Principles and Applications of Piezoresponse Force Microscopy

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Outline

- **Introduction**
  Ferroelectrics and scanning force microscopy

- **Piezoresponse Force Microscopy**
  Principles, elementary theory

- **Technical aspects of PFM**
  Electromechanic vs electrostatic effect
  Vertical vs lateral imaging
  Local vs global excitation

- **PFM and Extrinsic effects**
  Materials properties and data interpretation
  Surface contamination,cross-talk, tip artifacts

- **Summary**

Historical Remarks

1986 **Invention of the atomic force microscope (Binnig, Quate and Gerber)**

1989 **Quate suggested the use of SFM for imaging of ferroelectric domains**

1990 **First observation of 180º domain walls in GMO crystal by noncontact SFM (Saurenbach and Terris). Resolution is 5 µm**

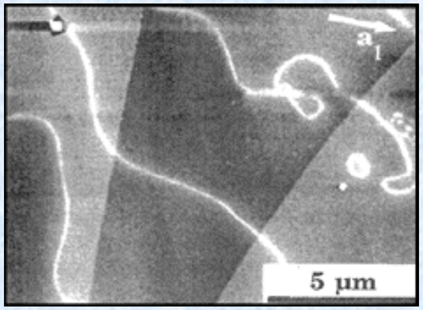
1992 **Imaging of poled regions in PvDF films (Guethner and Dransfeld)**

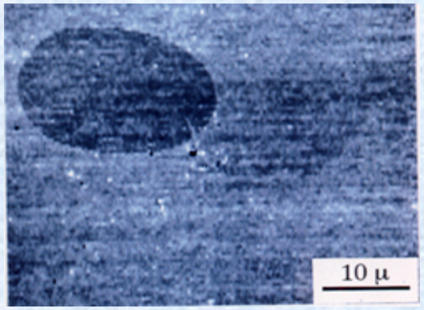
1993 **First *nanoscale* observation of 180º domain walls in a GASH crystal by noncontact SFM (Luthi)**

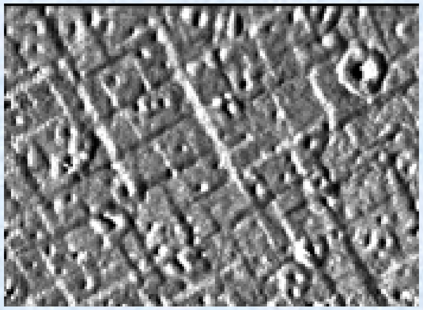
1994 **First nanoscale observation of as-grown domains in PZT thin films (Gruverman)**

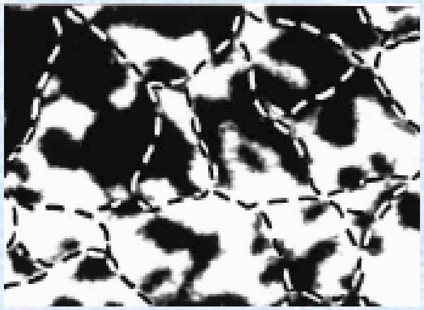
1998 **PFM switching in nanoscale ferroelectric structures (Alexe)**

2002 **Delineation of optimum imaging in PFM (Kalinin)**



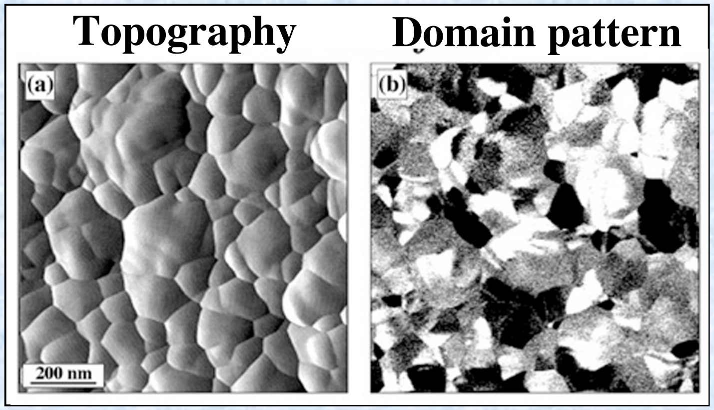




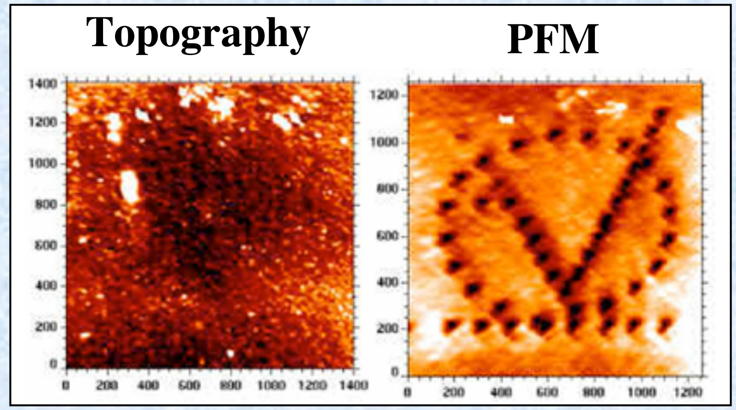


Examples of PFM Capabilities

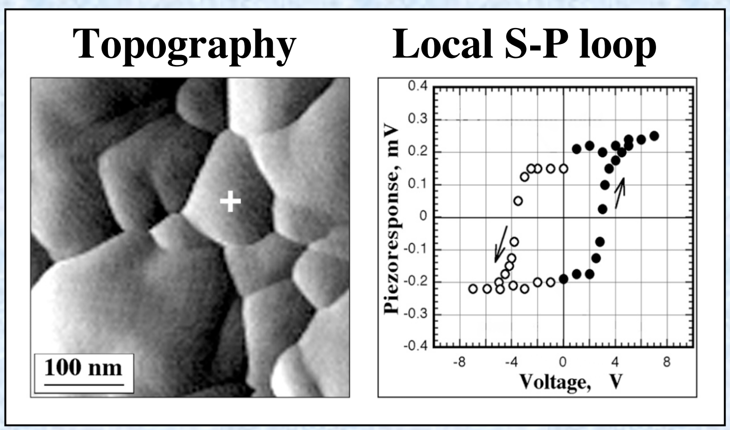
Polarization mapping



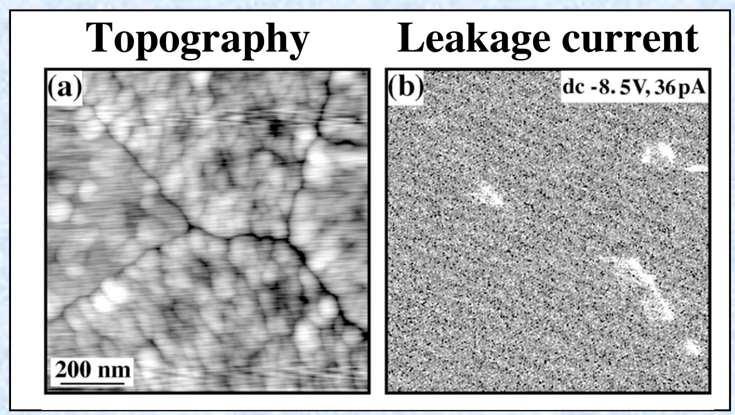
Domain patterning



Local hysteresis loop



Leakage current mapping



Comparison of SPM Methods for Domain Imaging

SPM Method	Advantages	Materials Studied	Drawbacks
EFM, SSPM	• Charge • Surface potential • Universal	Crystals: TGS, GASH, GMO, $BaTiO_3$, $PbTiO_3$, $LiNbO_3$	• Low-resolution • Surface sensitive
AFM, LFM	• High-resolution	Crystals: TGS, GASH, $BaTiO_3$, $PbTiO_3$	• Limited applicability • Surface sensitive
SNDM	• High-resolution • Dielectric studies • Universal	Crystals: $LiTaO_3$, $LiNbO_3$, SBN Thin films: PZT	• Surface sensitive
PFM	• High-resolution • Domain control • Capacitors testing • Universal	Crystals: TGS, $BaTiO_3$, KTP, $PbTiO_3$, SBN, $LiTaO_3$, $LiNbO_3$ Thin films: PZT, SBT, $BaTiO_3$, $PbTiO_3$	TBD

Electromechanical Coupling: Motivation to Study

Electromechanical coupling is an essential characteristic of a wide range of inorganic and organic materials alike

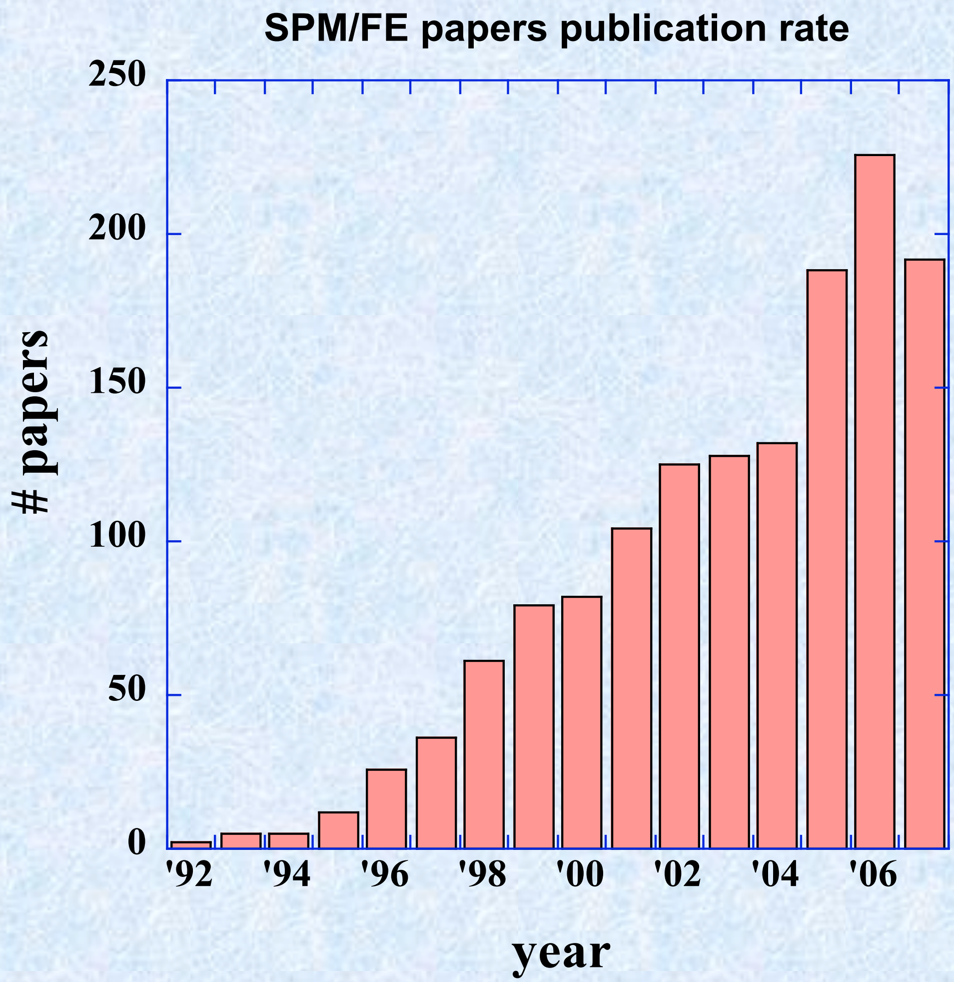
Materials:

- Ferroelectrics: $BaTiO_3$, $Pb(Zr,Ti)O_3$, PMN
- Piezoelectrics: ZnO, quartz
- Polymers: PVDF
- III-nitrides: GaN, AlN
- Biological materials: bones, wood, proteins, DNA

