Principles and Applications of Piezoresponse Force Microscopy

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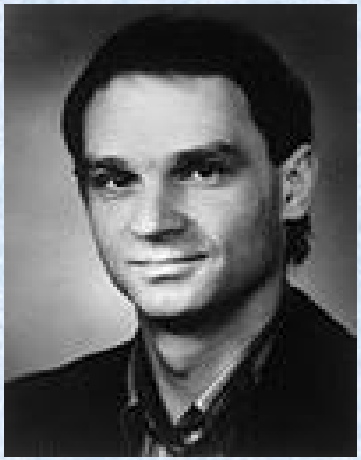
Outline

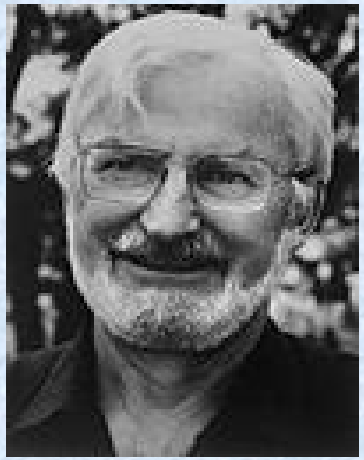
- Introduction
  Basics of scanning probe microscopy
- PFM and Ferroelectrics
  Domains, switching, scaling
- Piezoresponse Force Microscopy
  Principles, elementary theory, experimental setup
- PFM Characterization of Functional Materials
  Ferroelectrics, semiconductors, biomaterials
- Conclusion

History of Scanning Probe Microscopy

The Nobel Prize in Physics 1986

" for their design of the scanning tunneling microscope"





Gerd Binnig

Federal Republic of Germany

IBM Zurich Research Lab
Rüschlikon, Switzerland

Heinrich Rohrer

Switzerland

IBM Zurich Research Lab
Rüschlikon, Switzerland

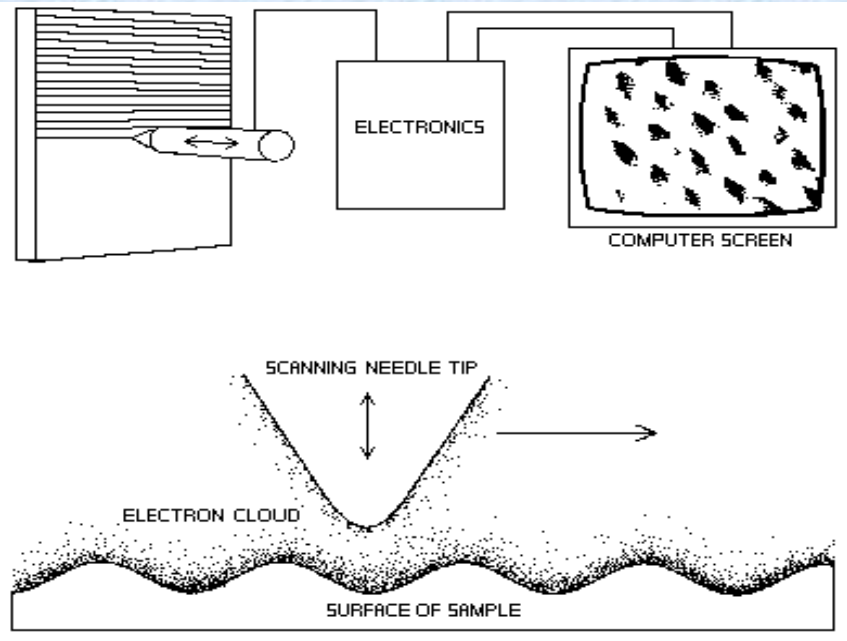
Concept of SPM: using the interaction of a small physical probe with a solid surface to obtain spatially resolved information about the surface.

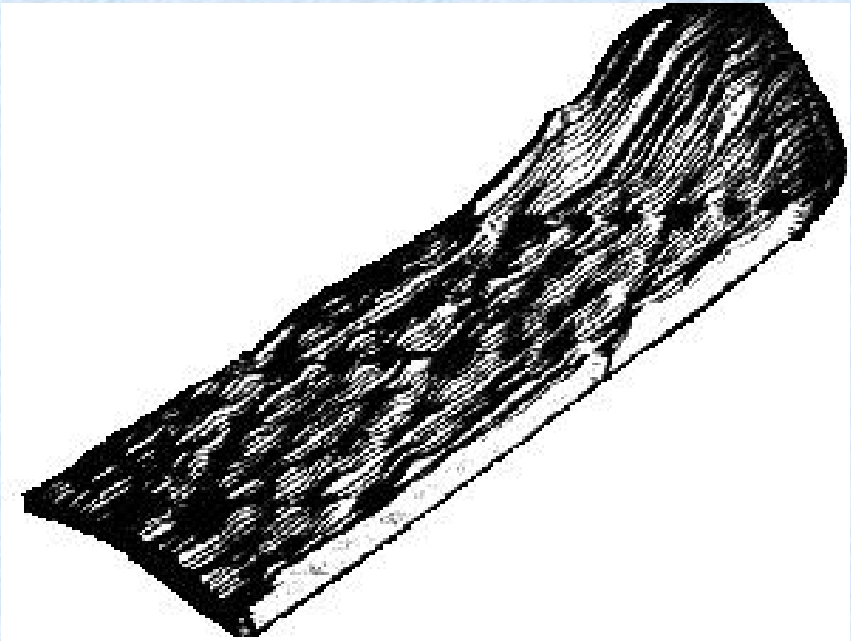
The (small) probe is scanned with respect to the sample, and the interaction is monitored.

The spatial position (x, y) of the monitored interaction is combined with the interaction information to construct a map of the probe-sample interactions.

http://www.nobel.se/physics/laureates/1986/index.html

History of SPM





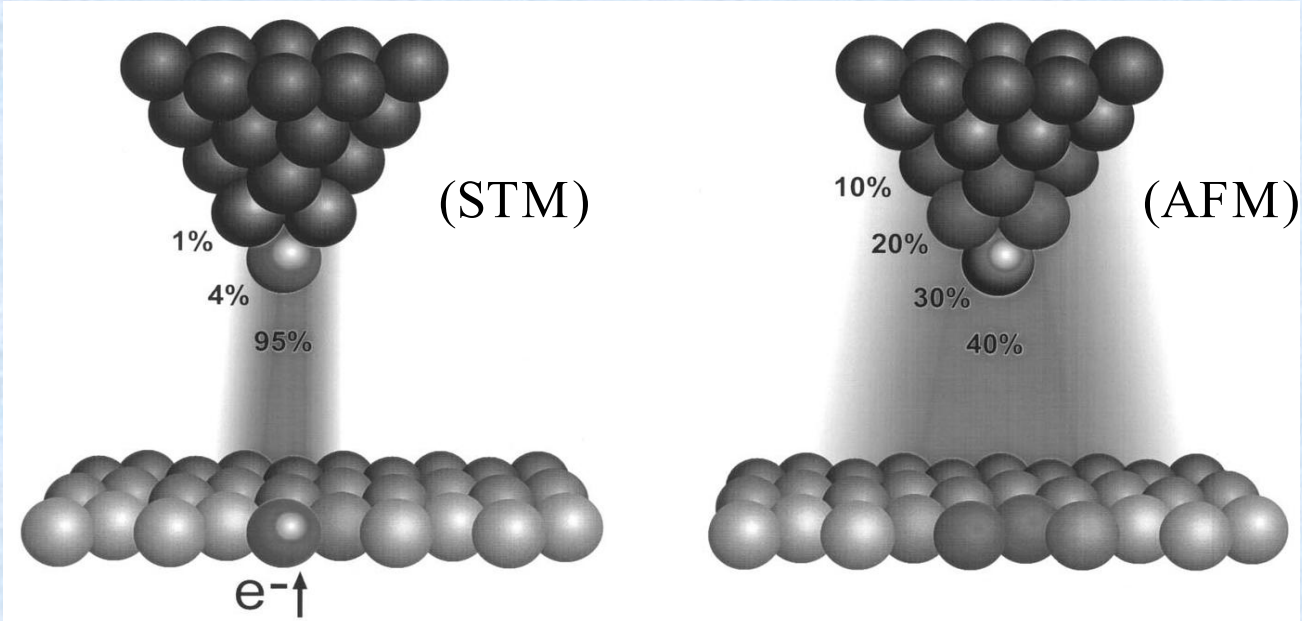
Here is a crude schematic of the STM invented in 1981 by Binnig and Rohrer, which opened a new field of science and has led to many advancements in technology.

Although the STM provides sub-angstrom resolution in all three dimensions, it is limited to conductive and semiconductive materials.

Scientific American, August, 1985

Concept of an Atomic Force Microscope

The AFM was invented in 1986 by Binning, Quate, and Gerber when they realized that the forces exerted by the tip on the sample could be used to map the topography of a sample.



An STM gives true atomic resolution. Because the dependence of the tunneling current on the tip-to-sample separation is exponential, only the closest atom on a good STM tip interacts with the closest atom on the sample. For AFMs, the dependence of cantilever deflection on tip-to-sample separation is weaker. The result is that several atoms on the tip interact simultaneously with several atoms on the sample.

Park Scientific Instruments

Feedback mechanism maintains a constant tunneling current in STM and constant force in AFM.

Historical Remarks

1981 Invention of the scanning tunneling microscope (G. Binnig and H. Rohrer)

1986 Invention of the atomic force microscope (G. Binnig, C.F. Quate and Ch. Gerber)

1989 C. F. Quate suggested the use of SFM for imaging of ferroelectric domains

1990 First observation of 180º domain walls in $Gd_2(Mo_3O_4)_3$ single crystal by noncontact SFM (F. Saurenbach and B. D. Terris). Spatial resolution is 5 μm

1992 Imaging of microscopic poled regions in PvDF films using the piezoresponse mode (P. Guethner and K. Dransfeld)

1993 First nanoscale observation of 180º domain walls in a single crystal of GASH by noncontact SFM (R. Luthi et al)

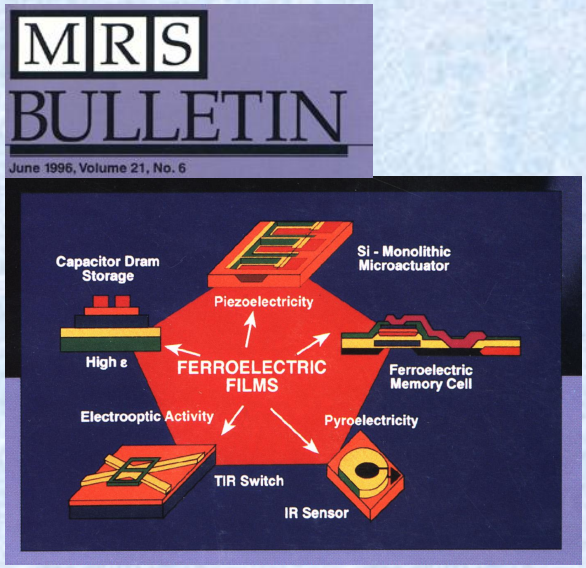
1998 Fabrication and switching in nanoscale ferroelectric structures (M. Alexe et al)

2002 Domain switching in FeRAM capacitors by PFM (A. Gruverman et al)

2003 First writing and imaging of 8 nm domains by SNDM (Y. Cho et al)

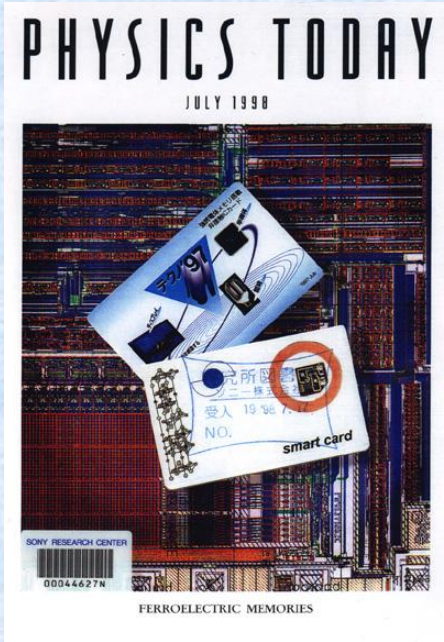
Ferroelectrics Today

Ferroelectrics have been around for more than 80 years;
Came to attention of engineers when barium titanate was discovered



Wide spectrum of properties and applications:

- Switchable polarization - nonvolatile FeRAM
- High dielectric constant - varistors, DRAM
- Piezoelectricity - transducers, actuators, MEMS
- Electro-optical activity - filters, switchers
- Pyroelectricity - IR sensors



