Микро- и наноэлектромеханические системы на базе сегнетэлектрических структур и методы их исследования

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• Introduction
• Overview of MEMS
• Basics of piezoelectric effect in bulk materials and thin films
• Piezoelectric measurements: Laser Interferometry
• Piezoelectric measurements: Piezoresponse Force Microscopy
• Relaxor ferroelectrics: nanoscale vs. macroscopic response
• Summary
Nanoscale ferroelectrics: processing, characterization and future trends

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Abstract

This review paper summarizes recent advances in the quickly developing field of nanoscale ferroelectrics, analyses its current status and considers potential future developments. This paper presents a brief survey of the fabrication methods of ferroelectric nanostructures and an investigation of the size effects by means of scanning probe microscopy. One of the focuses of this paper will be the study of kinetics of nanoscale ferroelectric switching in inhomogeneous electrical and elastic fields. Another emphasis will be made on tailoring the electrical and mechanical properties of ferroelectrics with a viewpoint of fabrication of nanoscale domain structures.
Special Issue on "Nanoscale Ferroelectrics", TUFFC, Dec. 06
Actuation principles used in MEMS

• Piezoelectric effect
  - strong force, low displacement, good scalability, hard to integrate, high efficiency, fast response

• Electrostatic effect
  - weak force, low to moderate displacement, non-linearity, most easy to integrate, large voltages even for small gaps

• Electromagnetic effect
  - high displacement, low to moderate force, limited by heating of coils, slow response, hard to integrate

• Thermal effect
  - strong force, large displacement, slow, hard to control, low efficiency
Other principles...

- **Shape memory effect**
  (austenite/martensite phase transition)
  - 5% strain (NiTi alloy),
  - slow response

- **Piezoresistivity**
  - easily processed
  - sensing only

- **Magnetostriiction**
  - processing can be complicated
    (Terfenol-D)
  - similar performance to piezoelectrics
Possibilities provided by Si technology

- **Most common structures**
  - Electrostatic drive
  - Capacitive sensor

- **Complex geometries**
  - Large strain with moderate force
  - High sensitivity-large areas

- **Easy processing**
  - 30+ years of Si processing technology
  - Surface micromachining
  - Bulk surface micromachining
  - LIGA process, etc…
Advantages of MEMS

- IC Technology: Integrated Multiple Functions
- Precision: Improved Performance
- Batch Fabrication: Reduced Manufacturing Cost & Time
- Miniaturization: Portability, Ruggedness, Low Power Consumption, Easily & Massively Deployed, Easily Maintained & Replaced, Little Harm to Environment
MEMS technologies

- Bulk micromachining
- Surface micromachining
- Wafer bonding
- LIGA and similar techniques
- Others
  - MicroEDM
  - 3D lithography
  - Laser micromachining
Wet etching of Si

- Frontside Mask
- Backside Mask
- Boron-doped Si membrane
- Slanted {111}
- Top View
- Self-limiting etches
- Slanted {111} Vertical {111}
- <100>
- <110>
- Boron-doped Si membrane
Dry etching of Si
Surface micromachining

Deposit & pattern oxide

Deposit & pattern poly

Sacrificial etch

10 μm

Oxide

Poly-Si

Anchor

Cantilever

Si substrate

Si substrate

Si substrate
Piezoelectric micromotor (EPFL)

Fig. 1. Schematic drawing of the membrane with view onto the top side of the wafer and a schematic cross section through the films.

Fig. 2. Image of a cut through a membrane as obtained by scanning electron microscopy.

P. Muralt, A. Kholkin, M. Kohli, T. Maeder (Sens. Act. 96, 97 & 98)
### Motor performance vs. PZT routes

<table>
<thead>
<tr>
<th>Performance</th>
<th>Sol-gel</th>
<th>Sol-gel</th>
<th>Sputter</th>
<th>Sputter</th>
<th>Sputter</th>
</tr>
</thead>
<tbody>
<tr>
<td>no bias</td>
<td>94 kHz</td>
<td>+2 V</td>
<td>-2 V</td>
<td>no bias</td>
<td>-2 V</td>
</tr>
<tr>
<td>94 kHz</td>
<td>94 kHz</td>
<td>21 kHz</td>
<td>78 kHz</td>
<td>78 kHz</td>
<td>78 kHz</td>
</tr>
<tr>
<td>B_{10}</td>
<td>B_{10}</td>
<td>B_{00}</td>
<td>B_{10}</td>
<td>B_{10}</td>
<td></td>
</tr>
</tbody>
</table>