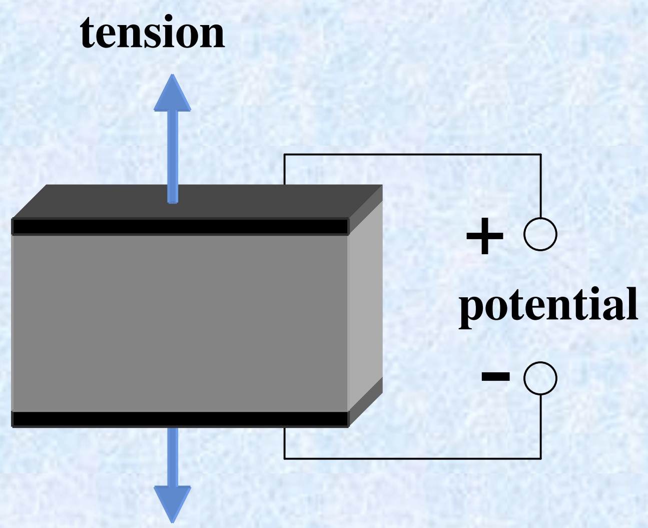
Studies:

- Characterization of electromechanical properties of materials
- Testing of micro- and nanoelectromechanical devices
- Explore relationship between polarity and materials properties
- Nanoscale structural characterization in biomaterials

SPM related publications



Piezoelectric Effect



Direct Piezoelectric Effect

$$D_j = d_{ij}^{dir} S_i$$

Converse Piezoelectric Effect

$$s_j = d_{ij}^{conv} E_i$$

E_m - electric field

s_{ij} - strain

d_{ij} - piezoelectric constant

Piezoelectricity/electrostriction:

- transducers, actuators, MEMS

In an ideal piezoelectric crystal, polarization P is related to mechanical stress s as

$$P_i = d_{ijk}\sigma_{jk}$$

where d_{ijk} - piezoelectric tensor

Piezoelectric tensor

Tetragonal material (4mm):

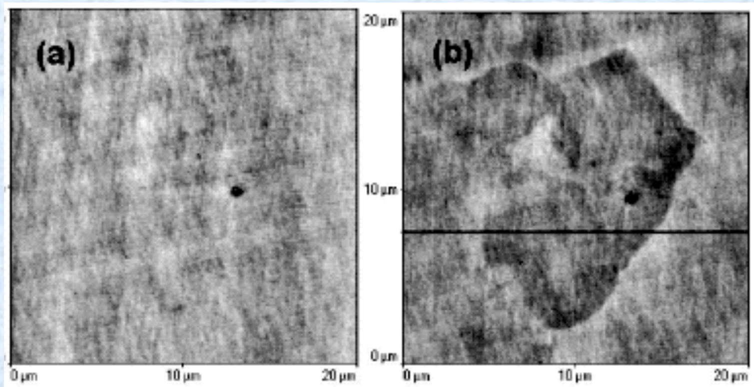
$$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}$$

Non-zero elements are determined by symmetry

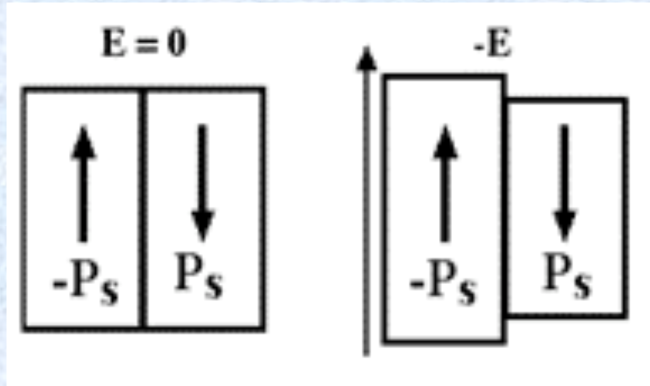
Domain Imaging via Static Piezoresponse

Polarization and piezocoefficients are linked via: $d_{ij} = \varepsilon_{im} Q_{jmk} P_{sk}$

Pinned domain in SBN crystal (topography); Imaging voltage 200 V, height difference 2 nm



Y.-G. Wang et al, PR B 61 (2000)



In piezoresponse: $\Delta L = \pm d_{33} V$

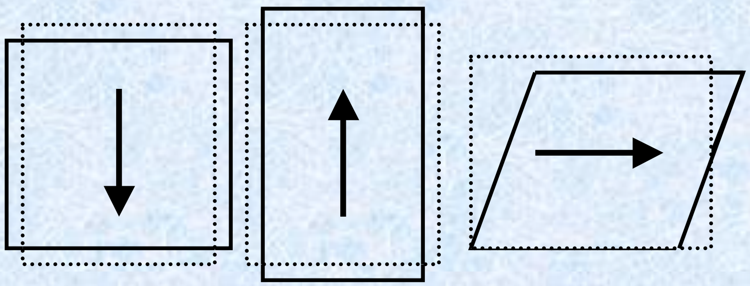
Imaging trade-off:

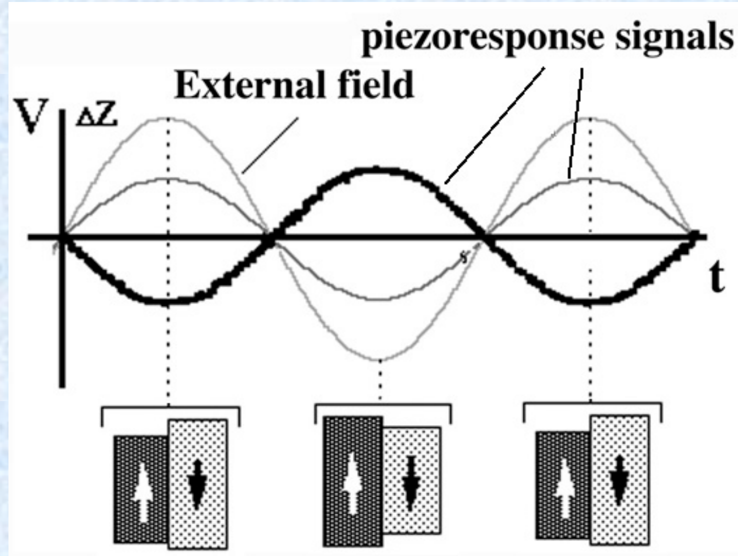
- The higher V, the better domain resolution
- Non-destructive imaging requires that $V < V_c$

Dynamic Piezoresponse increases sensitivity by 3 orders of magnitude

Domain Imaging via Dynamic Piezoresponse

Field is on





Field induced strain: $S_j = d_{ij} E_i$

Polarization and piezocoefficients are linked via: $d_{ij} = \varepsilon_{im} Q_{jmk} P_{sk}$

Sample deformation: $\Delta L = \pm d_{33} V$

Under modulation voltage $V = V_0 \cos(\omega t)$, surface vibrates as $\Delta L = \Delta L_0 \cos(\omega t + \varphi)$

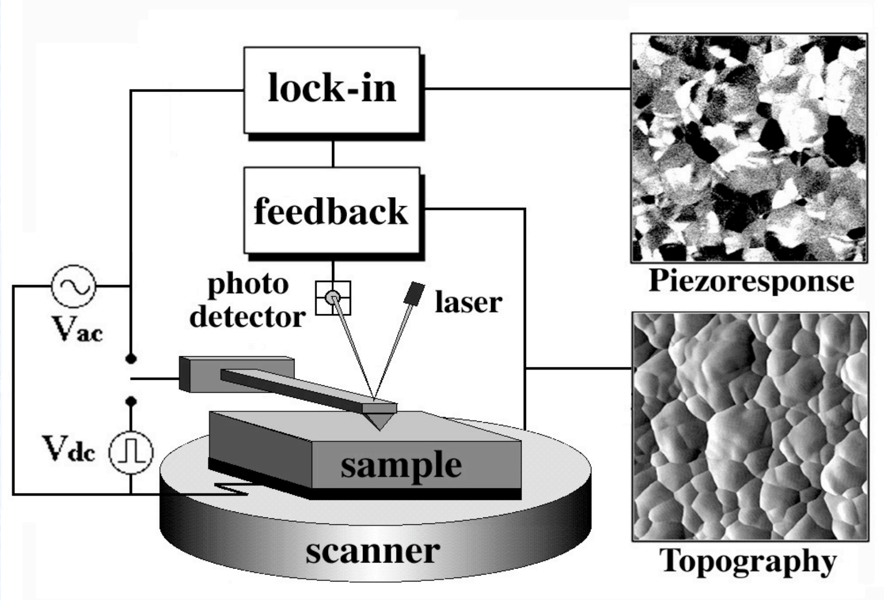
For P^+ ( ), φ=0º

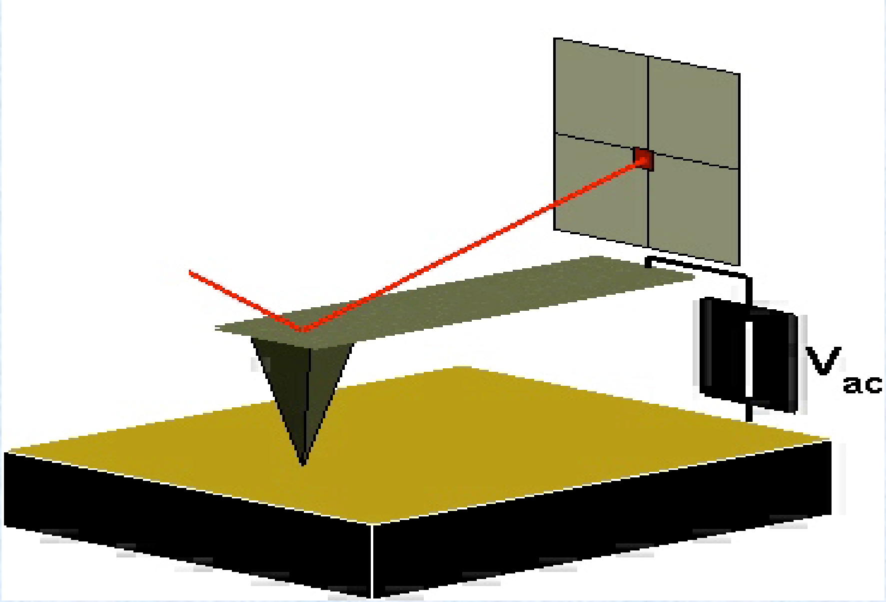
For P^- ( ), φ=180º

Vibration amplitude: $\Delta L_0 = d_{33} V_0$

Principle of Piezoresponse Force Microscopy

PFM is based on the field-induced mechanical response (converse piezoeffect)





AC voltage $V = V_0 \cos(\omega t)$

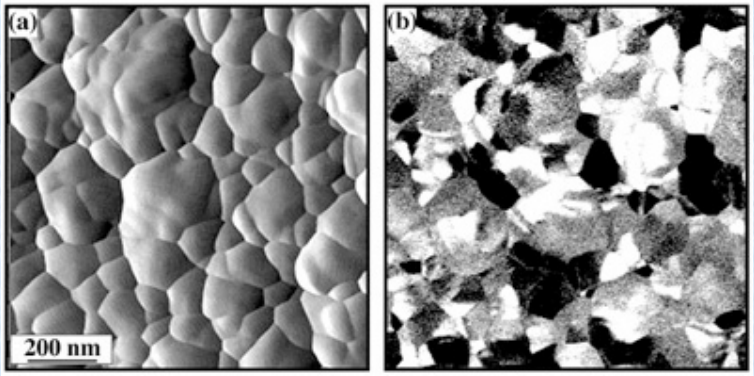
Surface displacement $\Delta z = d_{33} V_0 \cos(\omega t + \varphi)$