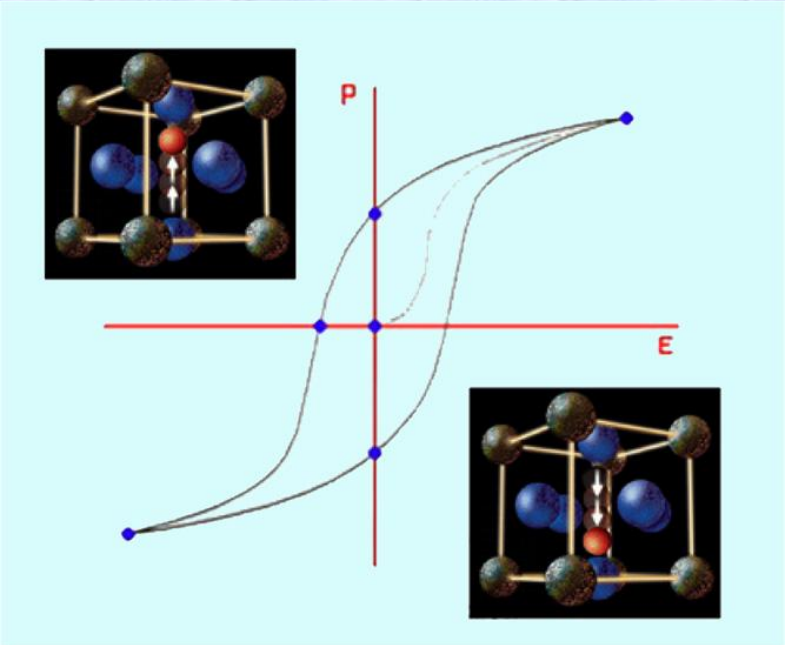
Novel applications:

- SPM-based ultra-high density data storage
- Ferroelectric lithography

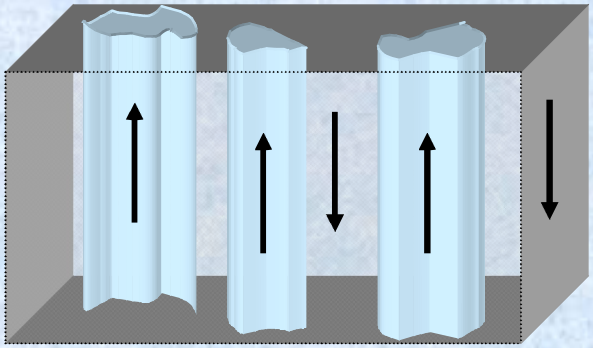
Ferroelectric Polarization

Free energy of the ferroelectric sample is reduced by domain formation and polarization screening

Ferroelectric Hysteresis
(polarization vs electric field)

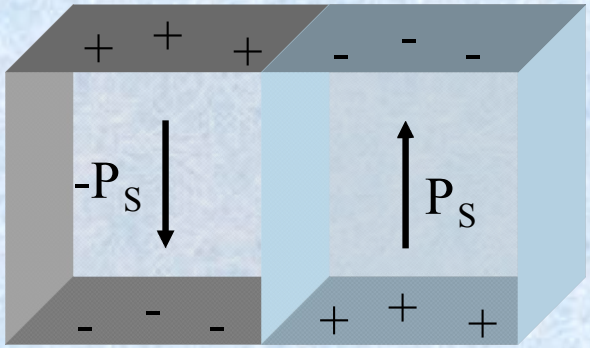


Domain formation

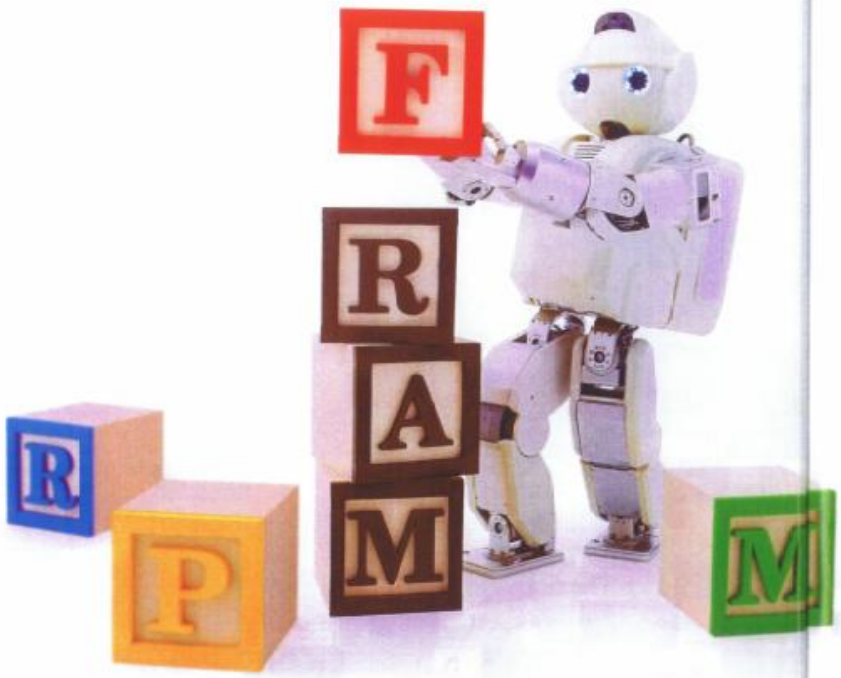


Domain wall width 1-2 unit cells

Screening of polarization



Random Access Memories



Resistive RAM (RRAM)
Phase-change RAM (PRAM)
Magnetic RAM (MRAM)
Ferroelectric RAM (FRAM)

THE POSSIBILITIES ARE INFINITE FUJITSU

選択は自由。
でも実績ある次世代メモリは、
FRAMだけです。

FRAMは、富士通が世界で初めて量産化。
高速書き込み/長寿命/省電力のアドバンテージで、
OA機器など幅広い用途で導入が進んでいます。

電源を切ってもデータを保持し、高速、高頻度で書き換え可能な次世代型不揮発性メモリ。多くのデバイスメーカーが開発を進めているなかで、いち早く量産化に成功したのが富士通のFRAMです。FRAMは、強誘電体膜をメモリセルに採用し、同じ不揮発性のE²PROMと比べ、書き込み回数約10万倍、書き込み時間1/30,000に下を実現します。しかも低消費電力で、E²PROMの置き換えや機器の性能向上、バッテリーレス化に貢献できることから、OA機器、AV、FA機器など幅広い用途で導入が進み、発売開始以来1億個を超える出荷実績を誇ります。今後、256Kビット、1Mビット品に加え、2Mビット品も発売予定。汎用メモリ製品の充実を図り、拡大するFRAMニーズにお応えしていきます。詳しい情報はこちらのホームページをご覧ください。<http://jp.fujitsu.com/microelectronics>

High Speed
FRAM
Power-Saving
Random Access

[FRAMメモリLSI製品ラインナップ]

■パラレルインターフェースFRAM

型番	FRAM容量	構成	アクセスタイム	電源電圧
MB85R256H	256Kビット	32K×8	70ns	2.7～3.6V
MB85R1001	1Mビット	128K×8	100ns	3.0～3.6V
MB85R1002	1Mビット	64K×16	100ns	3.0～3.6V

■シリアルインターフェースFRAM

型番	FRAM容量	構成	アクセスタイム	電源電圧
MB85RS256	256Kビット	32K×8	15MHz	3.0～3.6V

[利用分野(例)]

■多機能プリンタ
カウンタ、印刷管理、通信履歴管理
■オーディオ、ゲーム
リジュームデータ保存
■FA、計測機器
パラメーター設定、測定値設定
■デジタルカメラ、ビデオカメラ
撮影条件設定、補正値設定
■自動車、金融端末、自販機
取引履歴、バックアップ

※写真のロボットは、(株)富士通研究所と富士通データ・オペレーション(株)が共同開発した二足歩行型ヒューマノイドロボット「HOAP-3」

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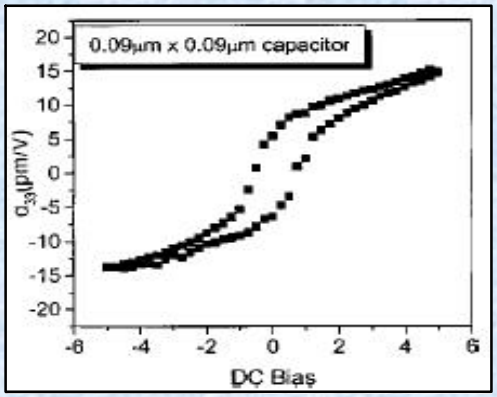
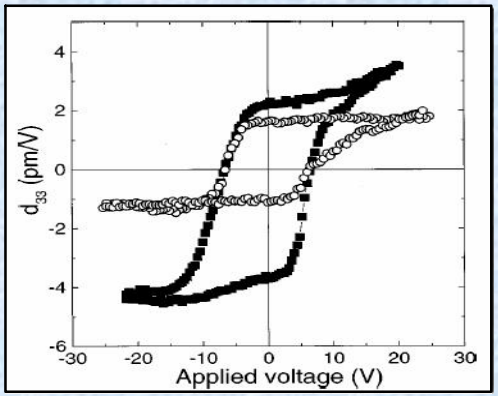
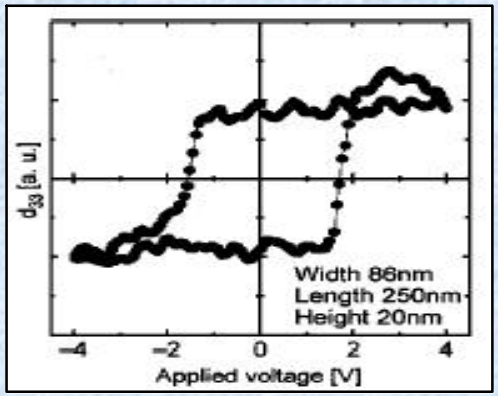
Ferroelectric Nanostructures



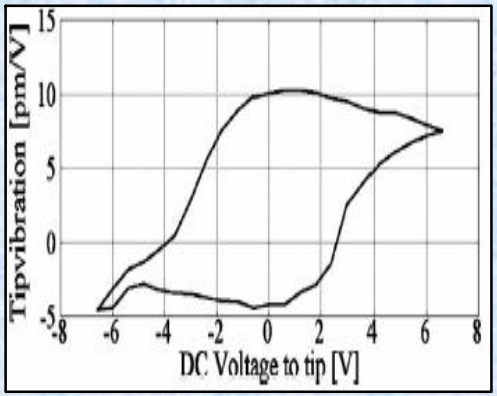
FIB-fabricated PZT capacitor
Ganpule et al, APL 75 (1999)



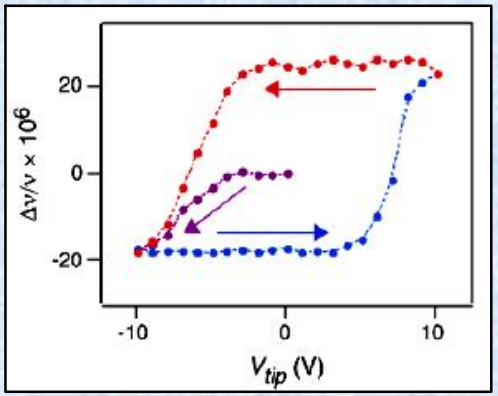
PZT cell array
Alexe et al, APL 75 (1999)



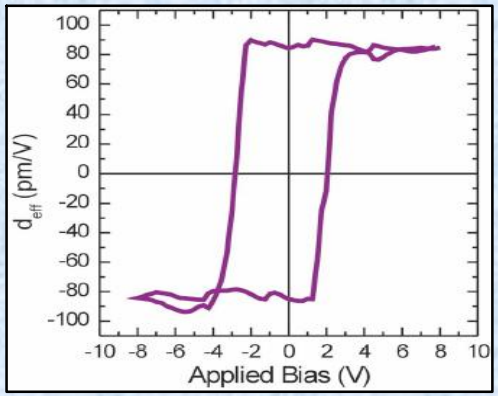
$PbTiO_3$ nanoislands
Nonomura et al, APL 86 (2005)



$PbTiO_3$ nanoislands
Buhlmann et al, APL 84 (2004)



$BaTiO_3$ nanowire
Yun et al, Nano Letters 2 (2002)



SBT nanotubes
Morrison et al, J. Phys. Cond. Matt. 15 (2003)

PFM allows testing the switching behavior of ferroelectric nanostructures

PFM: Ferroelectrics at the Nanoscale

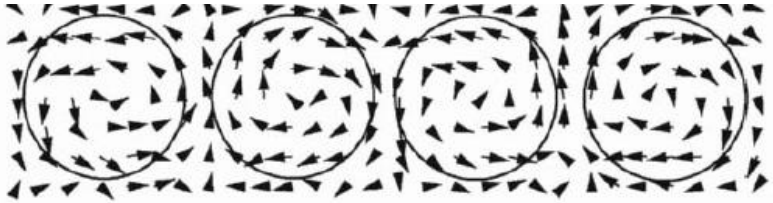
Fundamental issues

- High-resolution characterization
  Polarization mapping, local switching spectroscopy
- Investigation of size effects
  Instability of polar phase
- Control of local properties
  Manipulation of nanodomains

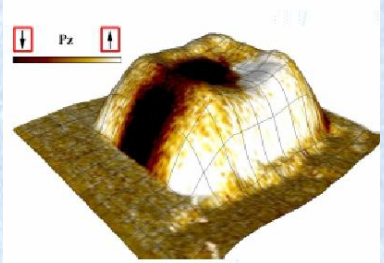
Application issues

- Testing microdevices
  High-density FeRAM, MEMS
- Addressing reliability issues
  Imprint, fatigue, dielectric breakdown
- Nanofabrication tool
  Ferroelectric lithography, data storage

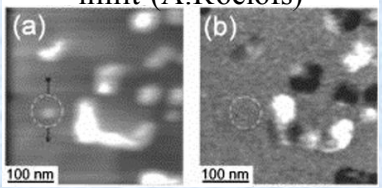
Local dipoles in PZT nanoparticles at low T (I.Naumov)



