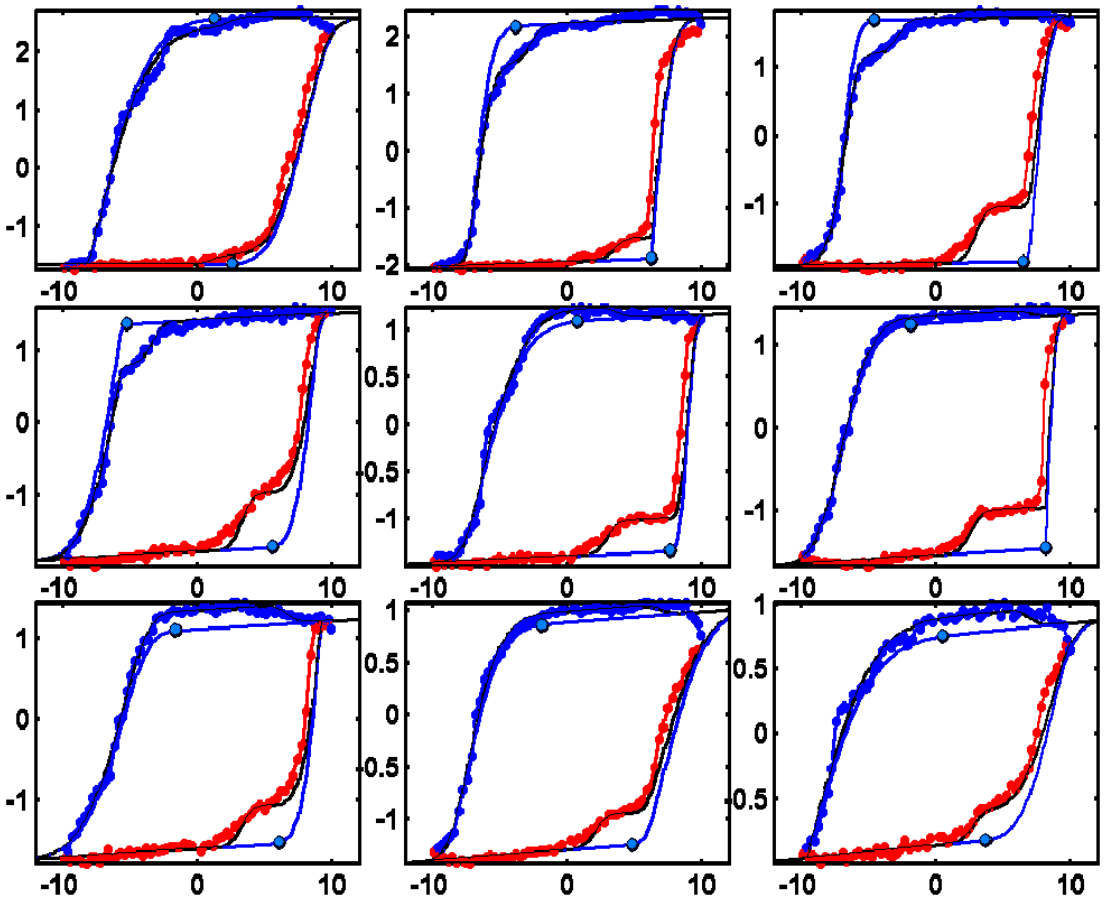
Spatial Variability of Loop Fine Structure