Phase: domain polarity

Magnitude: local piezocoefficient

DC bias: hysteresis loop and local switching

PZT thin film



Topography **Piezoresponse**

• Animation courtesy S. Jesse, ORNL

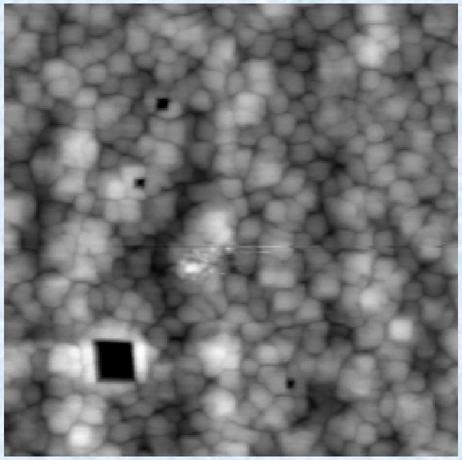
Phase and Amplitude Imaging in PFM

PFM phase and amplitude signals provide information on different properties

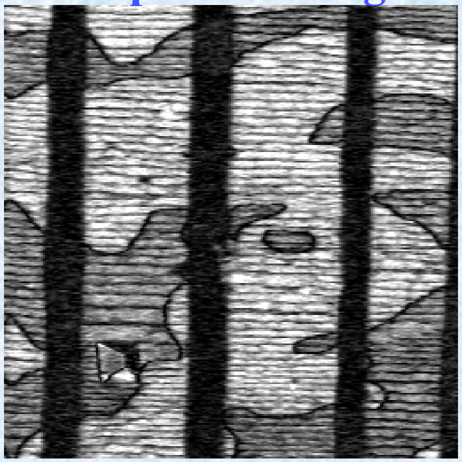
Amplitude recording:
piezocefficient

Phase recording:
polarization direction

Topography

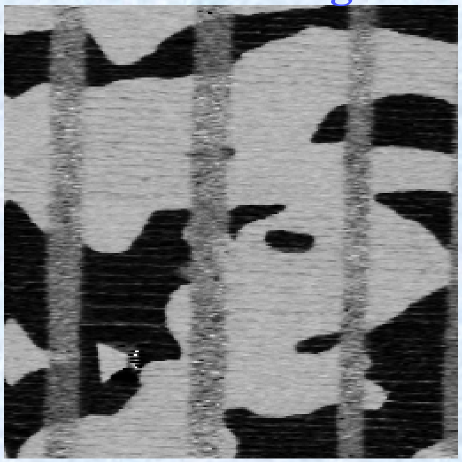


Amplitude image



$$\Delta d = d_{33}E$$

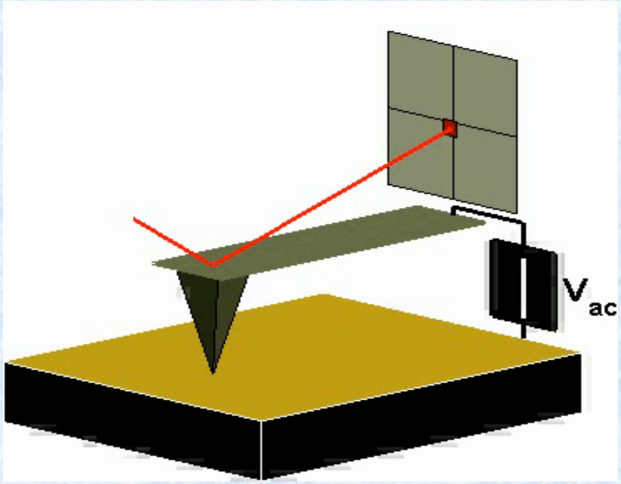
Phase image

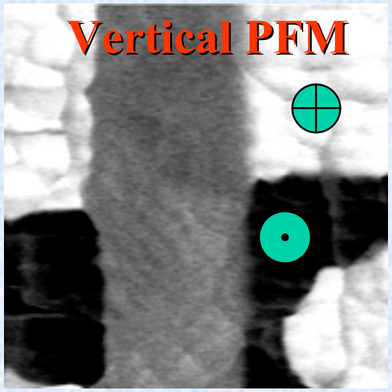


For P^+, φ=0º; For P^-, φ=180º

Vertical and Lateral PFM detection

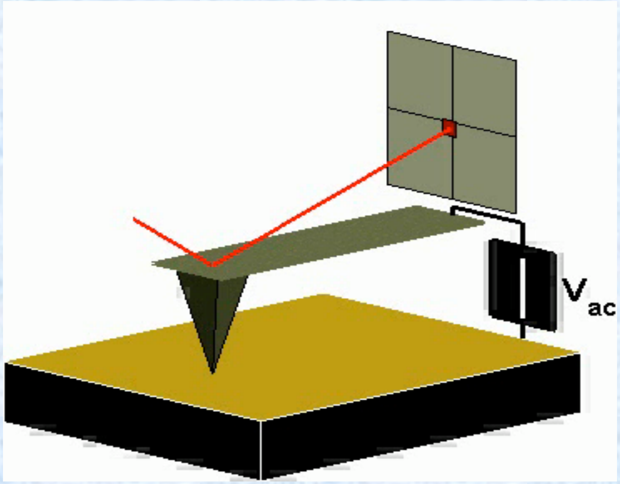
Vertical PFM

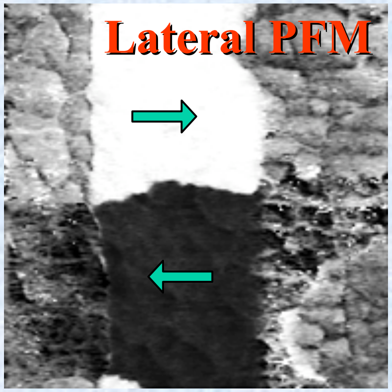




$$\Delta Z = \pm d_{33} V \cos(wt + \varphi)$$

Lateral PFM



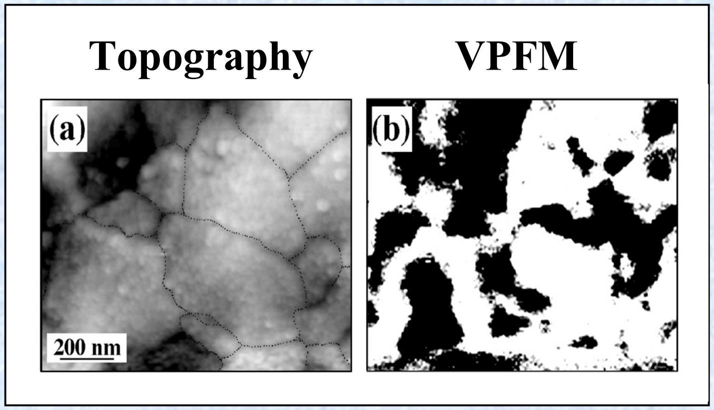


$$\Delta L = \pm d_{15} V \cos(wt + \varphi)$$

• **Animation courtesy S. Jesse, ORNL**

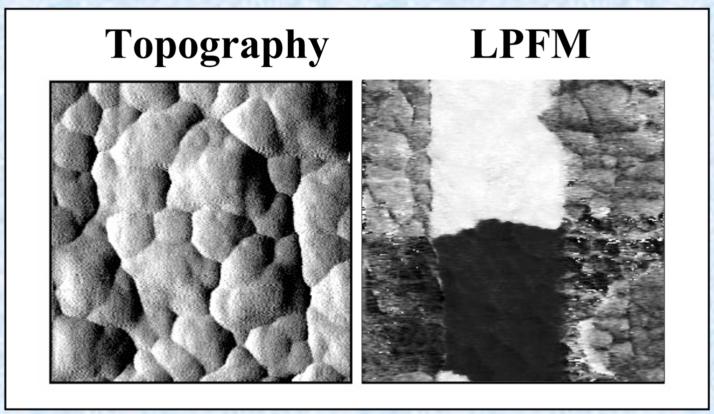
PFM: Out-of-Plane vs In-Plane Polarization

PZT (001) film



$$\Delta L = \pm d_{33} V \Rightarrow d_{33} \propto P_s$$

$PbTiO_3$ (100) film



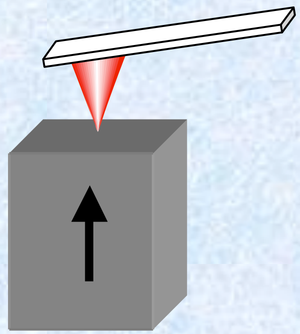
Tetragonal perovskite

$$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}$$

Vertical PFM

Lateral PFM (x)

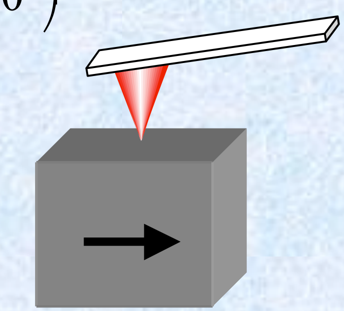
Lateral PFM (y)



Rotated by 90°

$$\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & d_{15} \\ d_{31} & d_{33} & d_{31} & 0 & 0 & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \end{pmatrix}$$

Lateral PFM (x)