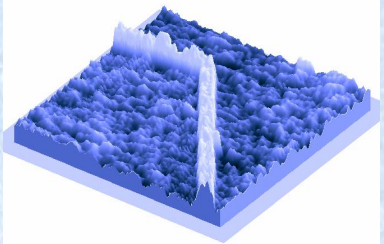
PZT nanocell (M.Alexe)

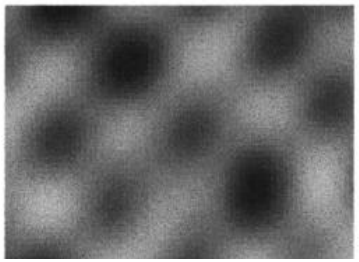


Testing the paraelectric limit (A.Roelofs)

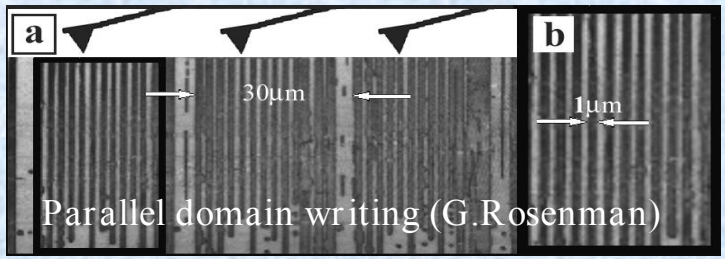


Ag nanowire on LNO





Tbit density data storage in LTO (Y.Cho)

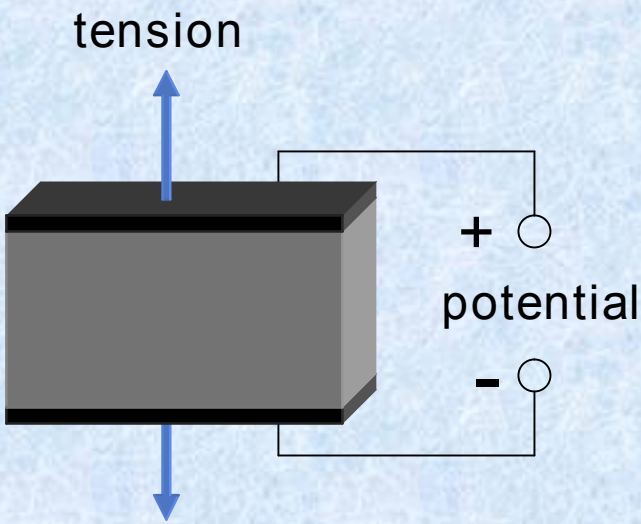


Parallel domain writing (G.Rosenman)

Principles of Piezoresponse Force Microscopy

- Experimental setup
- Elementary theory
- Local vs integral
- Vertical and Lateral PFM
- 3-dimensional PFM

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):

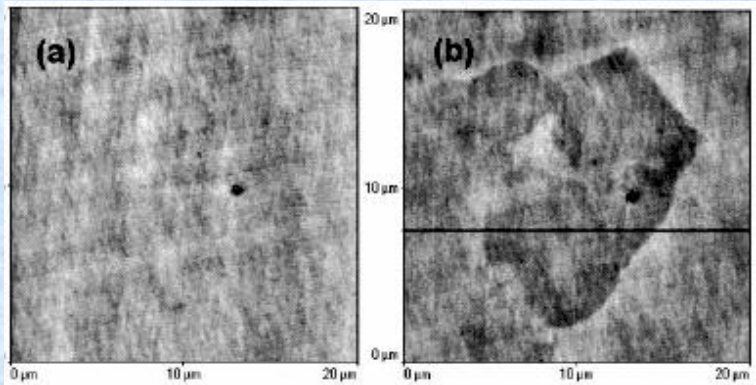
$$\begin{pmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{pmatrix}$$

Non-zero elements are determined by symmetry

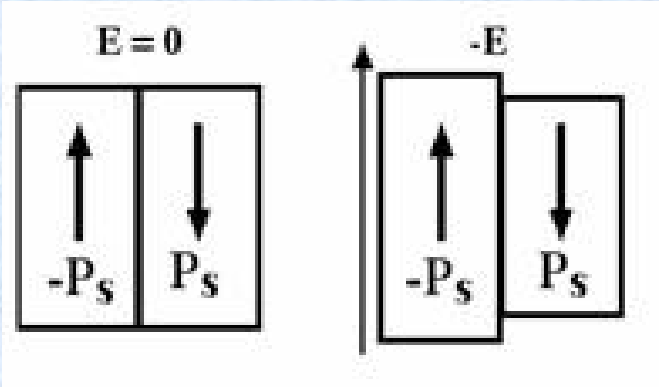
Domain Imaging via Static Piezoresponse

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:

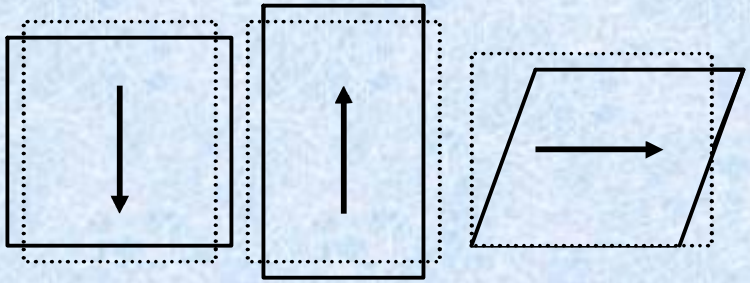
- The higher V, the better domain resolution
- Non-destructive imaging requires that $V < V_c$

Dynamic Piezoresponse increases sensitivity by 3 orders of magnitude

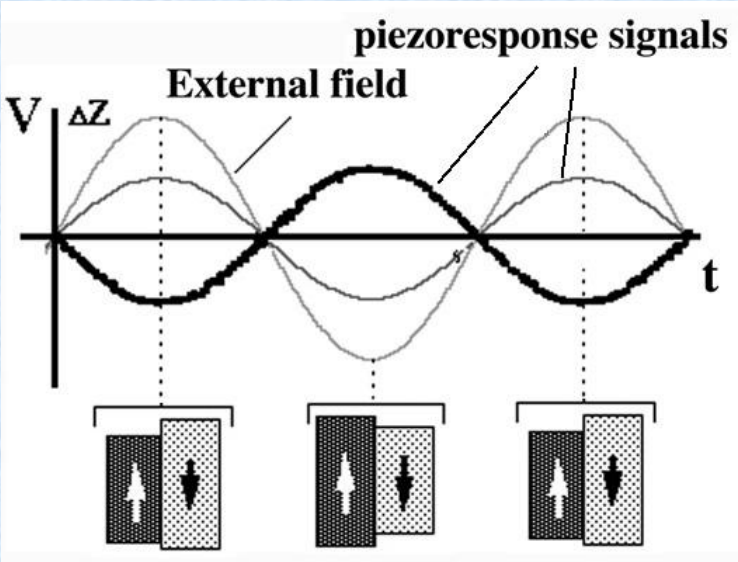
Principle of PFM

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

Field is on



Strain is polarization dependent



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

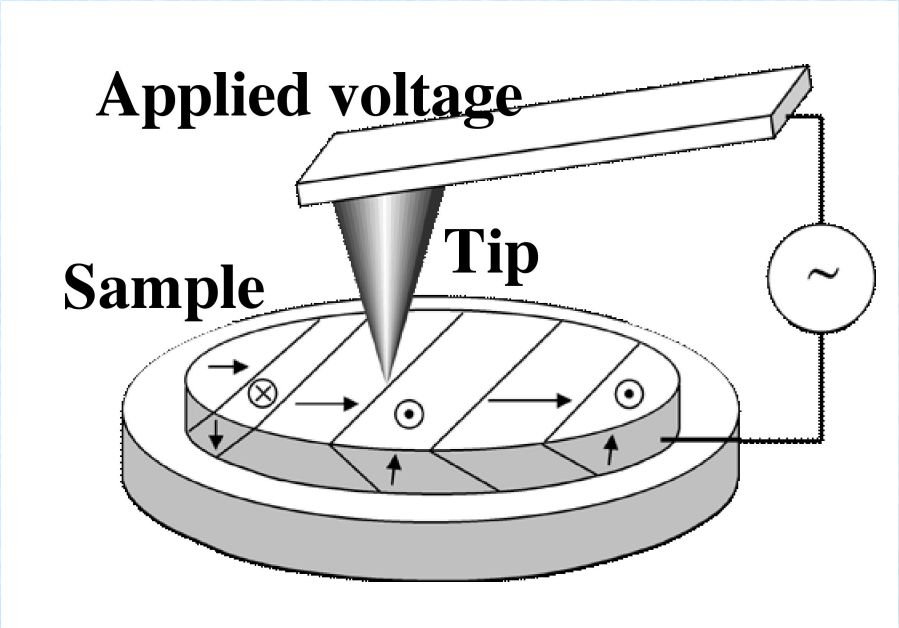
Under modulation voltage $V = V_0 \cos(\omega t)$, surface vibrates as $\Delta L = \Delta L_0 \cos(\omega t + \varphi)$

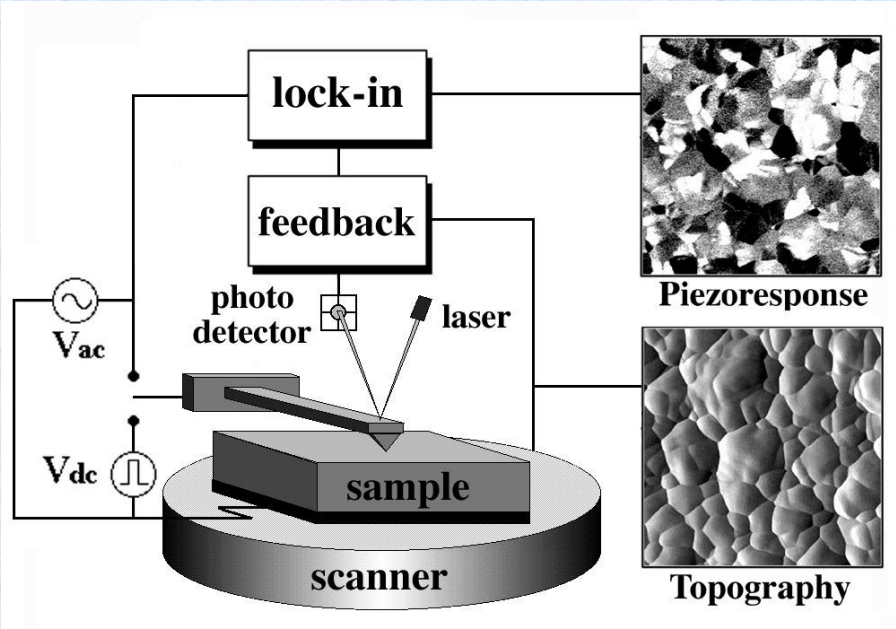
For P^+ (⬇), φ=0º

For P^- (⬆), φ=180º

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

PFM Experimental Setup





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

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

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)

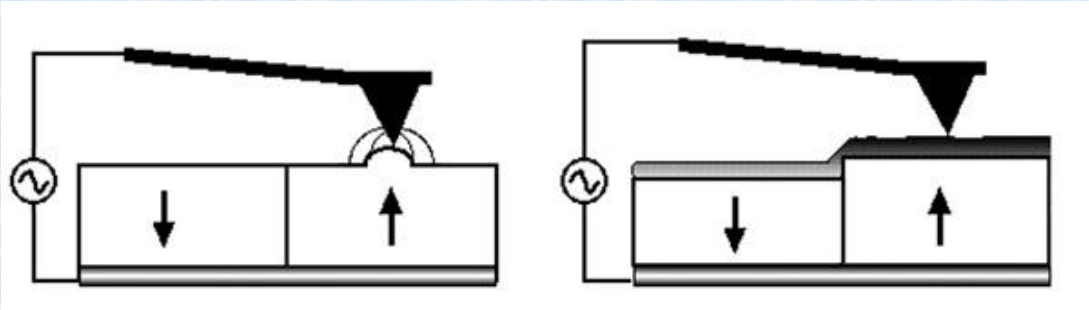
$$d_{33} = 2\chi_{33}Q_{33}P_{s3}$$ Expansion/contraction

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

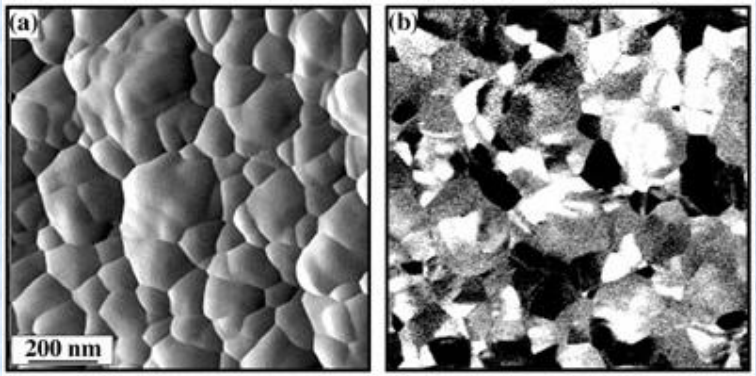
$$d_{34} = 2\chi_{33}Q_{44}P_{s2}$$ Shear