Topography



Nucleation bias map

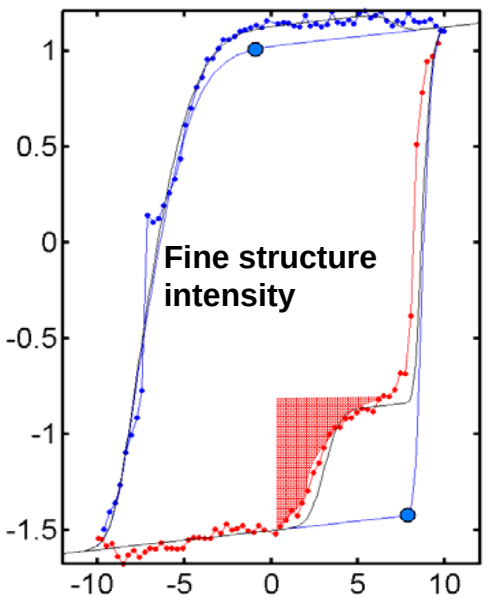




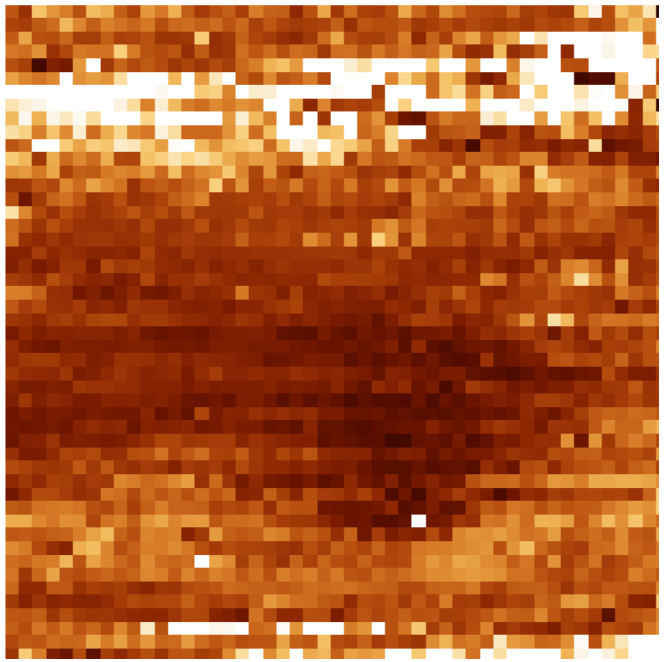
- The fine structure evolves systematically along the surface

Spatial Variability of Loop Fine Structure

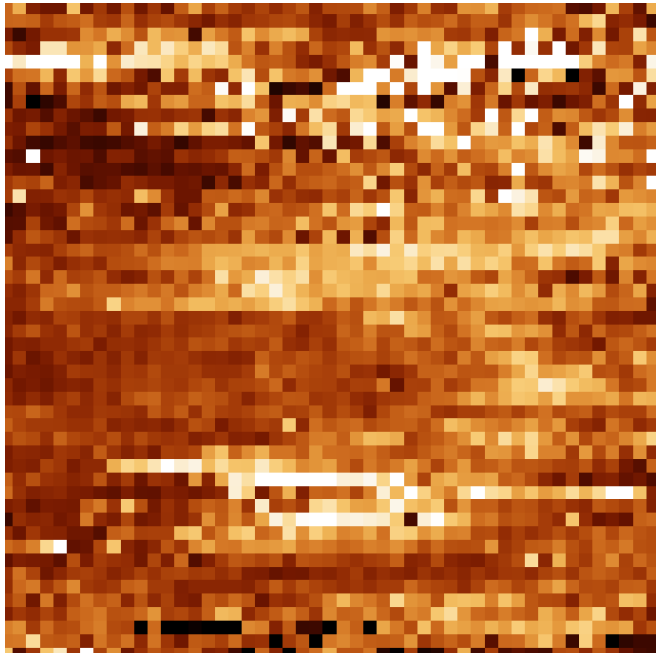
Hysteresis loop



Nucleation bias map



Fine Structure Intensity Map

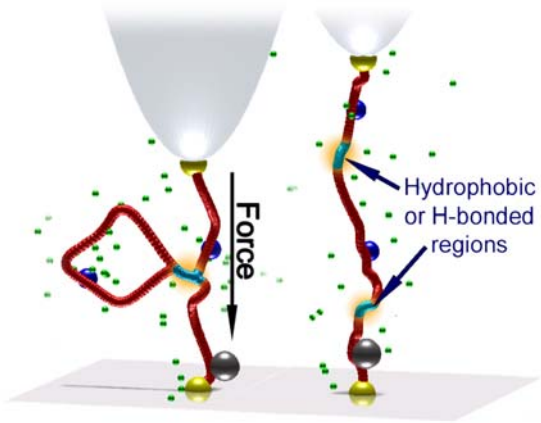


- Behavior consistent with a single defect signature
- Defect size is ~ 40-50 nanometer, likely limited by resolution
- A threading dislocation?

Future: Defect Effect on Local Phase Transitions

Force-Induced Transitions

Unfolding spectroscopy

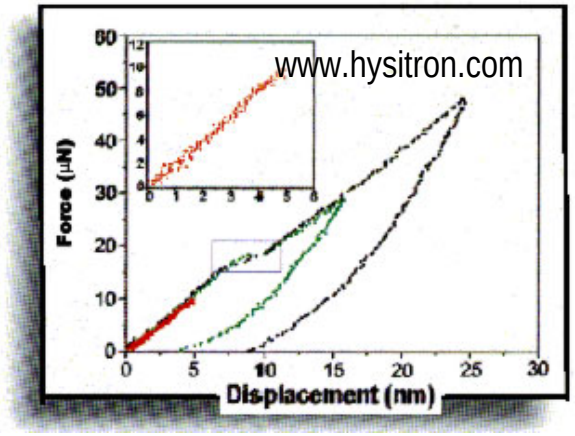


- Energies ~ kT: stochastic
- Reversible
- Only one parameter measured
- Need molecule hunting