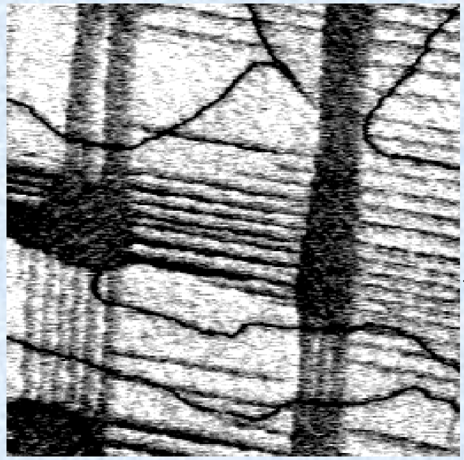


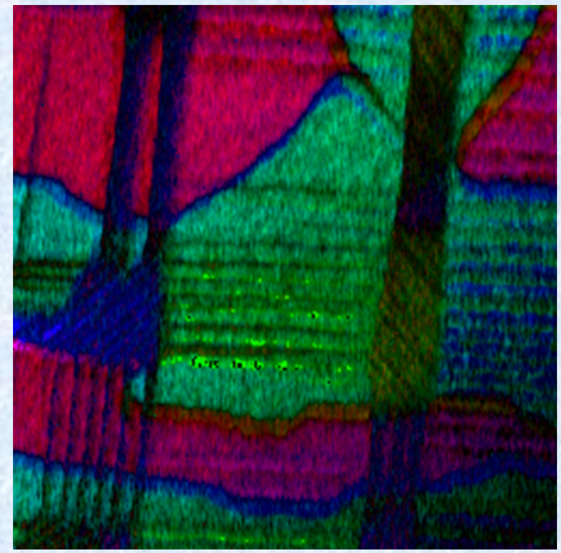
Color Representation of 2D PFM Data

VPFM

VPFM phase

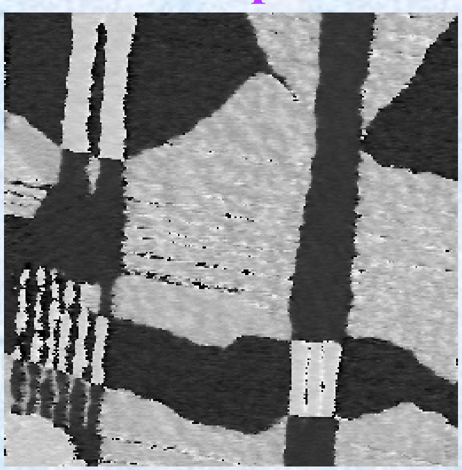
VPFM amplitude



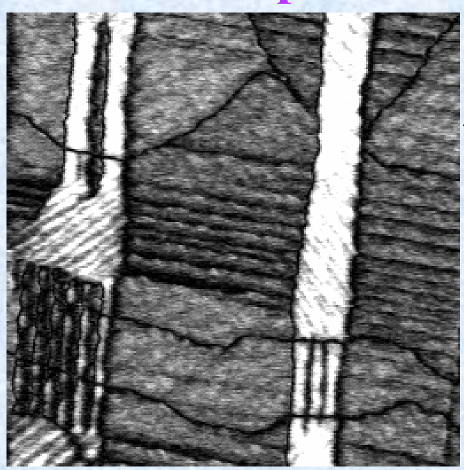


LPFM

LPFM phase



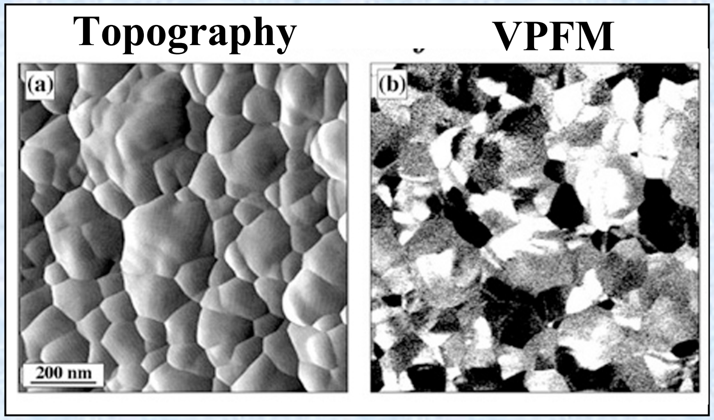
LPFM amplitude



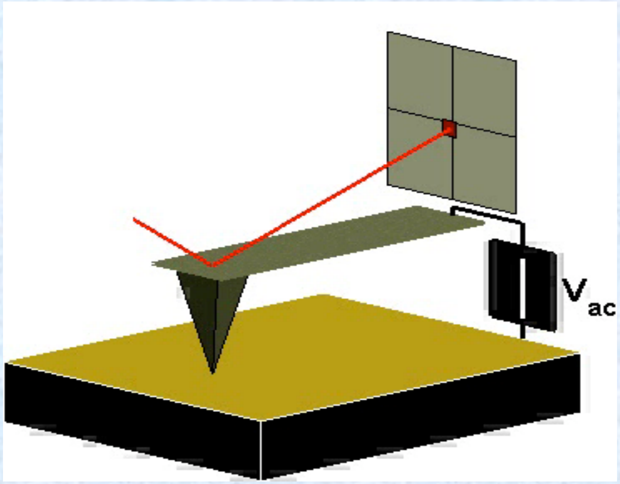
• Sample courtesy H. Funakubo

PFM of Polycrystalline Ferroelectrics

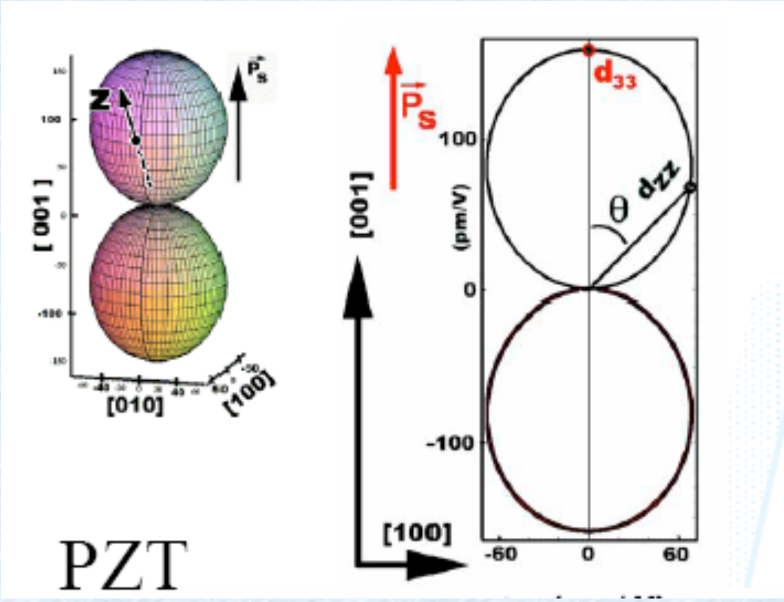
Randomly oriented grains



- P_s is not proportional to d_{33}
- Signal depends on d_{33}, d_{31}, d_{15}



VPFM surface for tetragonal Pb(Zr,Ti)O_3



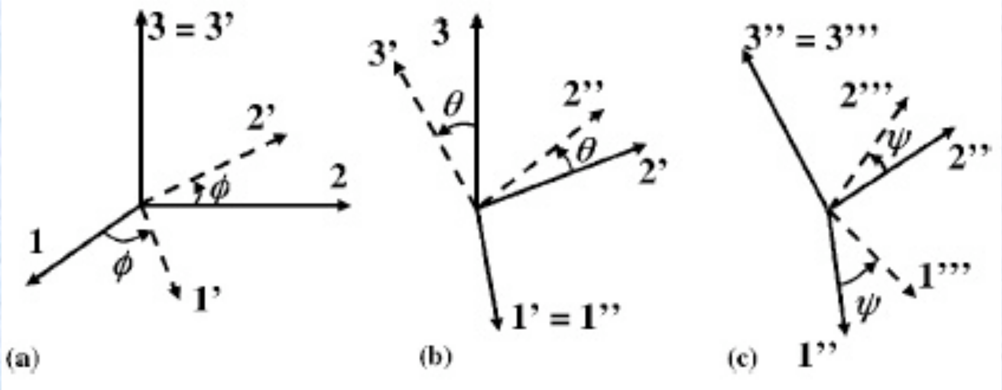
$$d_{zz}(\theta) = (d_{31} + d_{15})\sin^2\theta\cos\theta + d_{33}\cos^3\theta$$

Harnagea et al, Integrated Ferroelectrics 38, 23 (2001)

• Animation courtesy S. Jesse, ORNL

Crystal Orientation Effect on PFM

PE tensor in the laboratory system of coordinates $d_{ij} = A_{ik} d^0_{kl} N_{lj}$



Transformations for transition from crystal to laboratory coordinate system

In general case:

VPFM:

$$d_{zz} = (d_{31} + d_{15}) \sin^2\theta \cos\theta + d_{33} \cos^3\theta$$

LPFM:

$$d_{zx} = -(d_{31} - d_{33} + (d_{15} + d_{31} - d_{33}) \cos 2\theta) \cos\psi \sin\theta$$

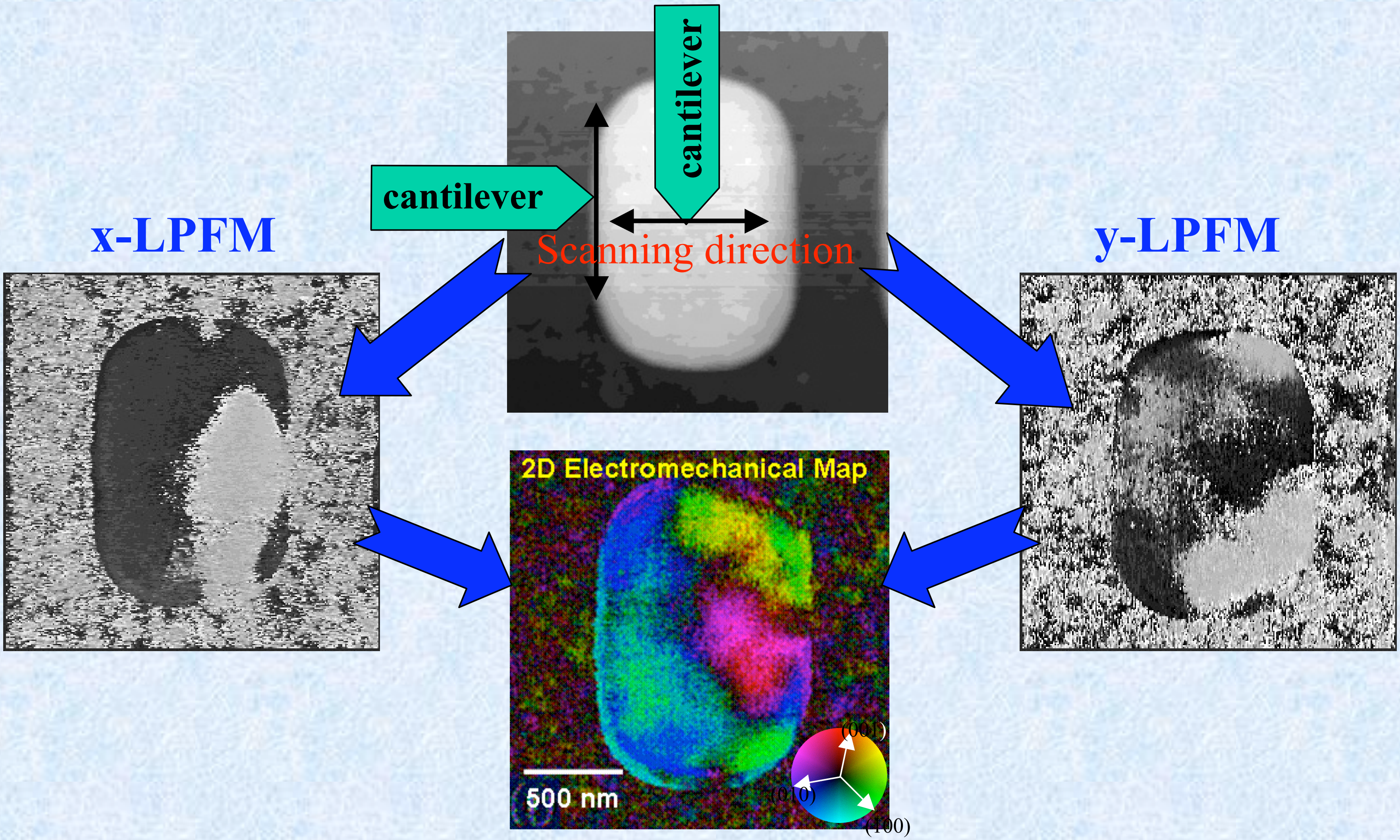
$$d_{zy} = -(d_{31} - d_{33} + (d_{31} + d_{31} - d_{31}) \cos 2\theta) \sin\psi \sin\theta$$

- **From 3D PFM data either the piezoelectric constants d_{ij} or local orientation map (θ , ϕ, ψ) can be obtained**
- **For materials with known constraints on possible crystallographic orientation polarization reconstruction can be performed**

Kalinin et al, Microsc. Microanal. (2006)

2D PFM imaging in (111) PZT capacitor

In-plane polarization mapping in poled capacitor



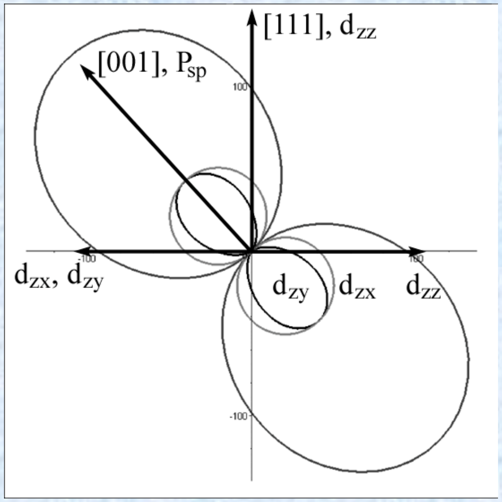
3D Reconstruction of Polarization in a PZT Capacitor

Simple case where possible directions are known: PZT (111)

VPFM: $d_{zz}(\theta) = (d_{31} + d_{15})\sin^2\theta\cos\theta + d_{33}\cos^3\theta$