**Speed per a.c. voltage**

\[ F = 2.4 \times 10^{-4} \text{ N} \]

(\text{rpm/V}_{\text{r.m.s.}})

- Sol-gel: 140 rpm/V_{\text{r.m.s.}}
- Sputter: 32 rpm/V_{\text{r.m.s.}}
- Speed: 80 rpm/V_{\text{r.m.s.}}

**Torque per a.c. voltage**

\[ F = 2.4 \times 10^{-4} \text{ N} \]

(\text{nN m/V}_{\text{r.m.s.}})

- Sol-gel: 4.3 nN m/V_{\text{r.m.s.}}
- Sputter: 1.8 nN m/V_{\text{r.m.s.}}
- Torque: 3.9 nN m/V_{\text{r.m.s.}}

**Torque per a.c. voltage**

\[ F = 9.8 \times 10^{-4} \text{ N} \]

(\text{nN m/V}_{\text{r.m.s.}})

- Sol-gel: 12 nN m/V_{\text{r.m.s.}}
- Sputter: 3.2 nN m/V_{\text{r.m.s.}}
- Torque: 11 nN m/V_{\text{r.m.s.}}

---

![Graph showing motor performance vs. excitation frequency](image)

The graph illustrates the relationship between torque per voltage and excitation frequency for different PZT routes. The sol-gel PZT and sputtered PZT are compared, showing distinct trends in performance.
Piezoelectricity: Coupling between mechanical and electrical energies

32 Crystallographic point groups

- 11 Centrosymmetric
- 21 Non-centrosymmetric
  - 20 Piezoelectric
    - 10 Pyroelectric
      - Ferroelectrics
    - 10 Non-pyroelectric
  - 1 Non-piezoelectric (432)
Direct piezoelectric effect:
Charge= \( d \times \text{force} \) or
\[
D = d \times X \quad \text{(stress)}
\]

Converse piezoelectric effect:
Dispacement= \( d \times \text{Voltage} \) or
\[
x \quad \text{(strain)} = d \times E
\]
or in general form
\[
x_{ij} = \alpha_{ij}^{X,E} \Delta T + s_{ijkl}^{T,E} X_{kl} + d_{ijk}^{T,X} E_k
\]
\[
D_i = p_i^{X,E} \Delta T + d_{ikl}^{T,E} X_{kl} + \varepsilon_{ij}^{T,X} E_i
\]

\((X, E)\) independent variables
Other choices of independent variables are possible:
\((X,D), (x, E), \text{and} (x, D)\)
Constitutive equations:

\[
\begin{align*}
    x_{ij} &= s_{ijkl}^E X_{kl} + d_{ijk}^E E_k \\
    D_i &= d_{ikl}^E X_{kl} + \varepsilon_{ij}^X E_j \\
    x &= s^D X + g D \\
    E &= -g X + \beta^X D \\
    \quad X &= c^E x - e E \\
    \quad D &= e x + \varepsilon^X E \\
    X &= c^D x - h D \\
    E &= -h x + \beta^X D
\end{align*}
\]

\[
\begin{align*}
    d &= \varepsilon^X g = e s^E \\
    g &= \beta^X d = h s^D \\
    e &= \varepsilon^X h = d c^E \\
    h &= \beta^S e = g c^D
\end{align*}
\]
Major piezoelectric coefficients

\[ d_{33} = \frac{(\Delta l/l)_l}{E} \]
\[ d_{13} = \frac{(\Delta l/l)_\perp}{E} \]
\[ d_{15} = \frac{(\Delta l/l)_{\text{shear}}}{E} \]
The choice of equations depends on boundary conditions:

**1D problem for a plate:**

\( E_1 = E_2 = 0, \quad E_3 \neq 0 \) but spatially constant \( \rightarrow \) choose \( E \) as one independent variable.