Single-molecule reactions

- Thermodynamics
- Kinetics
- Statistical physics

Nanoindentation

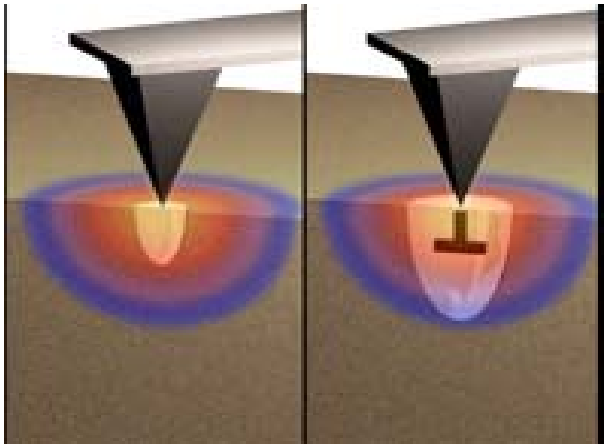


- Energies >> kT: deterministic
- (partially) Irreversible
- Only one parameter measured
- Strongly invasive

Nanomechanics

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

Bias-induced transitions



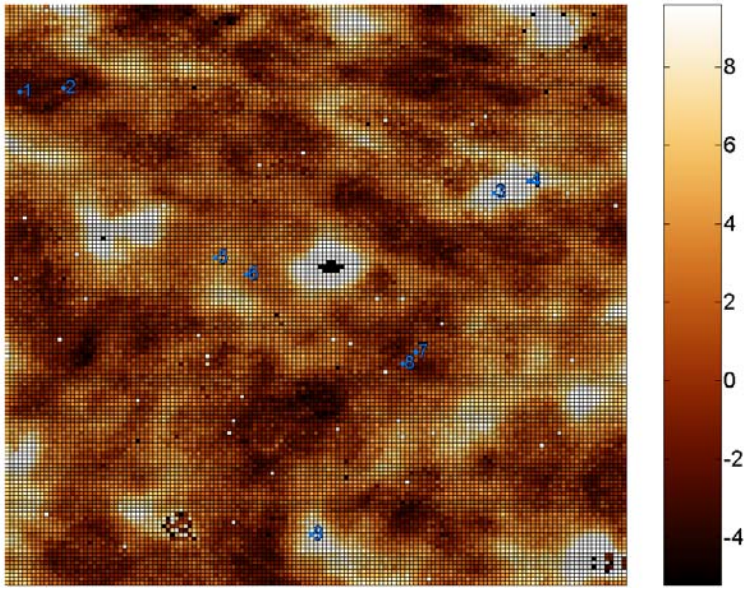
- Energies either >> kT or ~kT
- Can be reversible
- Many parameters can be measured