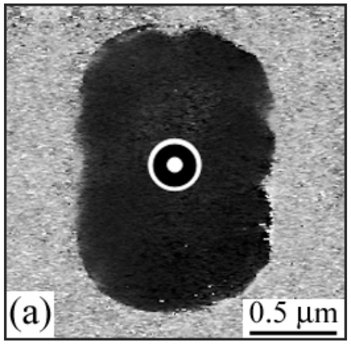
x-LPFM: $d_{zx}(\theta) = d_{31}\cos\theta$

y-LPFM: $d_{zy}(\theta) = (d_{33} - d_{15})\sin^2\theta\cos\theta + d_{31}\cos^3\theta$

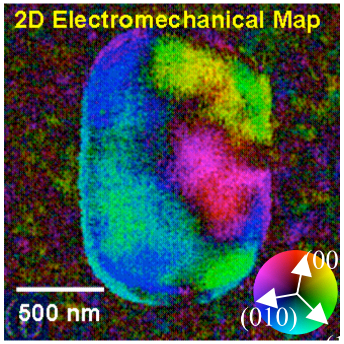


- **Poled capacitors, which appear uniformly polarized in VPFM, are in fact in a polydomain state**

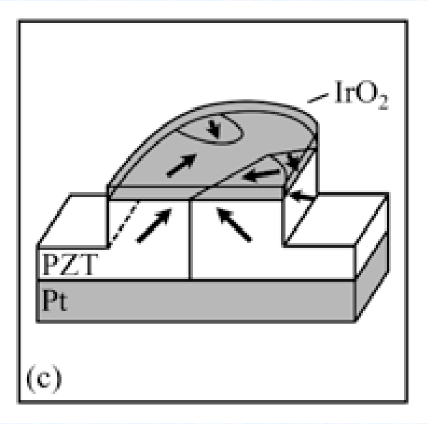
Out-of-plane polarization



2D in-plane map



3D reconstruction



Rodriguez et al, Appl. Phys. (2005)

Elementary Theory of PFM

Total response of the cantilever in contact with a ferroelectric:

$$A = A_{em} + A_{cap} + A_{nl}$$

Useful reference:
S. Kalinin and D. Bonnell, PRB (2001)

where

A_{em} - **electromechanical response**

$$A_{em} = d_{33}V_{ac} + 2\frac{M_{333}}{t}V_{ac}^2$$

A_{cap} - **capacitive/electrostatic response**

$$F_{cap} + F_{Coul} = \frac{1}{2}V^2\frac{dC}{dz} + \frac{\sigma CV}{2\varepsilon_0}$$

A_{nl} - **non-local (cantilever) response**

Can be neglected for most practical cases

For tetragonal phase of $BaTiO_3$ (E parallel to P_s)

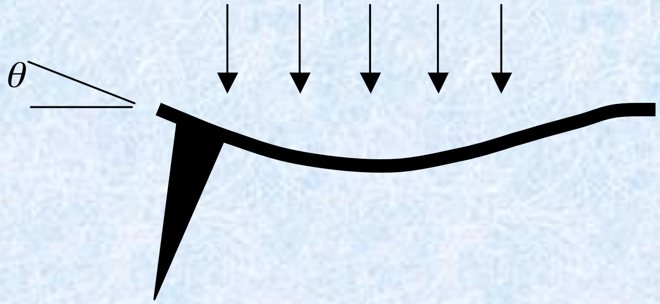
$$d_{33} = 2\chi_{33}Q_{33}P_{s3}$$ **Expansion/contraction**

$$d_{35} = 2\chi_{33}Q_{55}P_{s1}$$ **Shear**

$$d_{34} = 2\chi_{33}Q_{44}P_{s2}$$ **Shear**

Cancelled out

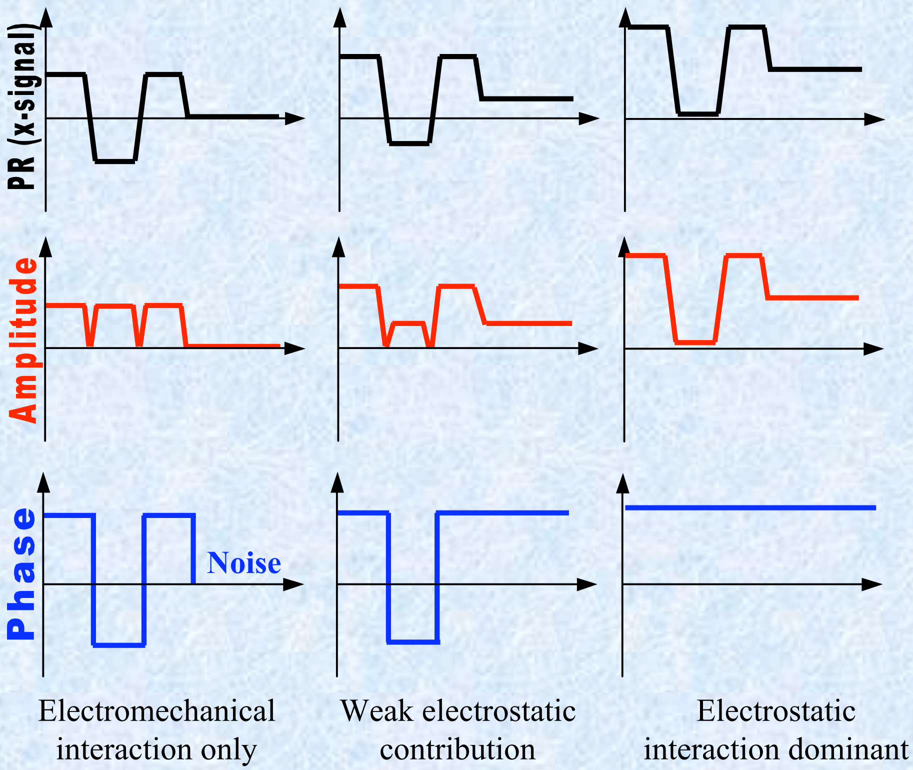
Electrostatic Contribution to PFM



Why quantifying PFM contrast is difficult:

- Tip is in contact - both electrostatic and electromechanical interactions contribute
- Total response contains both local and non-local contributions

Qualitative Aspects of Electrostatic Signal



PFM signal over positive domain

$$PR_+ = d_{33} + F_{nl}\left(V_{tip} - V_{av}\right)$$

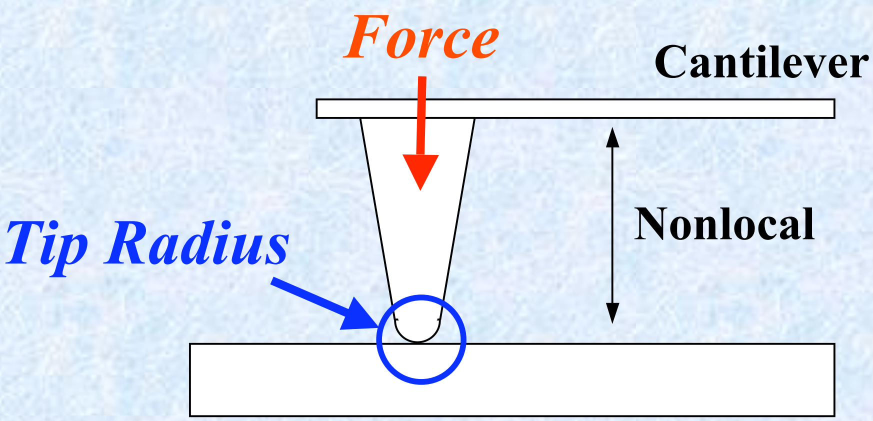
PFM signal over negative domain

$$PR_- = -d_{33} + F_{nl}\left(V_{tip} - V_{av}\right)$$

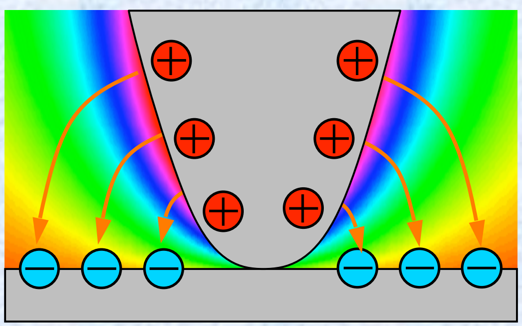
Stiffness criterion:

$$PR = d_{eff} + \frac{Lw\varepsilon_0 \Delta V}{48kH^2}$$

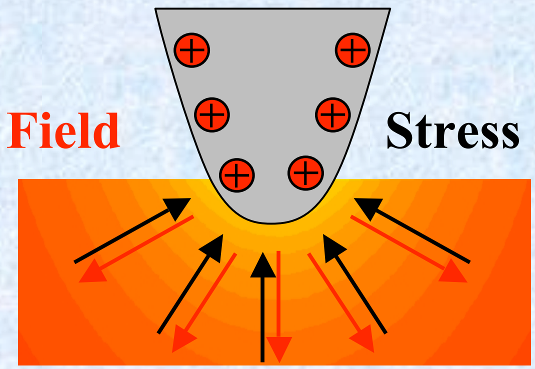
Various Imaging Regimes in PFM



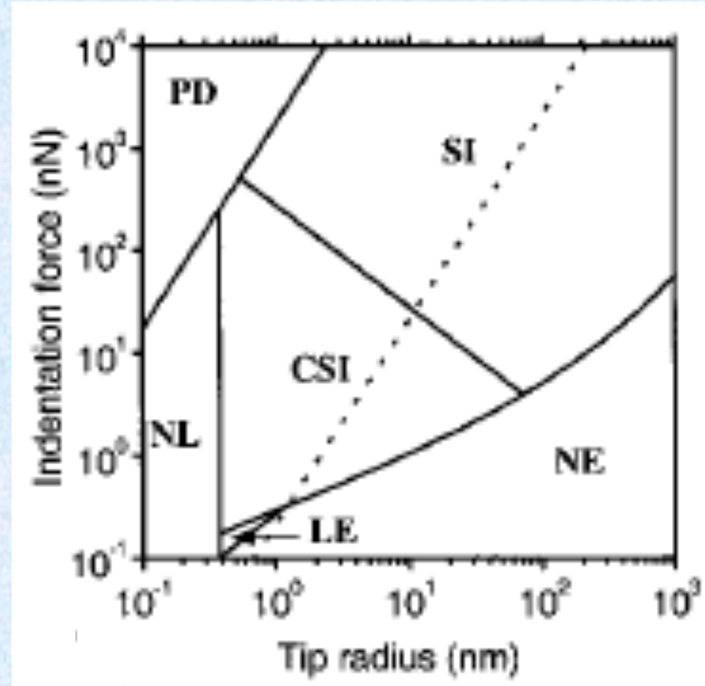
Local Piezoresponse Contrast



Electrostatic



Electromechanical



E - Electrostatic
NL - Non-local interactions
PD - Plastic Deformation
SI - Strong Indentation
CWI - Weak indentation

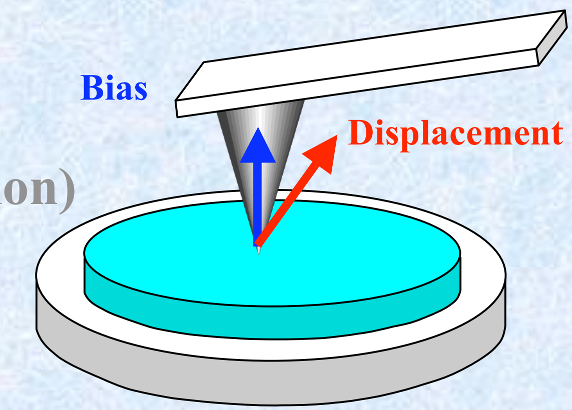
Kalinin and Bonnell, PR B (2002)

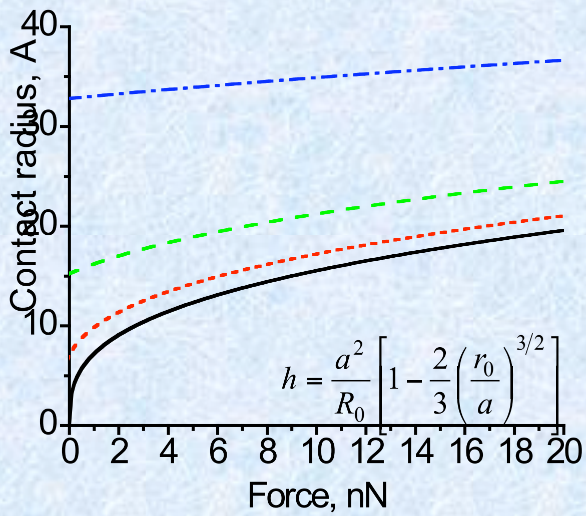
PFM Resolution Limits

Ideally, we want to probe electromechanical behavior with ~1 pm/V sensitivity at ~0.1- 1 V excitation bias on molecular (biosystems) and unit cell (ferroelectrics) level.