Cancelled out

Local vs Integral Excitation (Thin Films vs Capacitors)

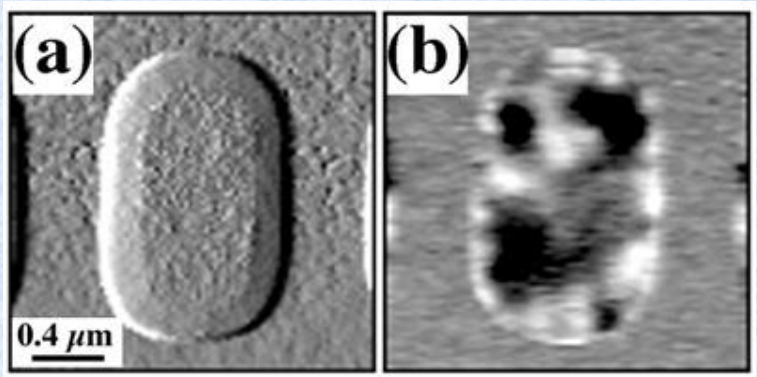


PZT thin film



Topography Piezoresponse

PZT capacitor



Topography Piezoresponse

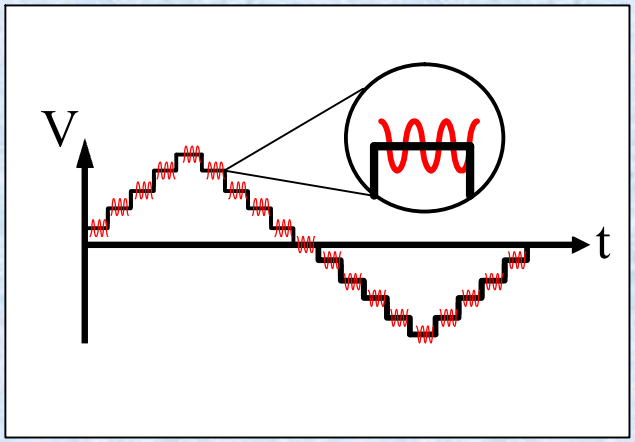
Local vs Integral Excitation (Thin Films vs Capacitors)

METHOD OF EXCITATION	ADVANTAGES	DRAWBACKS
Local (through the tip)	High lateral resolution Correlation between domain patterns and microstructure Control of nanoscale domains Analysis of domain wall structure and its interaction with microstructural features	Highly inhomogeneous electric filed Possible effect of surface contamination Difficult to quantify Asymmetric boundary conditions
Integral (through the top electrode)	Homogeneous electric field No electrostatic contribution Quantitative characterization	Lower lateral resolution Detrimental effect of top electrode on imaging resolution

PFM Spectroscopy: Local Hysteresis Measurements

Two different measurement procedures

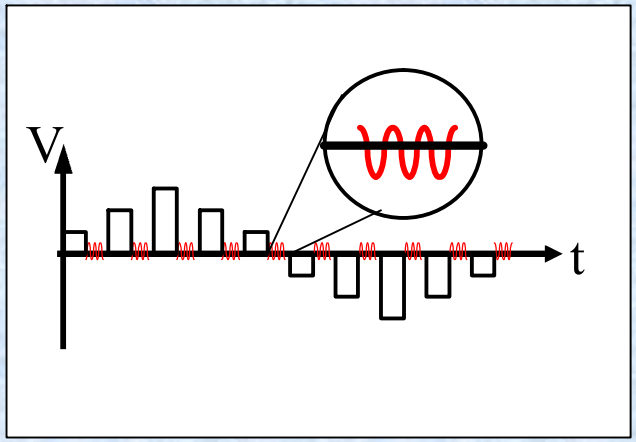
Step mode



In this mode, PFM signal can be affected by capacitance signal, hence it is more suitable for capacitors

Local PFM data can be directly related to the average macroscopic response

Pulse mode

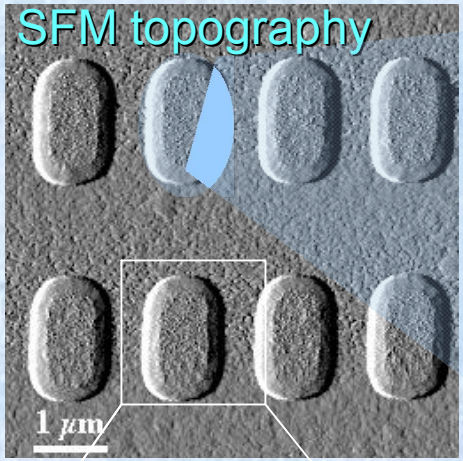


Capacitance signal is less significant, hence, it can be applied to thin films

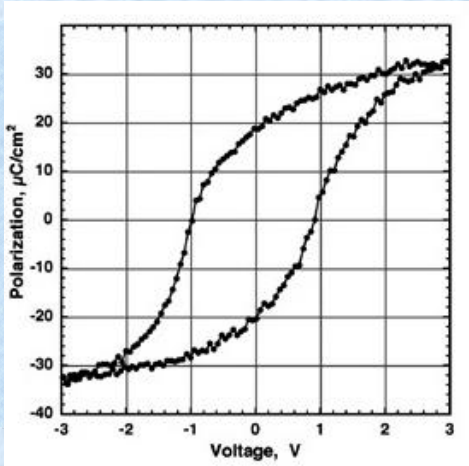
Measurements can be affected by the backswitching effect

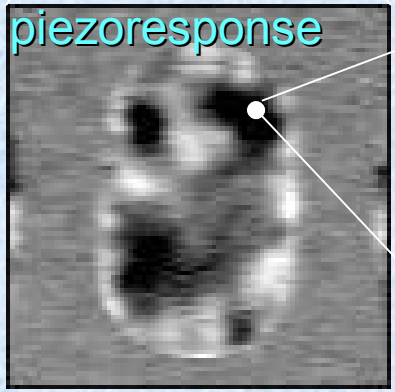
Testing FeRAM Capacitors

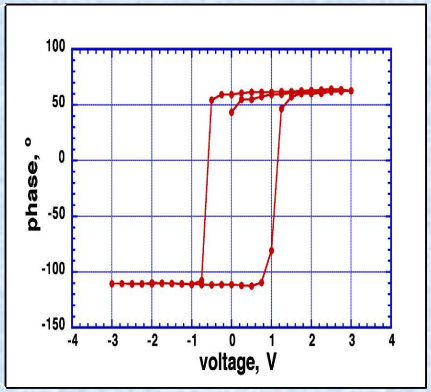
FeRAM PZT capacitors



Polarization loop







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

Separate Recording of Phase and Amplitude in PFM

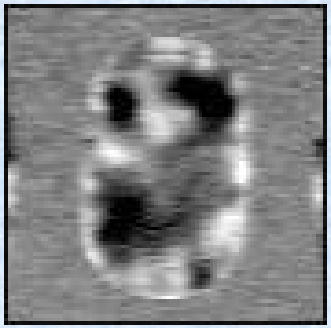
PFM provides information on local switching behavior within a capacitor
Measures absolute value of piezoelectric constant

Phase recording:

polarization direction

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

Mixed PFM image

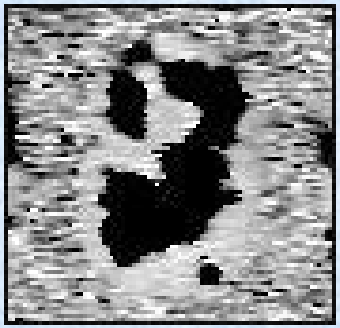


Amplitude recording:

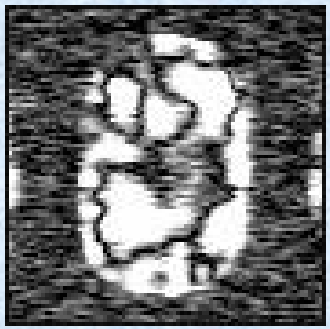
switchable volume

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

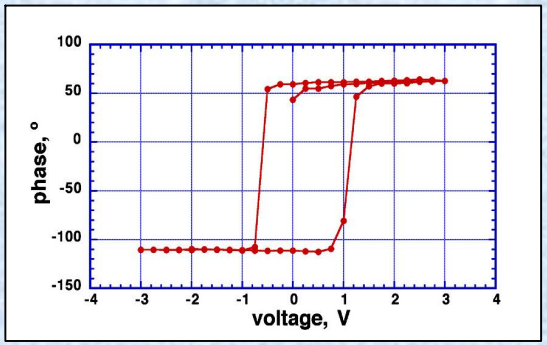
Phase image



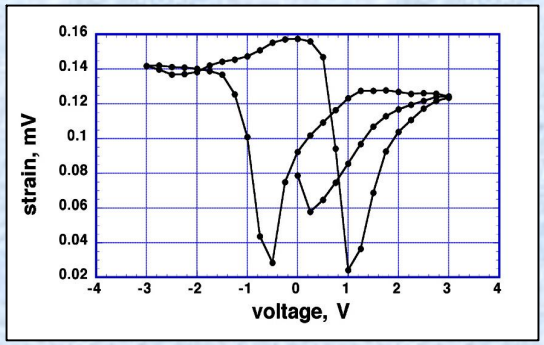
Amplitude image



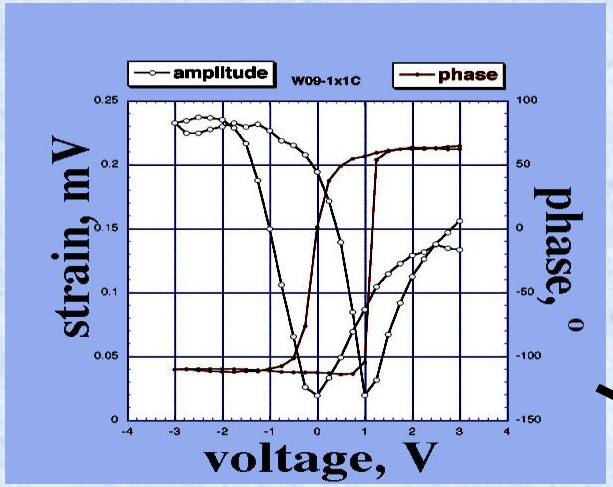
Phase loop

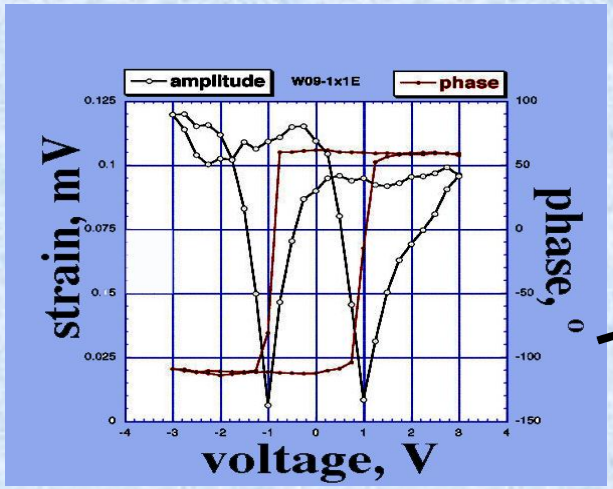


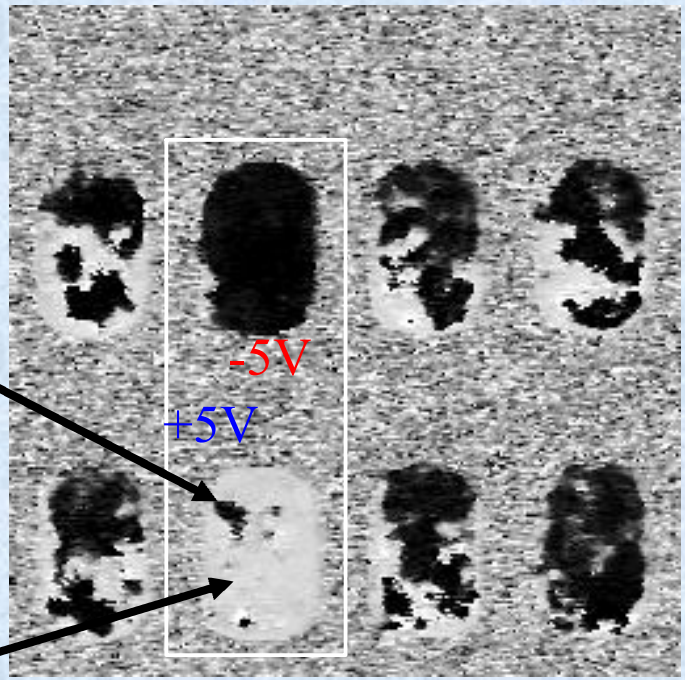
Amplitude loop



PFM: Addressing Random Bit Failure in FeRAM



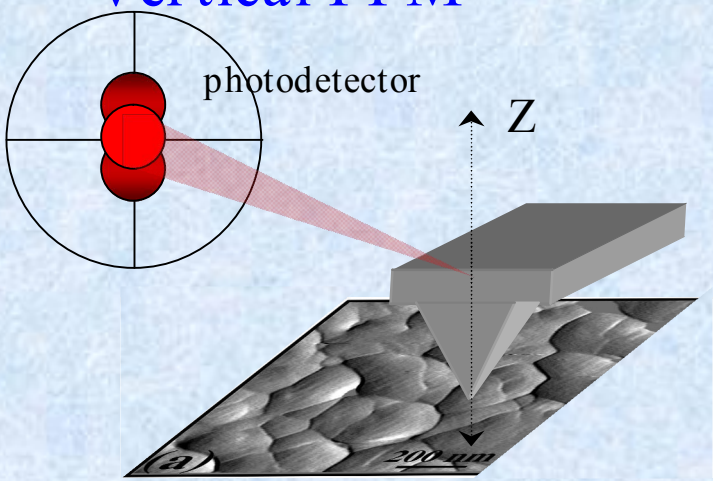




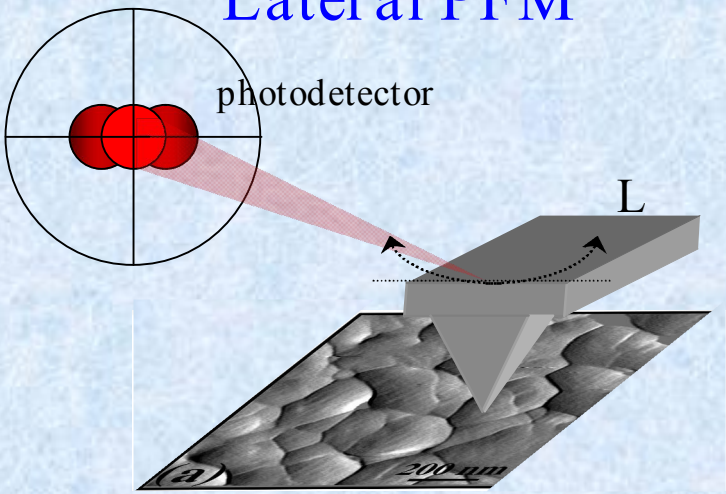
PFM allows localization of failing regions in FeRAM capacitors and assessment of mechanical stress and processing conditions on switching.