\( X_1 \neq 0, \quad X_2 = X_3 = X_4 = X_5 = X_6 = 0, \rightarrow \) choose \( X \) as the other independent variable.

\[
\begin{align*}
x_1 &= s_{11}^E X_1 + d_{31} E_3 \\
D_3 &= d_{31} X_1 + \varepsilon_{33}^X E_3
\end{align*}
\]
Clamping in thin films

Converse effect

Direct effect
For ideal clamping (thin film on thick rigid substrate) the equations:

\[
\frac{\sigma_1}{E_3} = e_{31,f} = \frac{d_{31}}{E} = e_{31} - \frac{c_{13}^E}{c_{33}^E} e_{33} \quad |e_{31,f}| > |e_{31}|
\]

Muralt 1996

\[
\frac{S_3}{E_3} = d_{33,f} = \frac{e_{33}}{c_{33}^E} = d_{33} - \frac{2s_{13}^E}{s_{11}^E + s_{12}^E} d_{31} < d_{33}
\]

Royer & Kmetik 1992

\[
\frac{D_3}{E_3} = e_{33,f} = e_{33} - \frac{2d_{31}^2}{s_{11}^E + s_{12}^E}
\]

Actuator:

\[
\sigma_{1,2} = -e_{31,f} E_3
\]

Sensor:

\[
D = e_{31,f} (S_1 + S_2) + d_{33,f} \sigma_3
\]

\[
S_3 = d_{33,f} E_3
\]
De-clamping in nanostructures

\[ \Delta d = d_{33}^{F_d} - d_{33}^{F_s} = \frac{2S_{12}}{S_{11}^F + S_{12}^F} d_{13} \]

Nagaranjan et al. APL (2002)
Advantages of piezoelectric actuation

- High strain (up to 3-4 %)
- Unlimited resolution
- Rapid response (µs range)
- Good scalability
- High generative force
- Low power consumption
- Unlimited reliability
- Problems with integration

Giant strain in (001)-oriented Pb(Zn, Nb)O$_3$-8%PT

$\text{d}_{33} \sim 2500 \text{ pm/V}$

Park & Shrout, JAP (1997)
Examples of piezoelectric MEMS

Acoustic pressure sensor (U. of Minnesota)

Piezoelectric micromotor (EPFL, Switzerland)
Examples of piezoelectric MEMS (cont.)

Piezo microswitch
Tilting micromirror
Cantilever array

 Courtesy of Inostek, Inc. (S. Korea)
Examples of piezoelectric MEMS (cont.)

Sensor/actuator for AFM

Smart wing for aircraft
Ferroelectric MEMS

• General features

- Small strains (1% max, 0.2%-0.5% more realistic)

Typically designs rely on “d_{31}” mode to increase strain:

  - diaphragms, bridges & cantilevers
  - High sensitivity to stress (stress-compensating layers)
  - Efficient electromechanical coupling (95% in some cases)

  - Weak hysteresis (in some compositions)

  - Excellent high-frequency potential

• Complicated processing

- Two or more metal cations in compositions of interest (PZT, d_{33} = 250-600 pm/V)

  - Typically contain Pb (need of lead-free materials)

  - Oxidizing process atmospheres
Non-ferroelectric MEMS

• **Non-ferroelectric piezoelectric MEMS**
  - ZnO $d_{33} \sim 4 \div 10$ pm/V (2 times larger than quartz)
  - AlN $d_{33} \sim 2 \div 6$ pC/N (compatible with Si$_3$N$_4$

  - Modulation of $n$ in ZnO-clad optical fiber

  **Much easier processing**
  - Relatively low-temperature growth

• **Comparatively small electromechanical response**

• **But must be deposited with specific crystallographic texture**
  - i.e., piezoelectric axis normal to substrate
  - $c$-oriented film for both ZnO and AlN
• **Advantages of FE MEMS**

- Potentially much larger piezoelectric response
  
  - $d_{33}$ values up to **2500 pm/V**

- As deposited, FE films are NOT piezoelectric and poling can produce piezoelectricity for any texture

- No crystallographic texture required

- In some cases, random orientation gives best results
**MEMS materials**

- **Same materials as in bulk ceramics**
  
Pb(Zr, Ti)O$_3$ (PZT) solid solution – ferroelectric
  
Pb(Mn$_{1/3}$Nb$_{2/3}$)O$_3$ – electrostrictors
  
Relaxor-PbTiO$_3$ solid solutions and new MPB systems
  
such as BiScO$_3$-PbTiO$_3$ (High $T_c$)

- **Most research still on Pb(Zr$_x$Ti$_{1-x}$)O$_3$ solid solution**
  
  - $x \approx 0.52$ (morphotropic composition) ideal
  
  - $d_{33}$ coefficients approach now above 200 pm/V (unclamping)