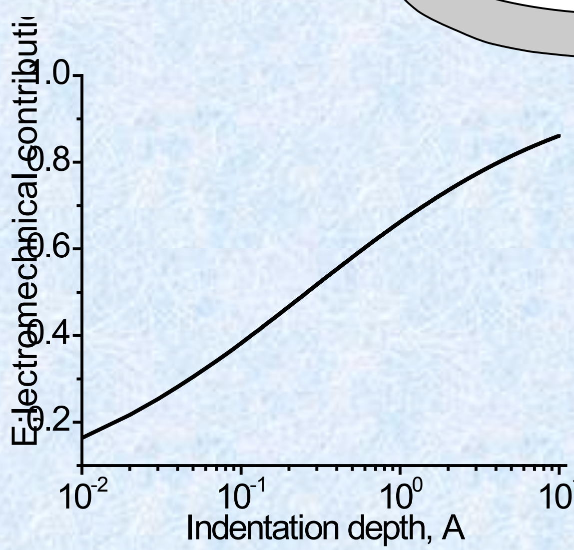
PFM limitations: contact mode technique

- **electrostatic tip-surface interactions**
- **formation of liquid necks at the tip-surface junction**
- **large contact force – large contact area (low resolution)**
- **difficult to use resonant enhancement**
- **probing dynamic processes**





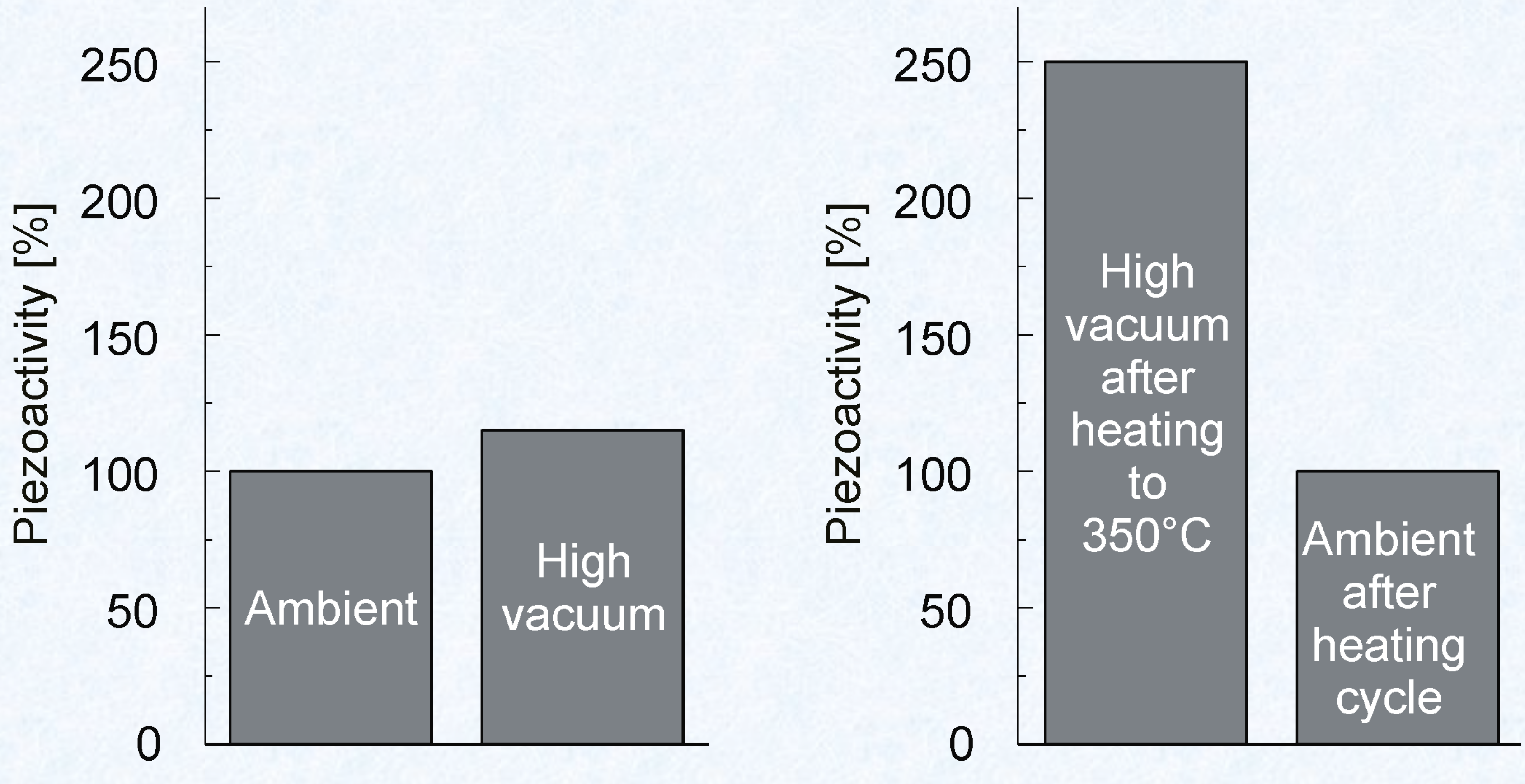
$$a^3 = \frac{R_0}{E^*}\left\{P + 3\sigma\pi R_0 + \sqrt{6\sigma\pi R_0 P + (3\sigma\pi R_0)^2}\right\}$$



$$PR = \alpha_a(h) d_3 \frac{k_1}{k_1 + k} + \frac{C'_{sphere}}{k_1 + k}(V_{dc} - V_s)$$

Surface Contamination Effect in PFM

PFM measurements of a $BaTiO_3$ single crystal

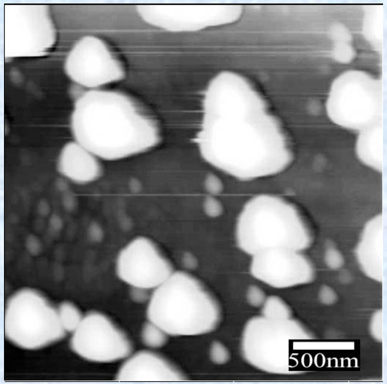


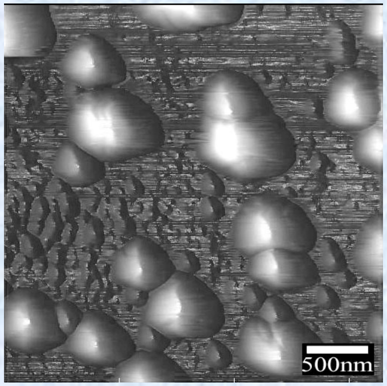
Peter, Ruediger, Waser, RSI (2006)

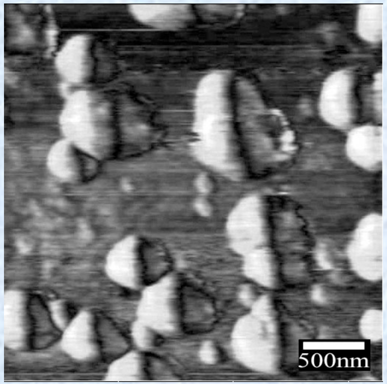
Topographic Cross-talk in PFM

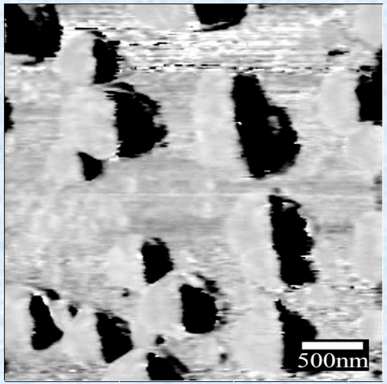
(001) PZT grains

Topography **Derivative** **VPFM amplitude** **VPFM phase**





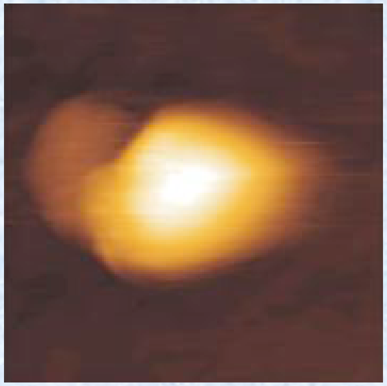
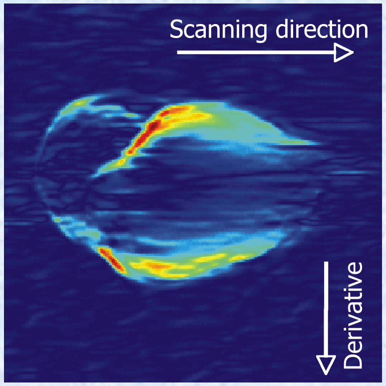


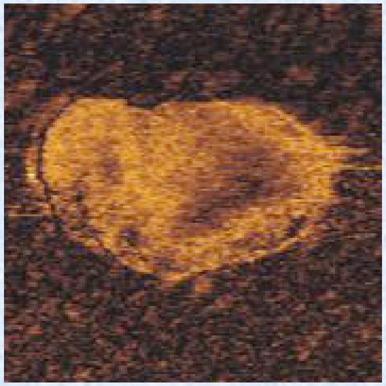
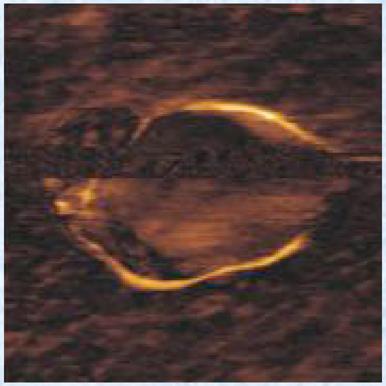


Data courtesy S.Kalinin

(001) $BaTiO_3$ grain

Topography **Derivative** **VPFM** **LPFM**

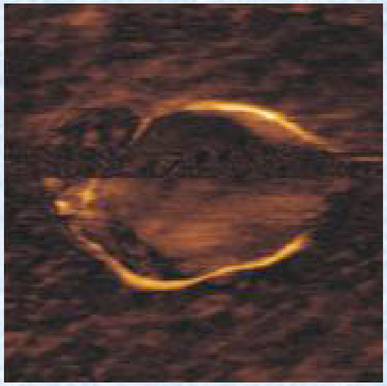



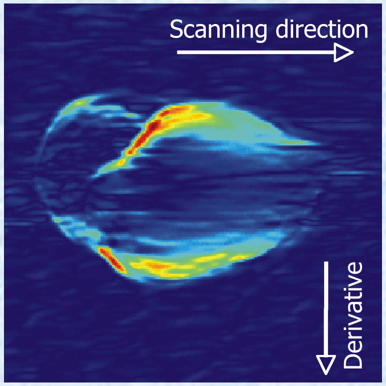



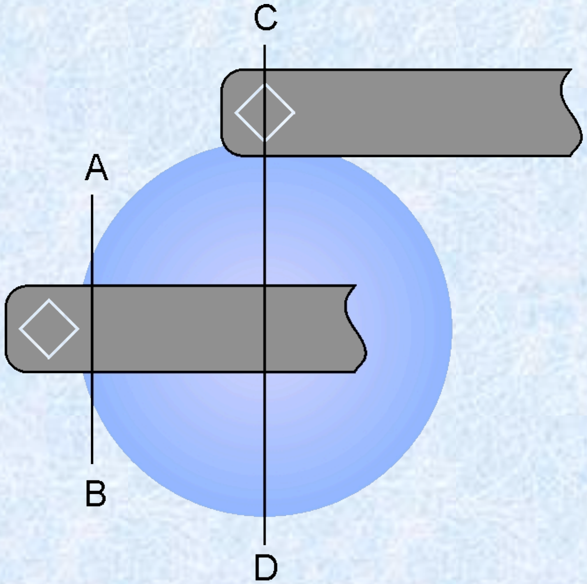
Peter, Ruediger, Waser, RSI (2006)