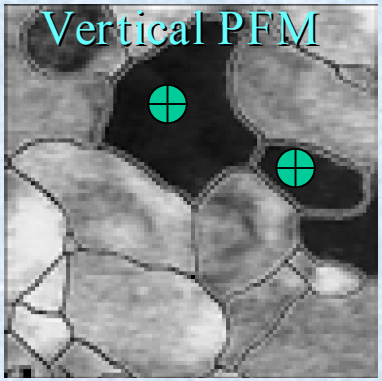
Schematics of Vertical and Lateral PFM detection

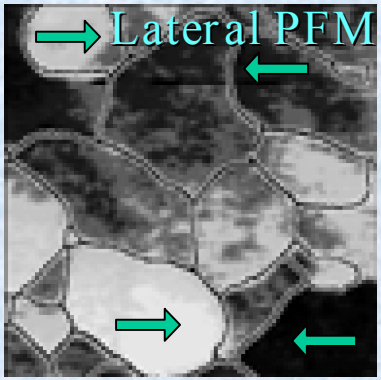
Vertical PFM



Lateral PFM







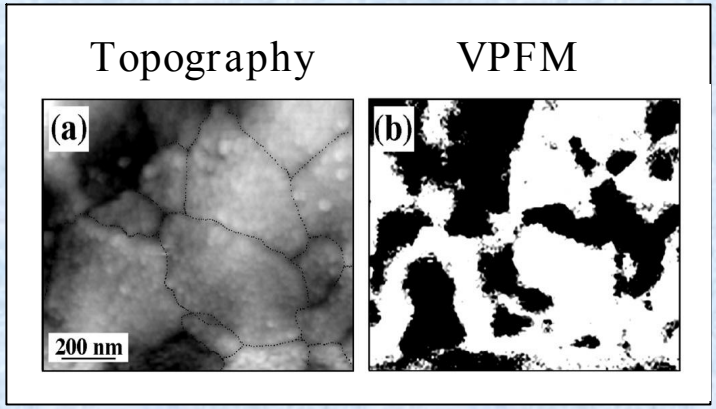
$$\Delta Z = \pm d_{33} V \cos(wt + \varphi)$$

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

Vertical + Lateral PFM(x,y) = vector PFM

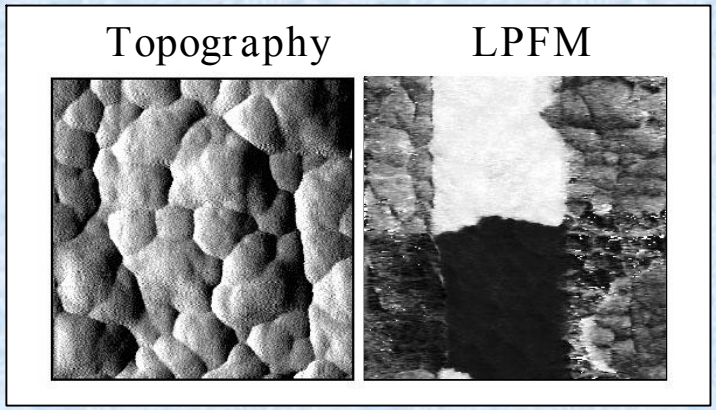
PFM: Out-of-Plane vs In-Plane Polarization

PZT (001) film



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

$PbTiO_3$ (100) film



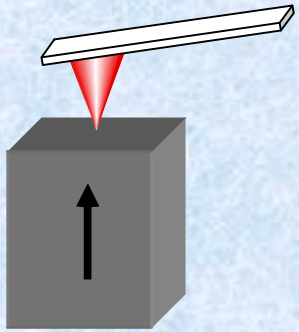
Tetragonal perovskite

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

Vertical PFM

Lateral PFM (x)

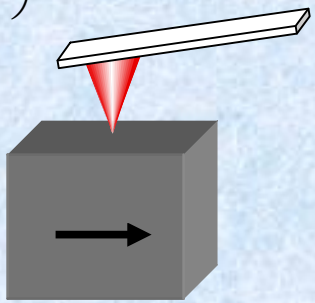
Lateral PFM (y)



Rotated by 90°

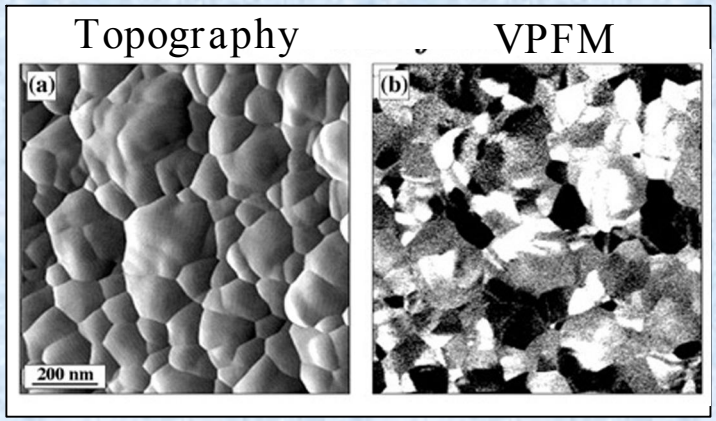
$$\begin{pmatrix} 0 & 0 & 0 & 0 & 0 & d_{15} \\ d_{31} & d_{33} & d_{31} & 0 & 0 & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \end{pmatrix}$$

Lateral PFM (x)

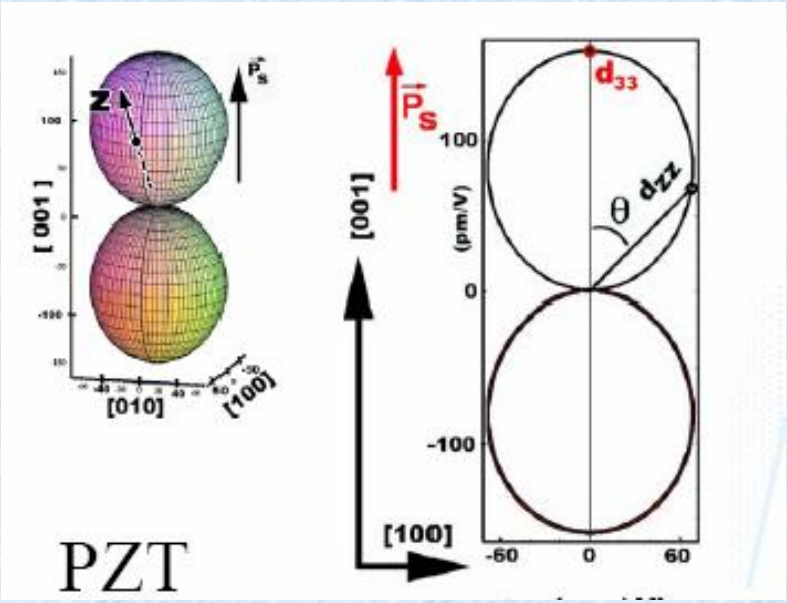


PFM of Polycrystalline Ferroelectrics

Randomly oriented grains



VPFM surface for tetragonal $Pb(Zr,Ti)O_3$



Randomly oriented grains:

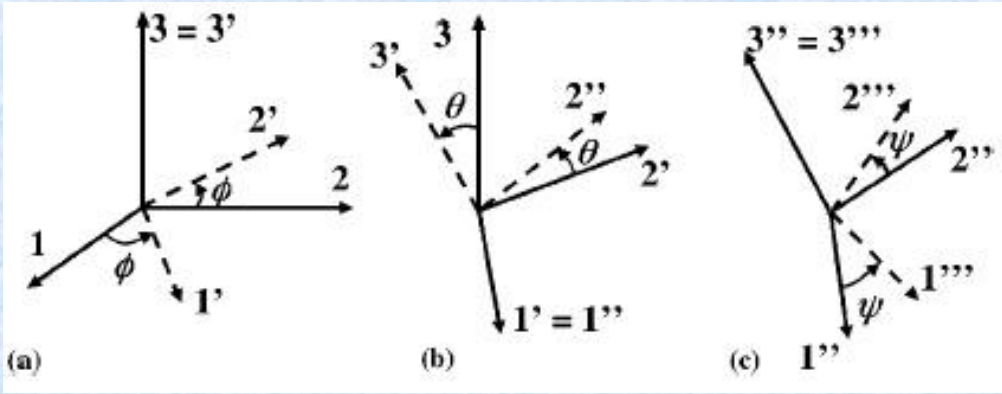
- P_s is not proportional to d_{33}
- Lateral components are non-zero
- Signal depends on d_{33}, d_{31}, d_{15}

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

Du et al, Jpn. J. Appl. Phys. 36, 5580 (1997)
Harnagea et al, Int. Ferroel. 38, 23 (2001)

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 (Kalinin et al, Microsc. Microanal., 2006)

In general case:

VPFM:

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

LPFM:

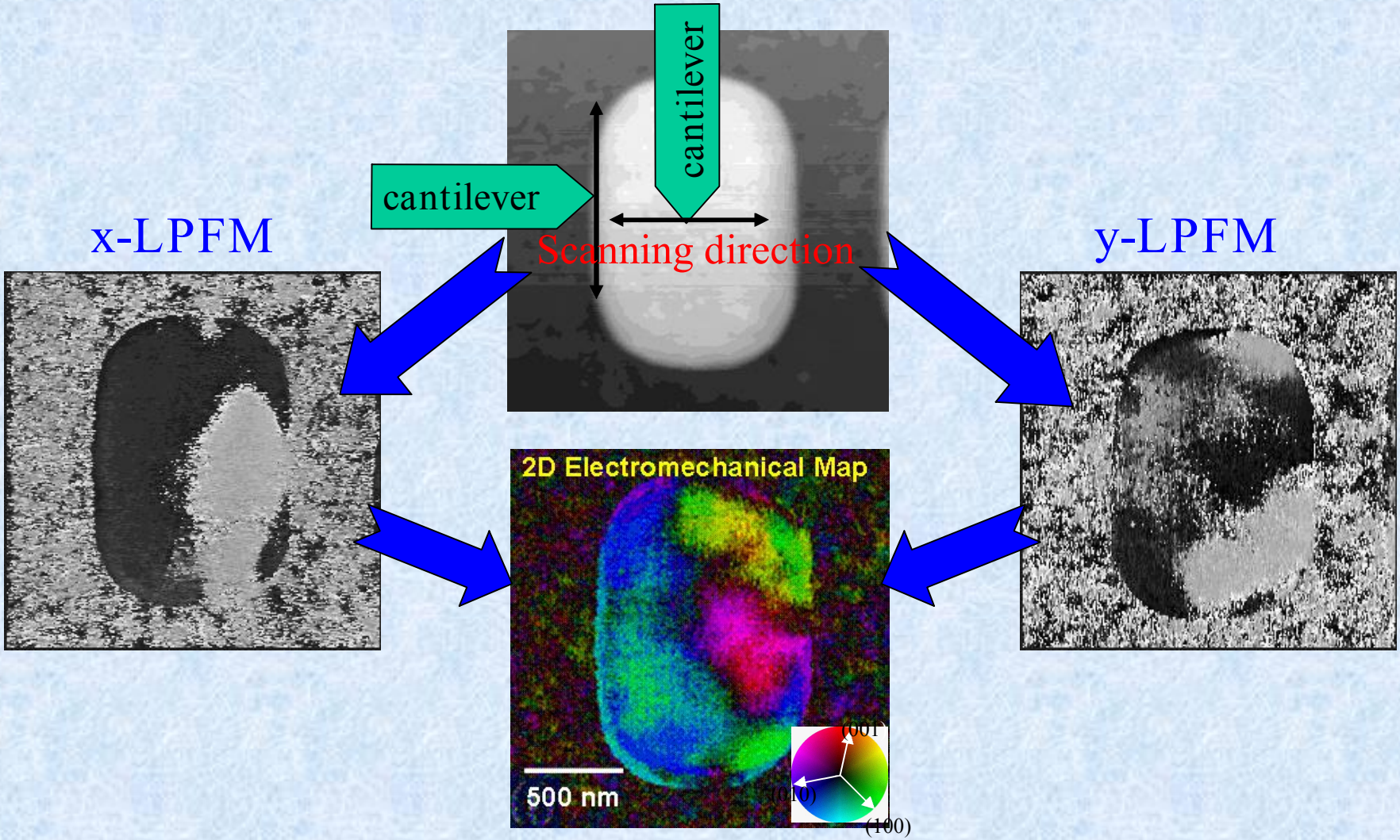
$$d_{zx} = -(d_{31} - d_{33} + (d_{15} + d_{31} - d_{33})\cos 2\theta)\cos\psi\sin\theta$$