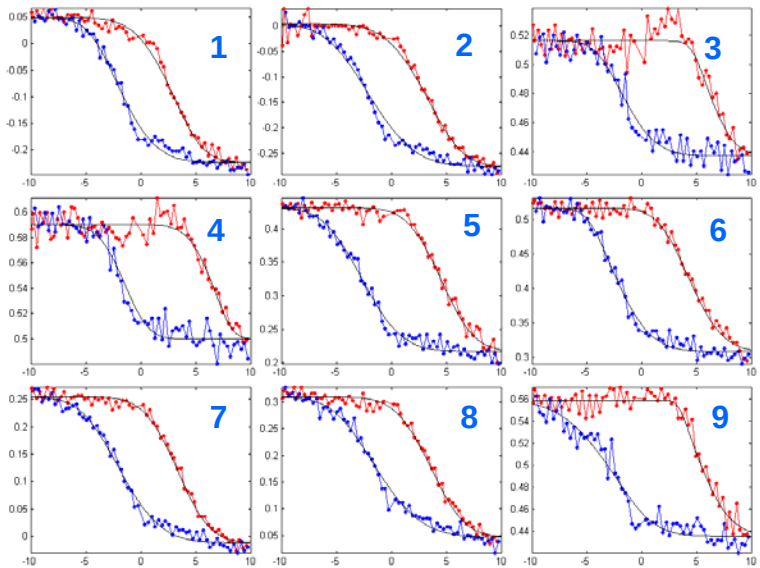
Nanoelectromechanics

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

Enabling tools in nanobiology and nanomechanics

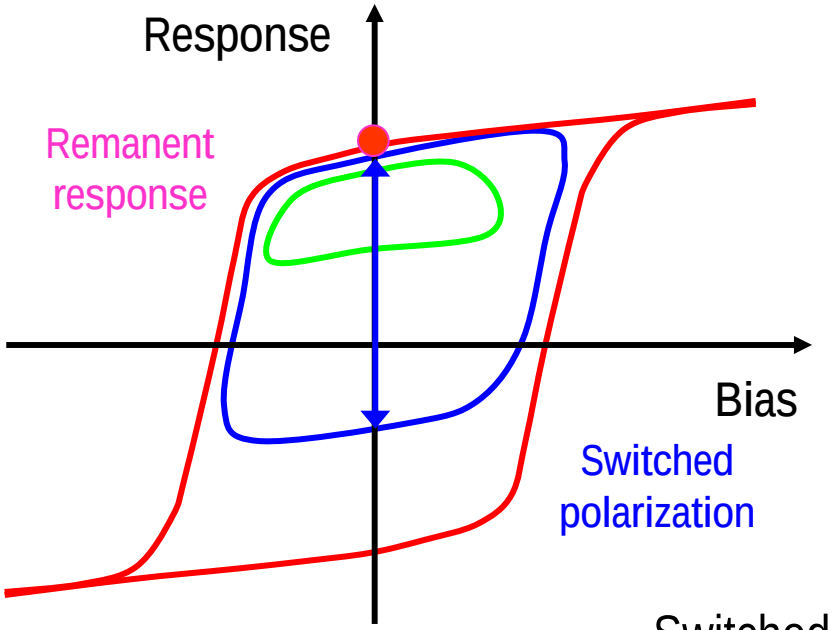
SS-PFM of Capacitor Structures



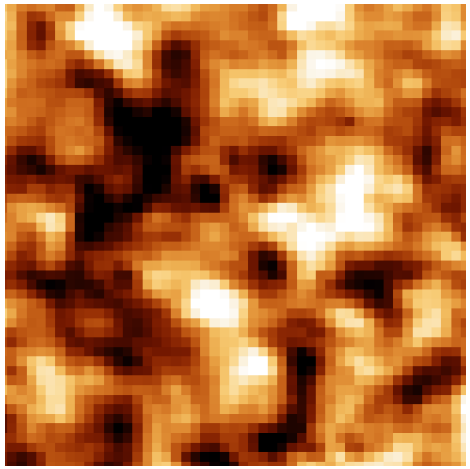


- Variability of switching behavior between different points
- 2D maps of loop parameters
- Very high resolution: 128x128x128 data points in 3D array
- Noticeable internal distribution of switching behaviors in capacitor

SS-PFM of Capacitor Structures

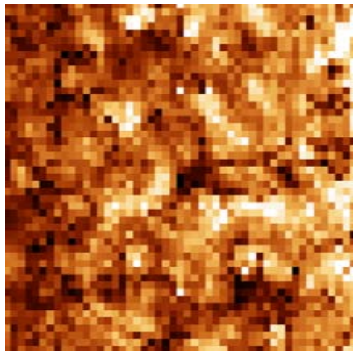


Remanent Response

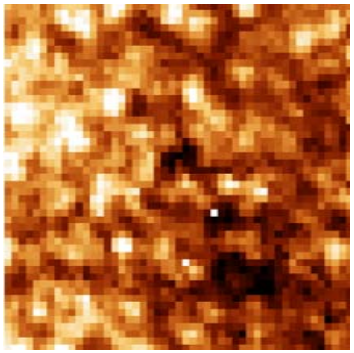


Switched Polarization

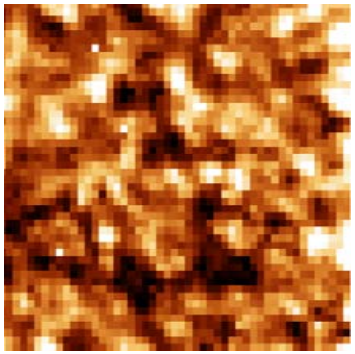
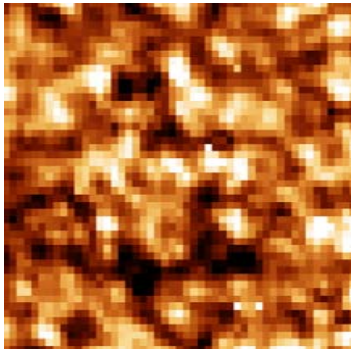
3 V



6 V



9 V



12 V