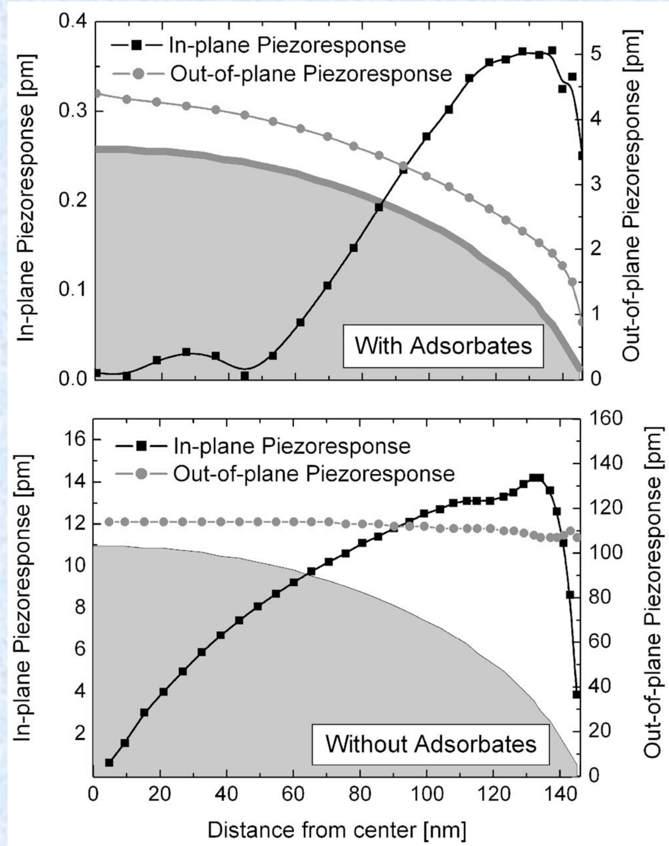
Topographic Cross-talk in PFM

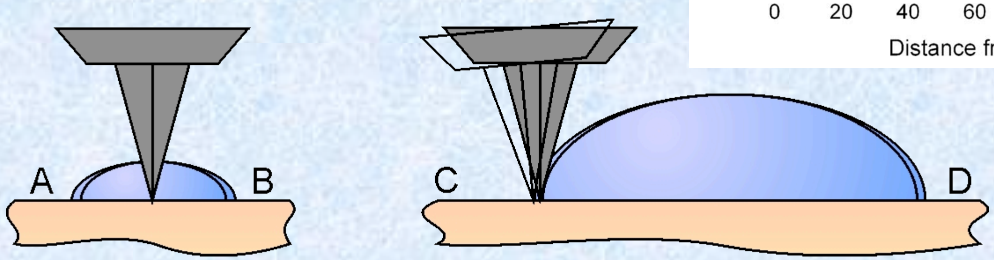
(001) $BaTiO_3$ grain





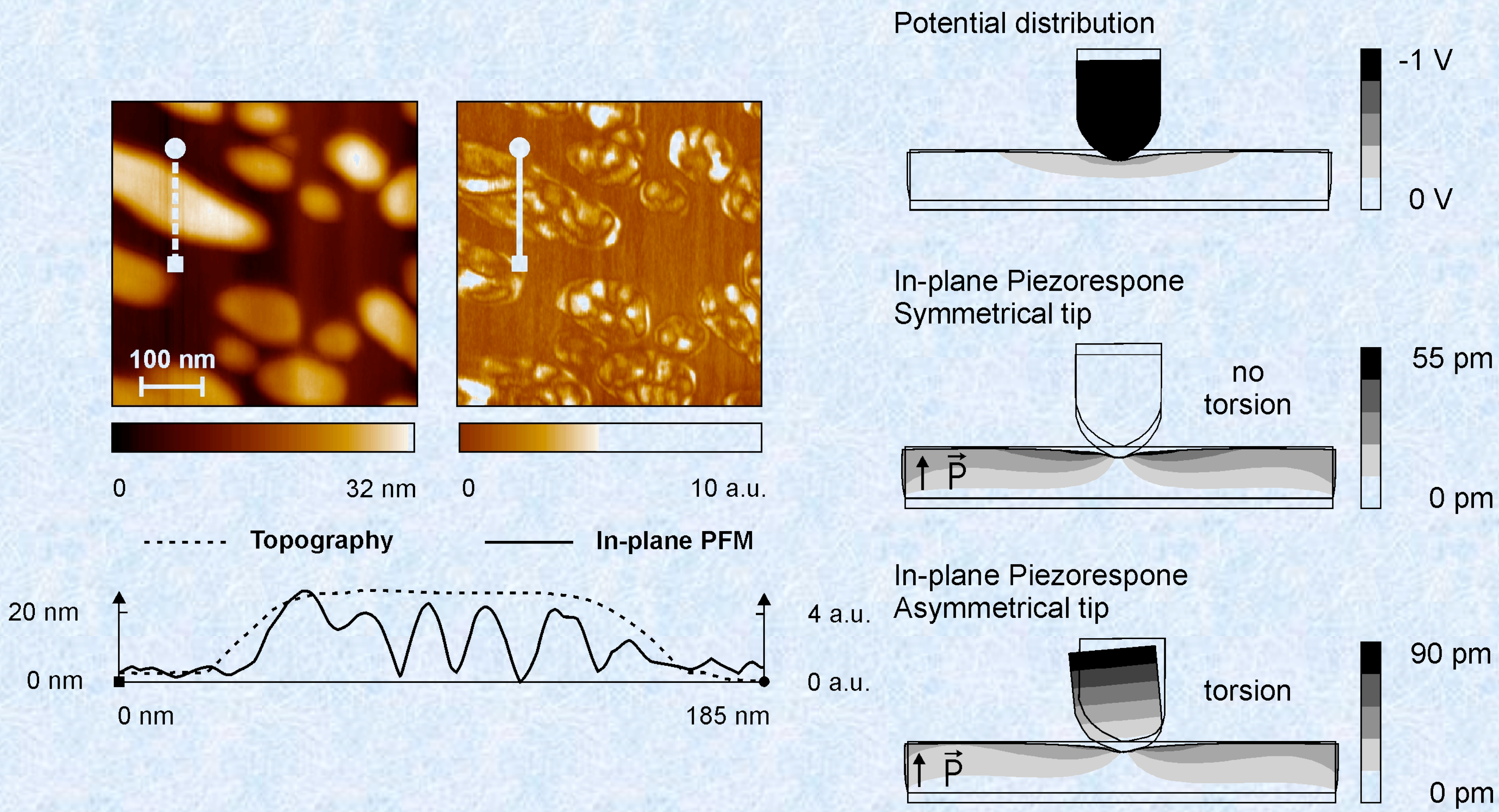






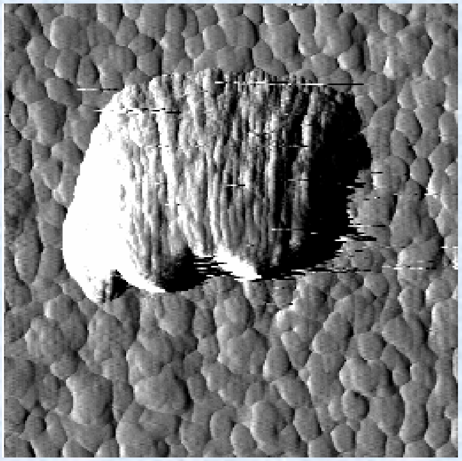
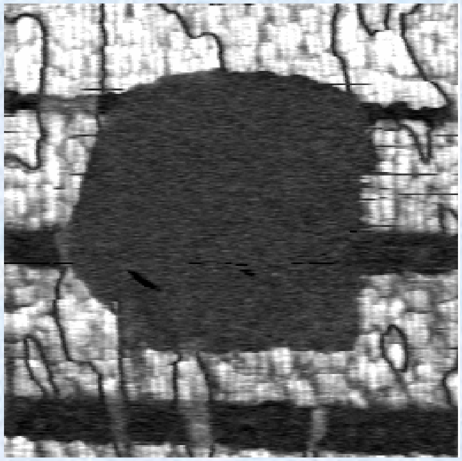
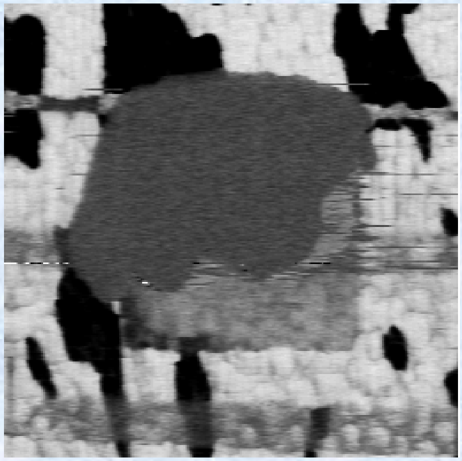
Slide courtesy A.Ruediger, RWTH

Tip Shape Effect in PFM



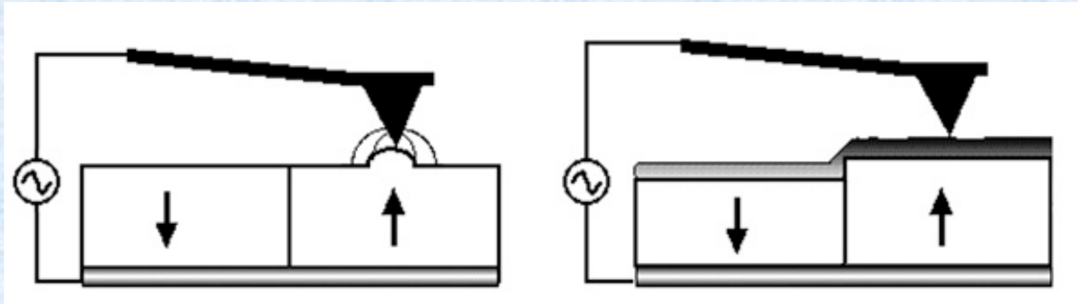
Slide courtesy A.Ruediger, RWTH

Surface Modification Effect in PFM

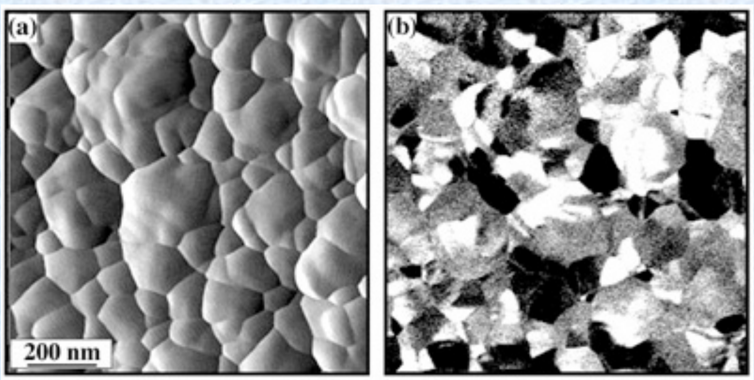
  

Built-up of foreign substance (tip material transfer, adsorbates) during long bias application results in surface modification and a change in PFM signal.