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

- 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

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)

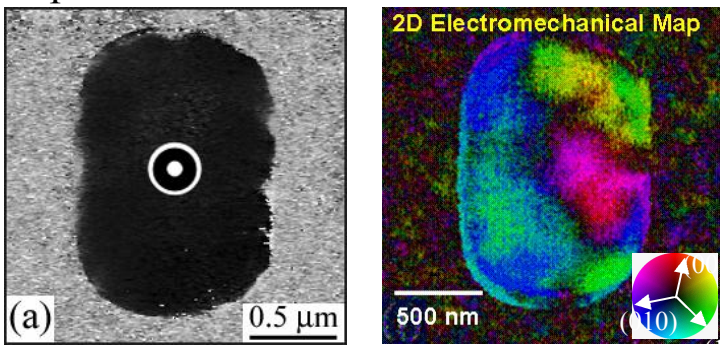
VPFM: $d_{zz}(\theta) = (d_{31} + d_{15})\sin^2\theta\cos\theta + d_{33}\cos^3\theta$

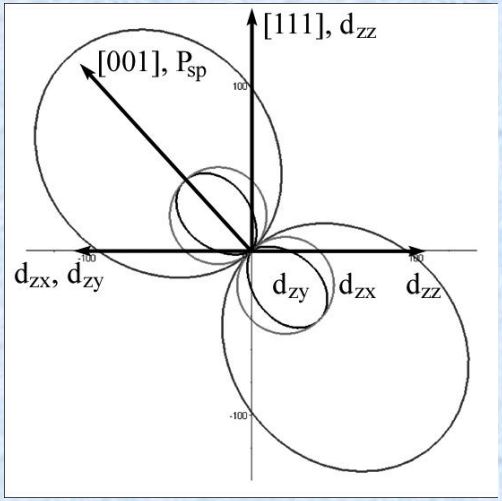
x-LPFM: $d_{zx}(\theta) = d_{31}\cos\theta$

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

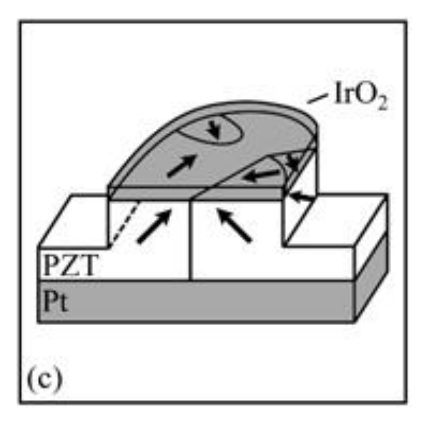
Out-of-plane polarization

2D in-plane map





3D reconstruction

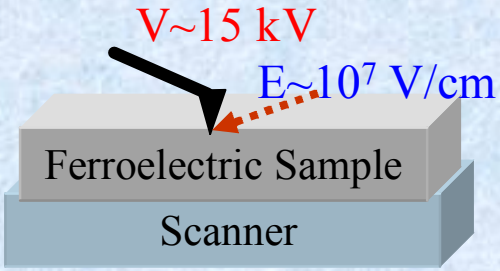


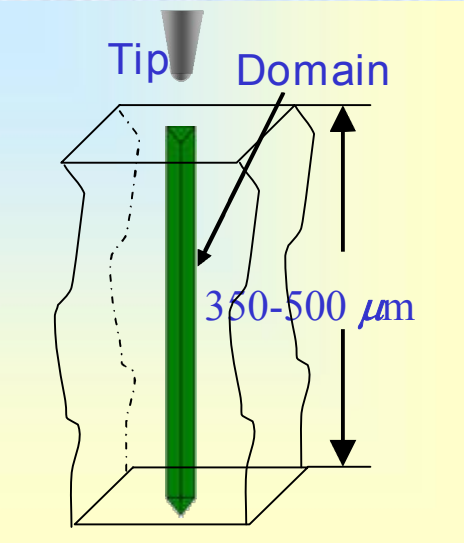
- Poled capacitors, which appear uniformly polarized in VPFM, are in fact in a polydomain state

B.J.Rodriguez, et al, Appl. Phys. A 80, 99 (2005)

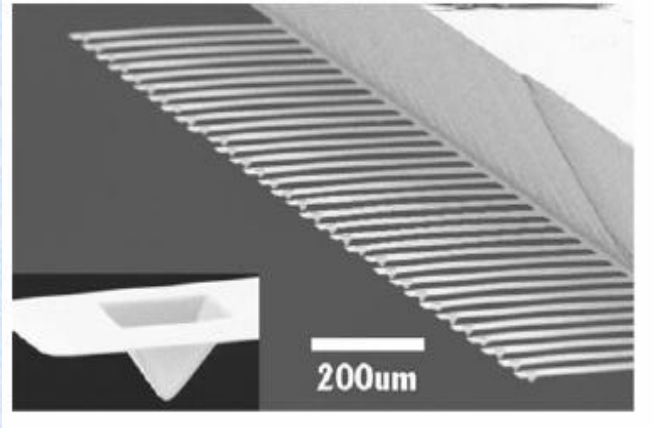
Nanodomain Engineering in Bulk Ferroelectrics

New phenomenon:
Domain breakdown

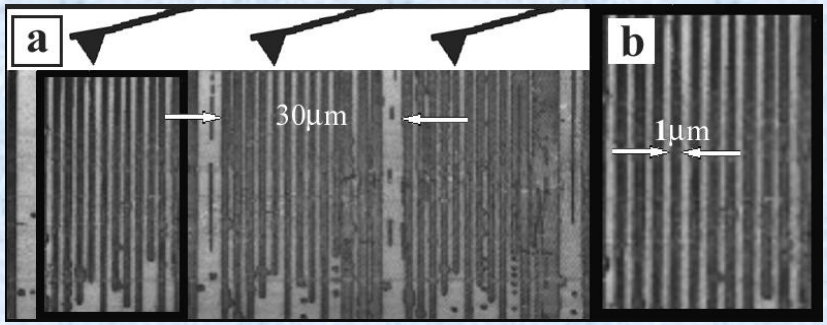




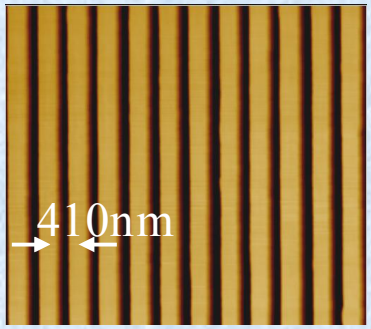
2D AFM tip array (Nanoink Inc.)



Parallel domain writing in RTP crystal



Nanodomain gratings in $LiNbO_3$ crystals
(500 μm thick)



Application in a new generation of
photonic and microelectronic devices

G. Rosenman, Y. Rosenwaks, P. Urenski, US Patent, 2003
G. Rosenman, et al, APL, 82, 103 (2003)

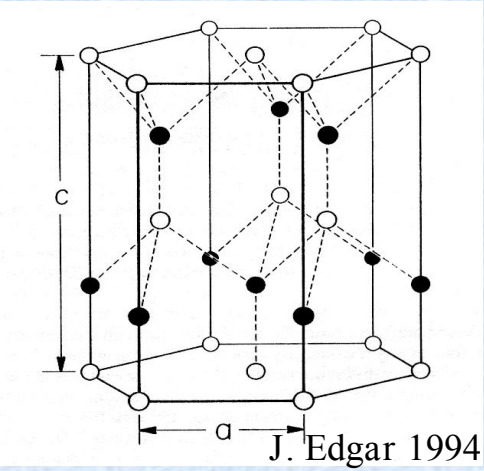
Slide courtesy of G. Rosenman

PFM Characterization of III-Nitride Materials

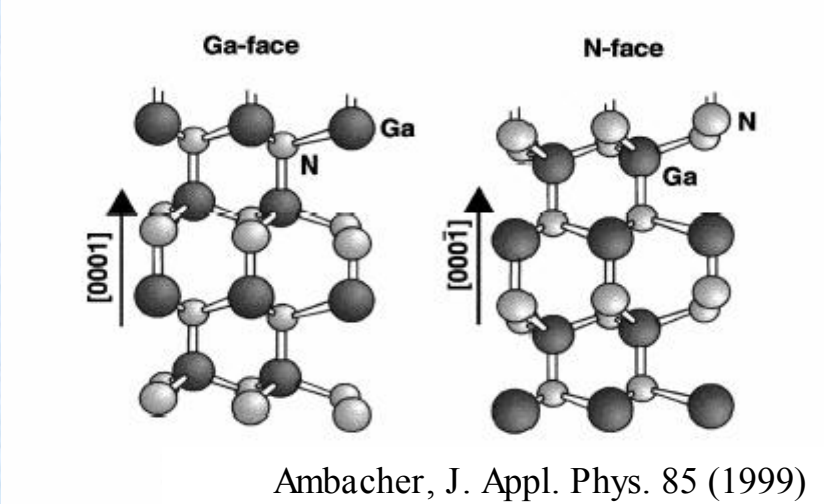
- Spatial variations and detection of inverse domains

PFM Studies of III-Nitrides

- Wurtzite Crystal Structure
- Piezoelectric and pyroelectric
- Crystals of opposite polarity will oscillate 180° out-of-phase



J. Edgar 1994

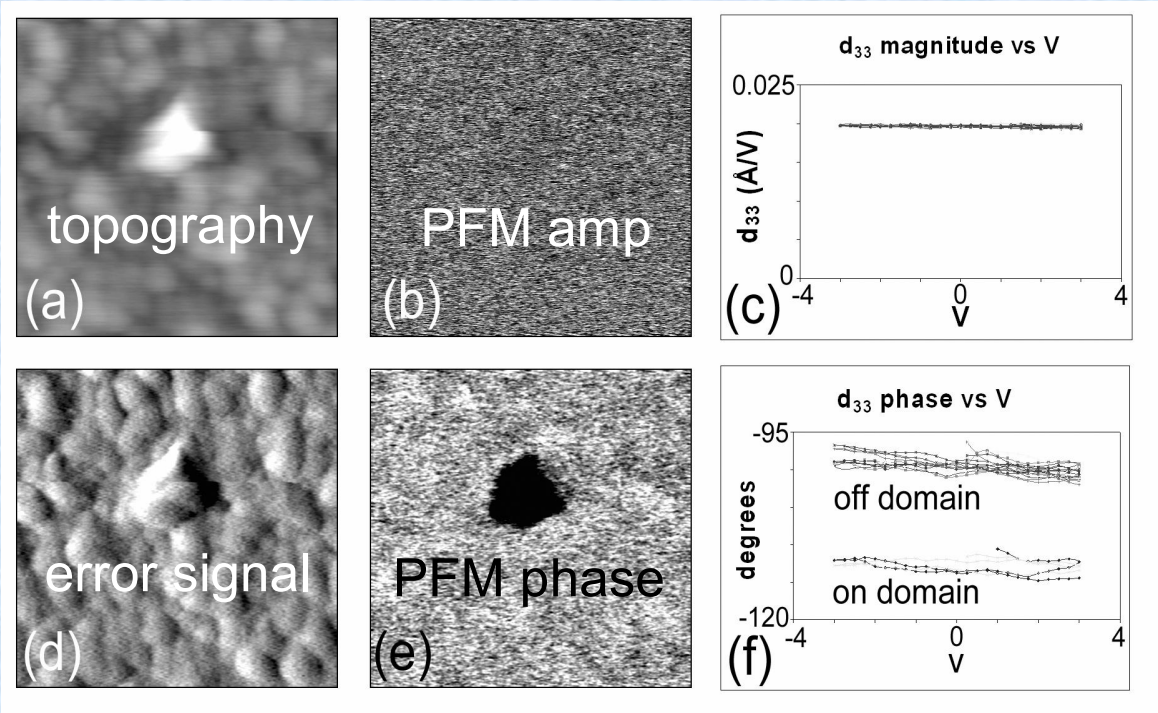


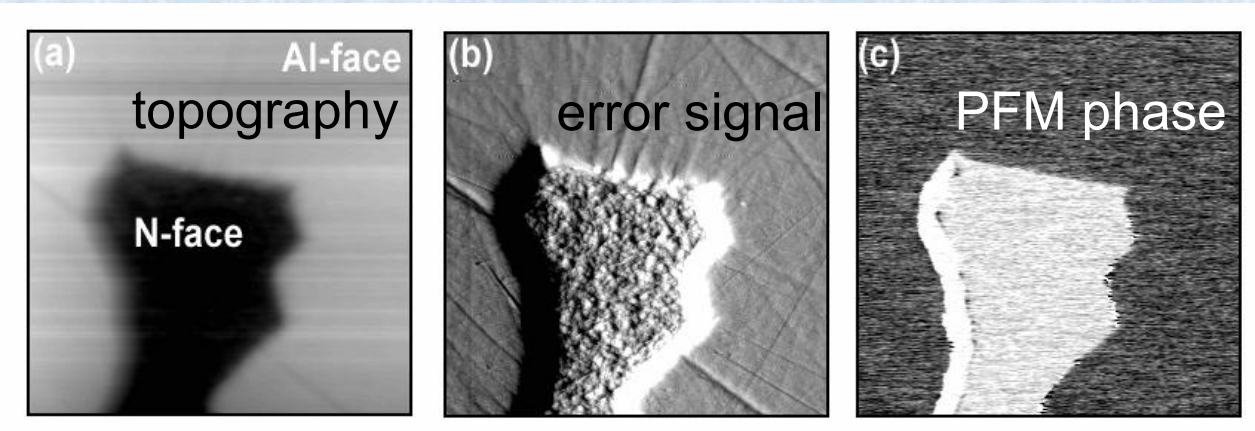
Ambacher, J. Appl. Phys. 85 (1999)

Each face has a different surface termination

PFM of AlN Thin Films and Crystals

Sputtered N-face AlN thin film with Al-face inversion domains
1.5 x 1.5 μm^2





AlN bulk crystal with N-face inversion domains grown by physical vapor transport
20 x 20 μm^2

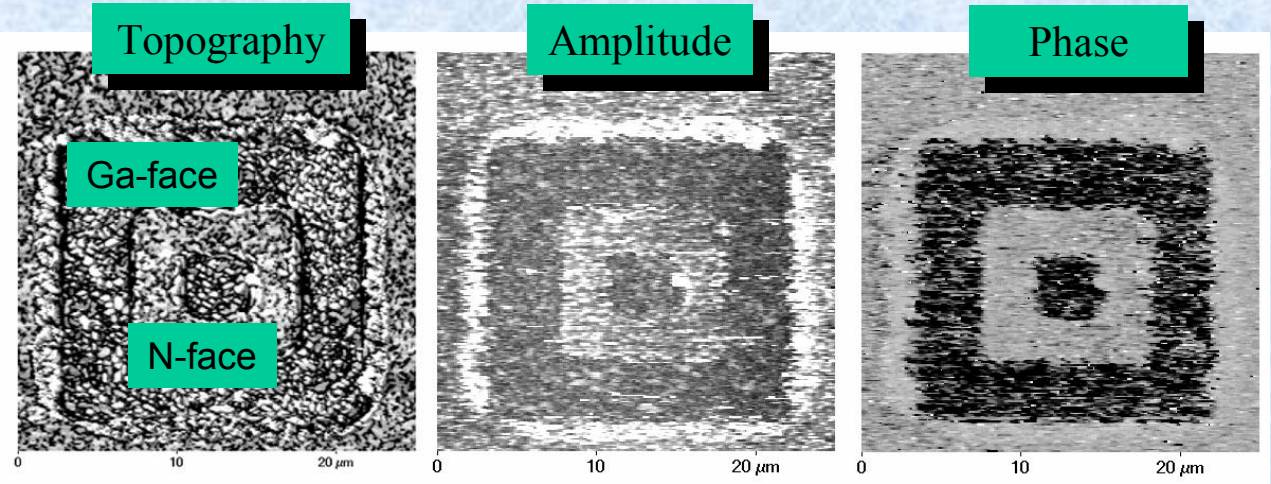
J. Cryst. Growth 281, 2005 & 246, 2002

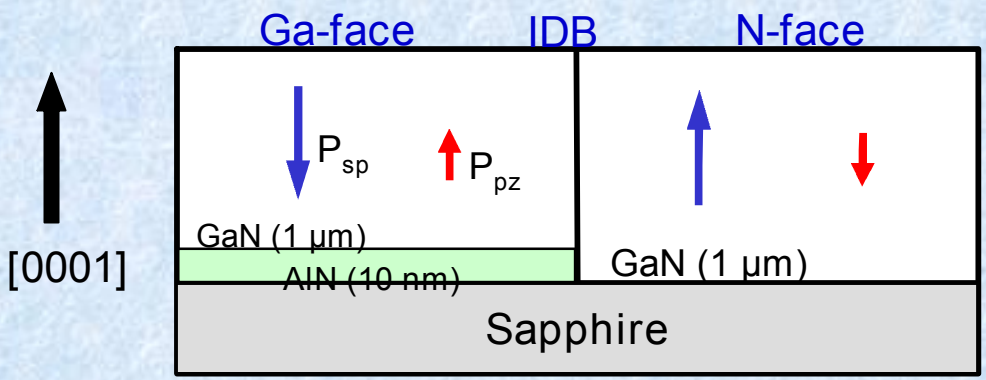
Sample courtesy of R. Dalmau, NCSU

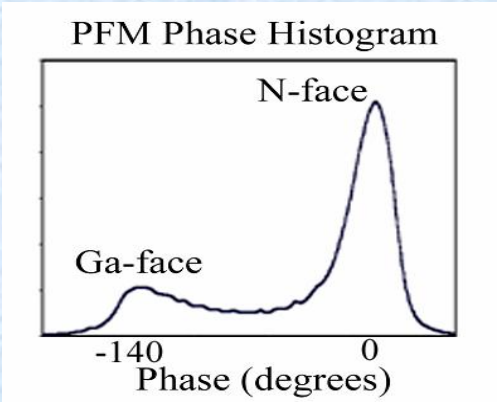
PFM Imaging of Ga- and N-Face GaN

- Previous example: PFM detected unwanted domains detrimental for device performance
- Now: controlled polarity growth of adjacent domains – lateral polarity heterostructure

PIMBE grown GaN with alternating concentric squares of Ga- and N-faces







Rodriguez et al, APL (2002)

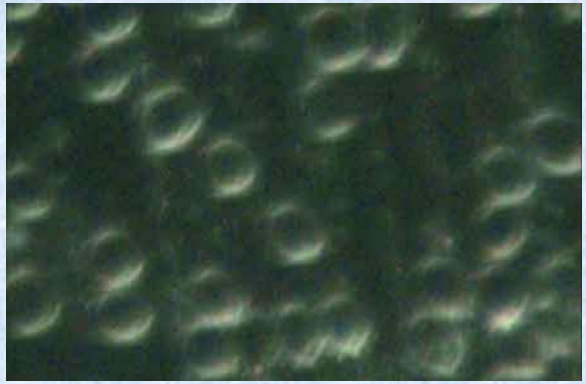
PFM Characterization of Biomaterials

- Electromechanical coupling and physical basis for biopiezoelectricity
- Nanoscale imaging of dental tissues: proteins vs mineralized matrix
- Molecular imaging

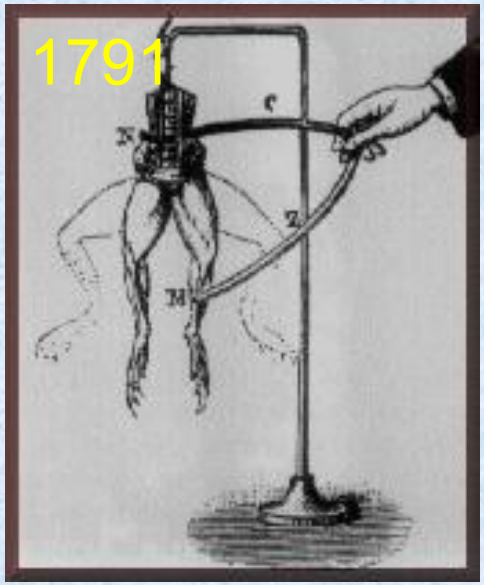
Electrical Phenomena in Biological Systems

Blackdevil angler fish uses bioluminescent to attract prey. Photo credit: Edith Widder/HBOI

The electric eel can generate a shock potential of up to 800 V



Surface charge of blood cells helps absorb nutrients, water or oxygen and to release toxins

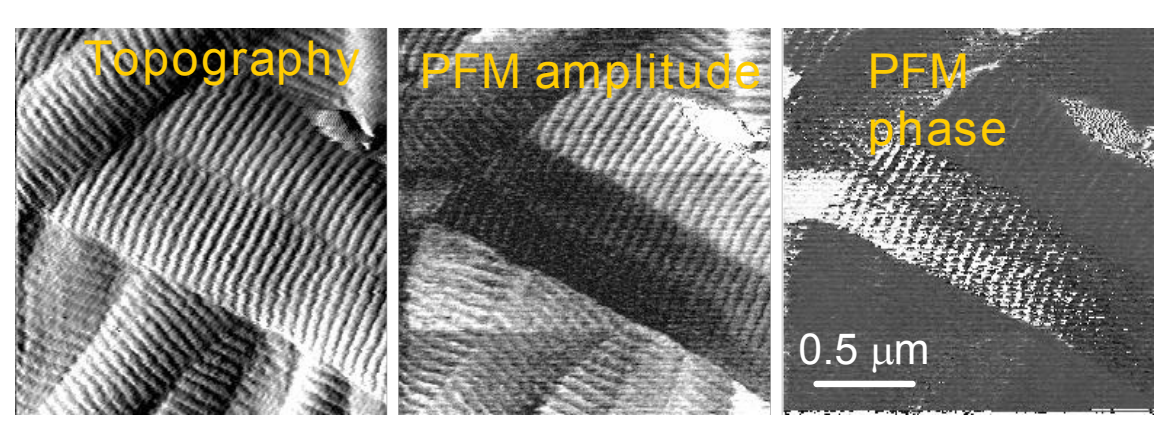


- Electrical phenomena in biosystems are known since Aristotle (650 AD)
- First scientific studies of biological electric potential by Galvani (1791): muscle contraction under an electric bias
- Living tissues display different type of electrical activity related to their functionaity: biorheology

Experimental observations of piezoeffect in biomaterials:

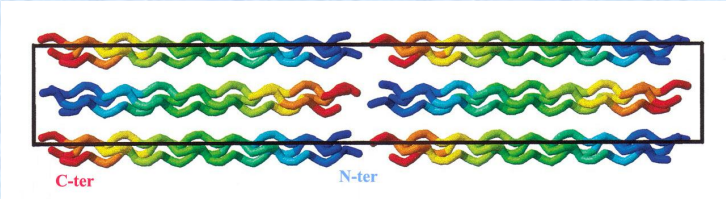
- Wood (Shubnikov, 1946; Bazhenov, 1950)
- Bone, tendon, silk, wool, fibrous proteins (Fukada, 1960)
- Collagen, cellulose, keratin

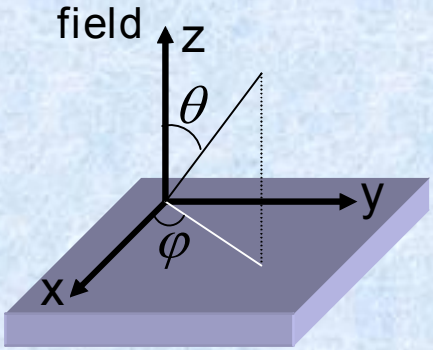
PFM Imaging of Collagen



Piezoelectric tensor of collagen

$$\begin{bmatrix} 0 & 0 & 0 & d_{14} & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & -d_{14} & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}$$





VPFM:

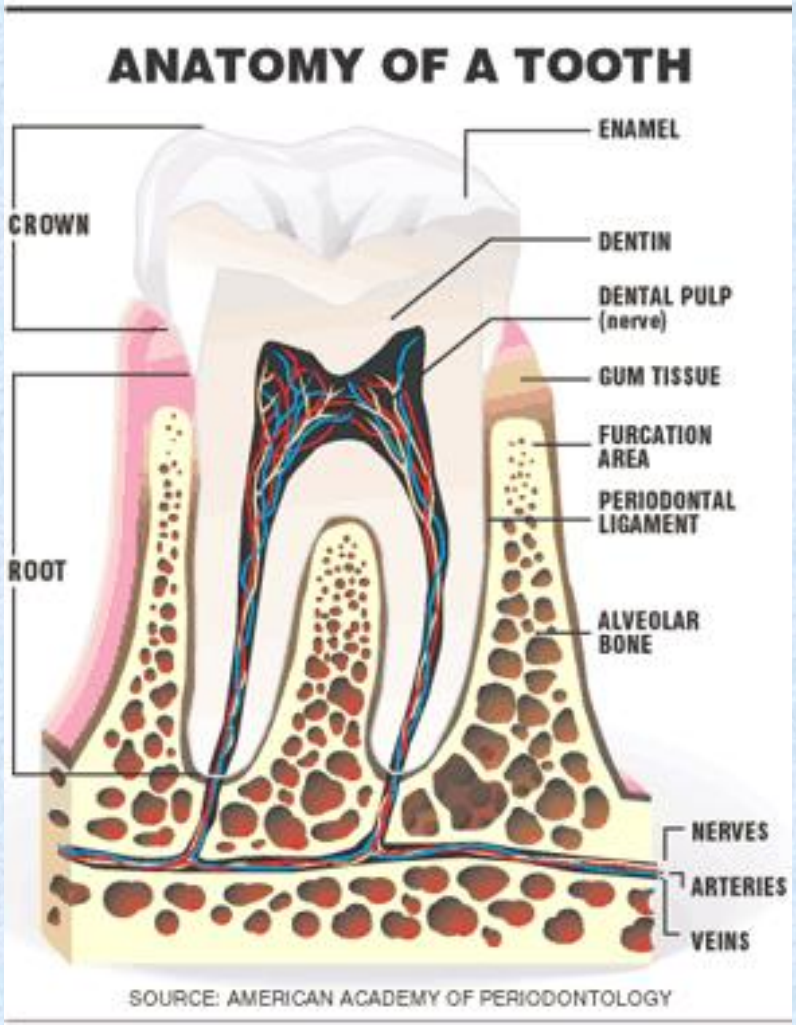
$$d_{33}^{1} = 0.5\cos\theta(d_{15} + d_{31} + d_{33} - (d_{15} + d_{31} - d_{33})\cos 2\theta)$$

LPFM:

$$d_{34}^{1} = -((d_{15} + d_{31} - d_{33})\cos 2\theta)\cos\varphi + d_{14}\cos\theta\sin\varphi)\sin\theta$$

$$d_{34}^{1} = -((d_{15} + d_{31} - d_{33})\cos 2\theta)\sin\varphi - d_{14}\cos\theta\sin\varphi)\sin\theta$$

Anatomy of a Tooth



Enamel - the outermost layer of tooth, elastic modulus 130 GPa (as hard as Ti)
Dentin - bulk of the tooth, elastic modulus 15 GPa

Dentine and enamel consist of the same calcium-phosphate crystal (hydroxyapatite, or HAP, $Ca_{10}(OH)_2(PO_4)_6$) but have different mechanical properties as they differ by the content of organic fibers.