Local vs Integral Excitation (Thin Films vs Capacitors)

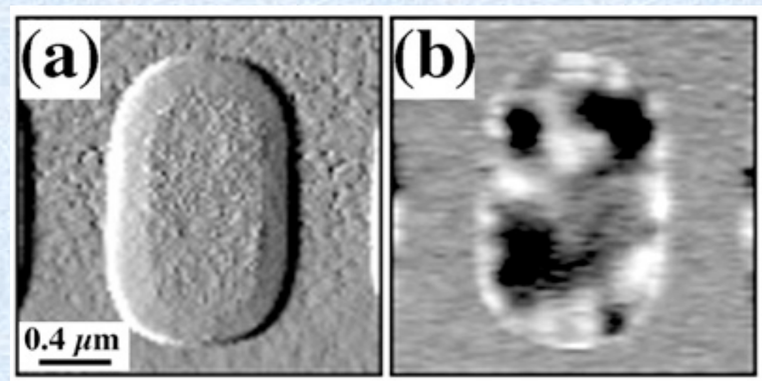


PZT thin film



Topography **Piezoresponse**

PZT capacitor



Topography **Piezoresponse**

Note: your ac power supply should be able to supply enough energy to generate piezoelectric oscillation in the capacitor.

Separate Recording of Phase and Amplitude in PFM

PFM provides information on local switching behavior within a capacitor
Measures absolute value of piezoelectric constant

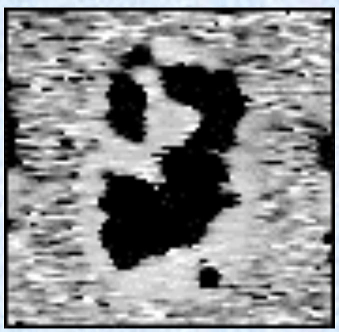
Phase recording:

polarization direction

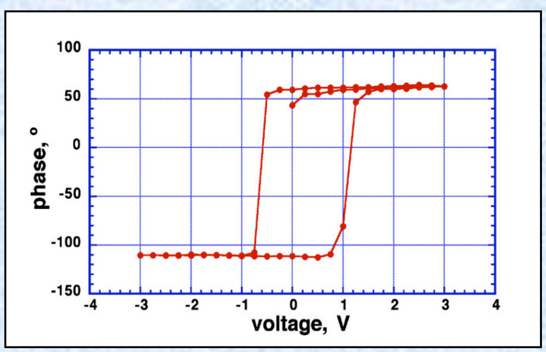
For P^+, $\varphi=0^o$; For P^-, $\varphi=180^o$

Mixed PFM image

Phase image



Phase loop



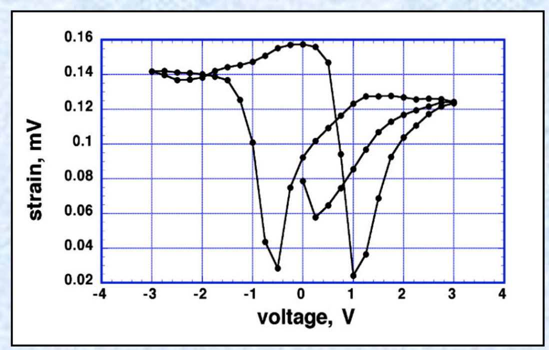
Amplitude recording:

switchable volume

$$\Delta d = \alpha d_{33} \int E(z)dz$$

Amplitude image

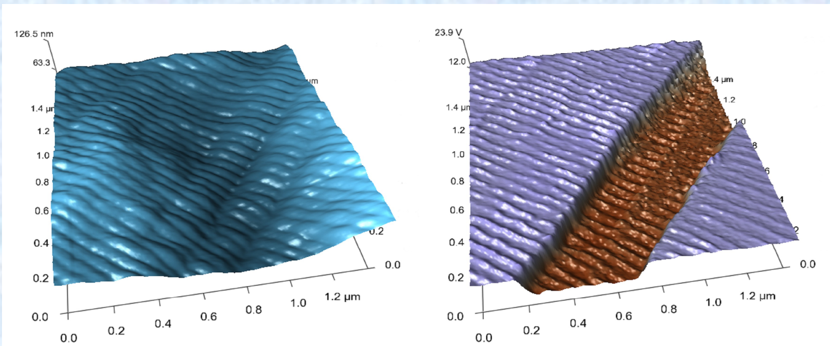
Amplitude loop



PFM Imaging of Piezoelectric Materials

Collagen fibers

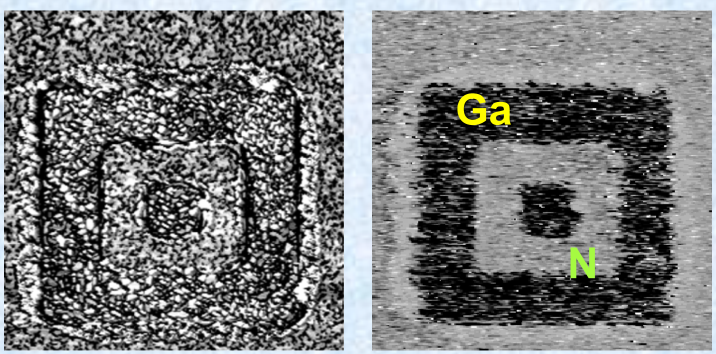
Topography **PFM phase**



- **Structural imaging in biomaterials**

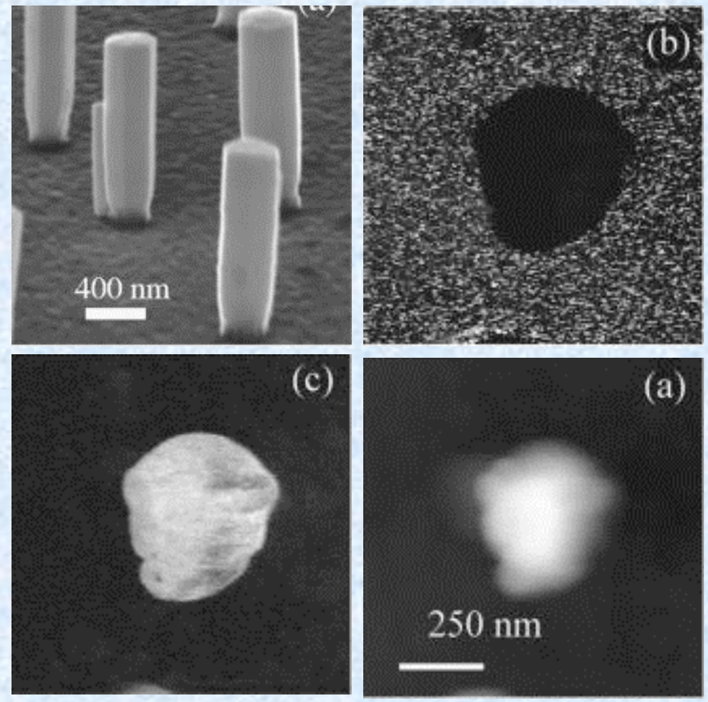
GaN films

Topography **PFM**



- **Detection of inverse domains in III-N semiconductors**

ZnO nanorods

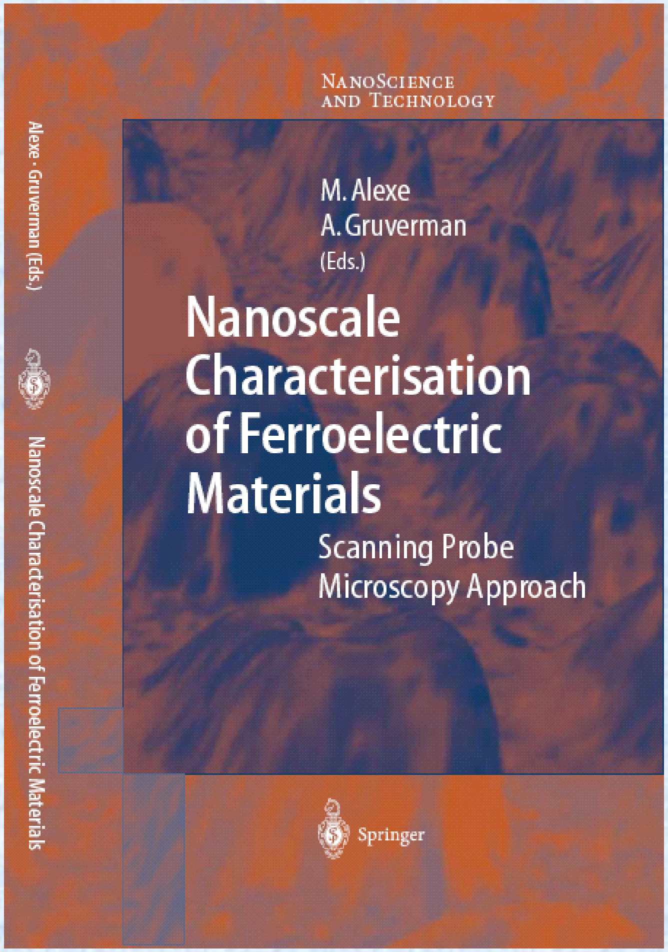


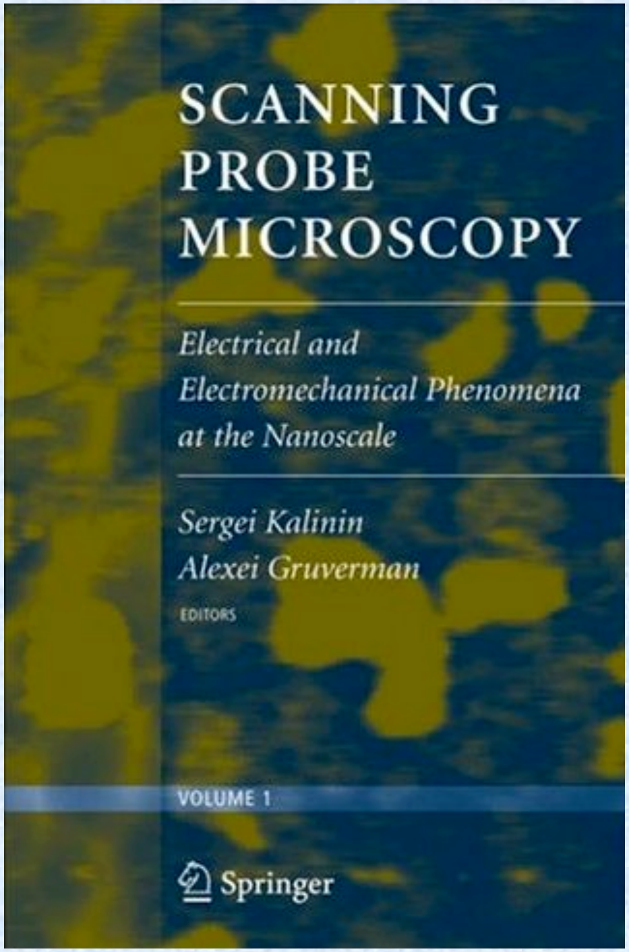
Scrymgeour et al, JAP (2007)

- **Evaluation of piezoelectric properties in nanostructures**

Books on PFM of Ferroelectrics

…presents recent advances in the field of nanoscale characterization of ferroelectric materials using SPM. ...addresses various imaging mechanisms of ferroelectric domains in SPM, quantitative analysis of the SPM signals, as well as nanoscale switching, scaling effects, and transport behavior.





Conclusion

- PFM has become a standard tool for investigation of nanoscale properties of ferroelectric materials

- PFM in combination with various SPM methods provides complementary information for quantitative analysis of surface and bulk properties of ferroelectrics

- PFM allows characterization of electromechanical and structural properties of a wide range of piezoelectrically active materials leading to a better understanding of material functionality down to the nanoscale level.