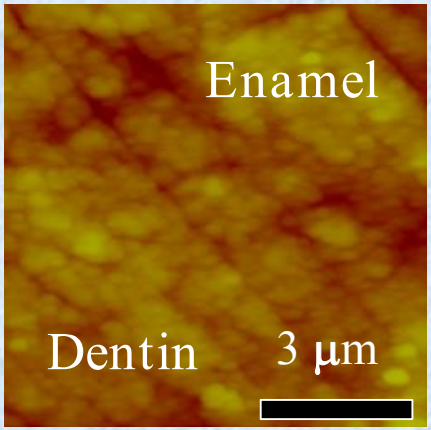
Enamel: 3-8% of enamelins and amelogenins;
Dentin: 30-40% of mostly collagen

HAP: centrosymmetric – no piezoelectric behavior
Collagen: non centrosymmetric - piezoelectric

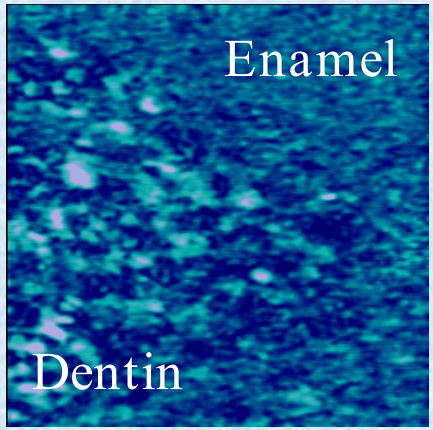
SPM opens a possibility to observe how proteins interact with hydroxyapatite crystals to form these tissues.

Properties on the Dentin-Enamel Interface

Topography



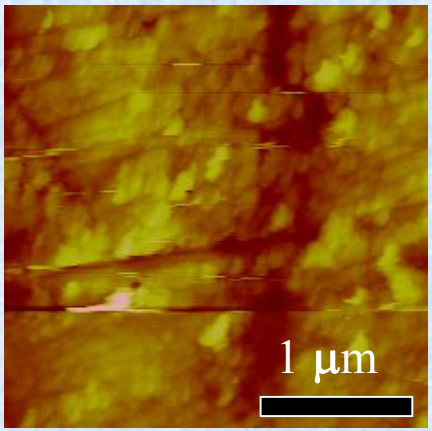
PFM ampl



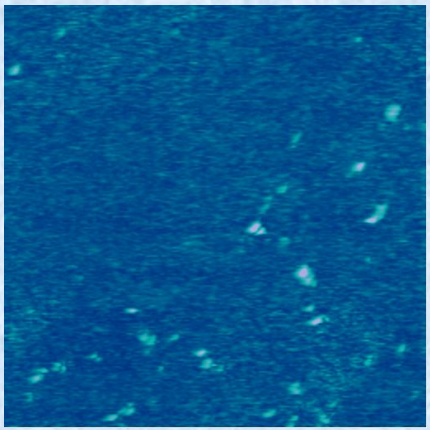
Enamel

Dentin

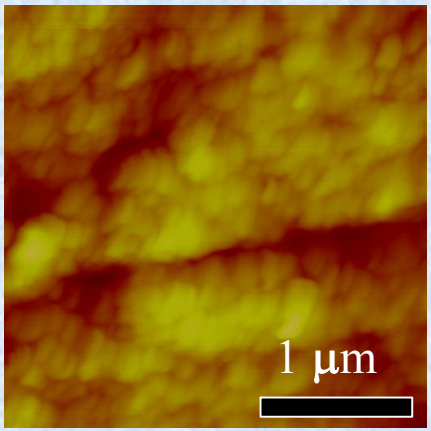
Topography



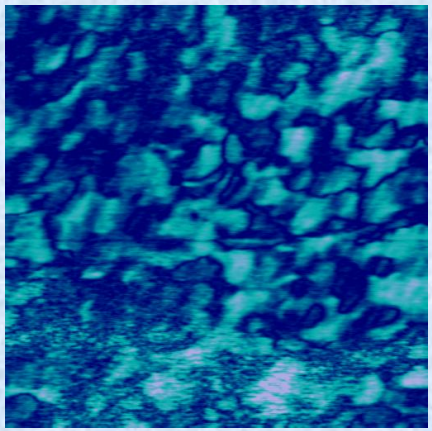
PFM ampl



Topography



PFM ampl

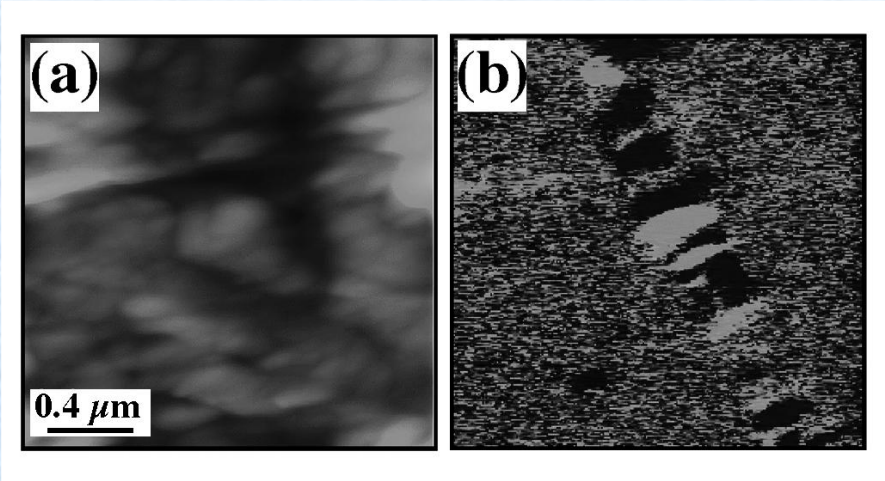


PFM images illustrate that dentin possesses a strong electromechanical coupling.

PFM for Dentin Structure

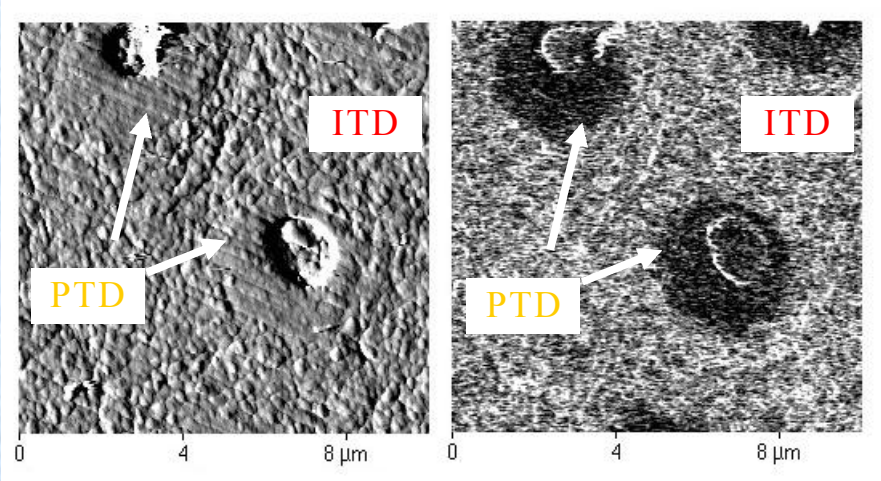
Rapid detection of collagen-type proteins in mineralized tissues

Tooth enamel



Dentin and enamel consist of hydroxyapatite $Ca_{10}(OH)_2(PO_4)_6$ crystals but have different mechanical properties as they differ by the content of organic fibers.

Tooth dentin



Peritubular dentin (PTD) is a tissue of increased mineral content that surrounds dentin tubules.

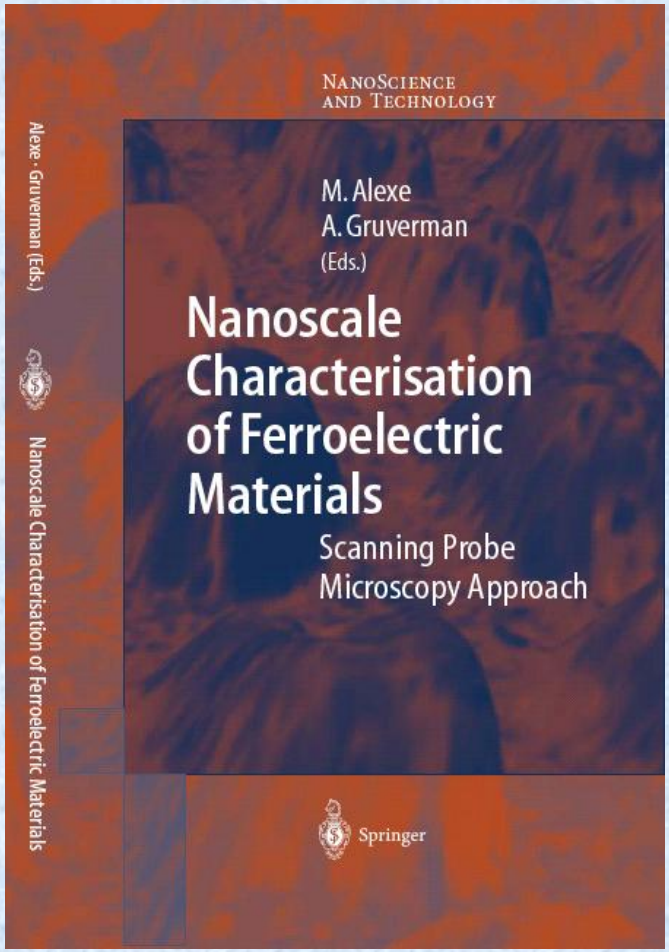
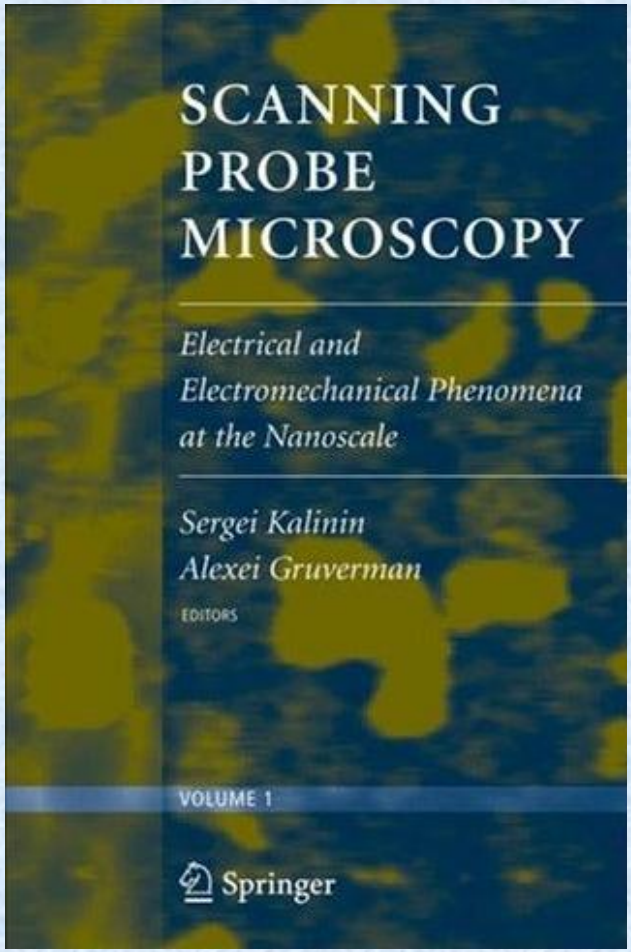
Gruverman et al, BBRC (2006)

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.

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.