  - **Non-lead containing compositions**
    
    - BaTiO$_3$, (Sr$_x$Ba$_{1-x}$)NbO$_3$, or (K,Na)NbO$_3$-based
    
    - difficult to process

- **Important observations**
  
  - bulk properties difficult to achieve in thin films
  
    - scaling effects
  
    - extrinsic vs. intrinsic contribution
Related issues

- **Intrinsic contribution to piezoelectricity**

\[ d_{ijk} = 2Q_{ijkl} \varepsilon_0 \varepsilon_{kl} P_l \]

large permittivity

large remanent polarization

- **Extrinsic contribution to piezoelectricity**

existence of non-180° domains

large spontaneous strain

multiple available domain variants

morphotropic compositions desirable

composition-induced symmetry transition
**PZT vs. lead-free materials**

Experimental evidence of domain wall contributions

Non-linearity

Temperature dependence of $d_{33}$

Aging

Q.M. Zhang et al, JAP 64, 6445 (1988)

R.Herbiet et al, Ferroelectrics 76, 319 (1987)

Q.M. Zhang et al, JAP 75, 454 (1993)
Theoretical predictions for extrinsic effect

\[ d_{\text{ext}} = 2\sqrt{2}(1 - \frac{\nu}{1-\nu})(Q_{11} - Q_{12}) \frac{P_s}{kD} \]

for \( D/H \ll 1 \)

\[ d_{\text{ext}} = 70 \text{ pm/V} \quad \text{PbTiO}_3 \]

\[ d_{\text{ext}} = 100 \text{ pm/V} \quad \text{PZT} \]
**Macroscopic characterization: laser interferometry**

- Vertical resolution – 0.003 Å
- Lateral resolution - 0.6 µm
- Frequency range <6 GHz

Piezoelectric measurements in thin films

Simultaneous $d_{33}$ and $\varepsilon$ measurements

Permittivity measurement

Precision LCR meter

Computer

$d_{33}$ measurement

V$_{ac}$ = 5 mV - 20 V

Laser beam

TE PZT film BE

Si substrate

Double beam laser interferometer
Substrate bending elimination

(a) Single beam

(b) Double beam

Graphs showing piezoelectric response vs. frequency and electric field.
Double-beam laser interferometer

Key issues

- Single-mode laser with improved stability
- Short optical path
- Reduced environmental noise
- Active stabilization of the optical path length difference

Sensitivity

Displacement (A) vs. Driving voltage (V)

X-cut quartz
- thickness 1.24 mm
- frequency 5 kHz

Stability

V_{out} (µV) vs. Time (h)

X-cut quartz
- frequency 5 kHz
- $E_{ac} = 40$ V/cm
Bending in single-beam interferometer

FIG. 2. (a) Deformation of the Si substrate induced by piezoelectric effect in the PZT film. Arrows indicate the edges of the top electrode. (b) Displacement of the top electrode as a function of the electrode diameter.
Typical values for PZT thin films

<table>
<thead>
<tr>
<th>Reference</th>
<th>Effective $d_{33}$* (pm/V)</th>
<th>Meas. technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>K.F.Etzold et al. (1990)</td>
<td>8</td>
<td>converse effect</td>
</tr>
<tr>
<td>Z.Surowiak et al. (1992)</td>
<td>70-120</td>
<td>direct effect</td>
</tr>
<tr>
<td>K.Lefki and G.J.M. Dormans (1994)</td>
<td>400</td>
<td>direct effect</td>
</tr>
<tr>
<td>J.-F.Li et al. (1994)</td>
<td>140</td>
<td>converse effect</td>
</tr>
<tr>
<td>H.D.Chen et al. (1995)</td>
<td>196</td>
<td>converse effect</td>
</tr>
<tr>
<td>A.L.Kholkin et al. (1996)</td>
<td>40-110</td>
<td>converse effect</td>
</tr>
<tr>
<td>F.Xu et al. (1997)</td>
<td>150</td>
<td>direct effect</td>
</tr>
</tbody>
</table>

*PZT films of MPB composition and thickness ≤1 µm

For undoped PZT ceramics $d_{33} \approx 230$ pm/V
Effect of the composition (sol-gel)

sol-gel PZT, thick. 0.3 μm, (111) orientation

- significant depoling for MPB and rhombohedral compositions
- $d_{33}$ for MPB composition is about half of the value for undoped PZT ceramics
Effect of the composition (sputtering)

sputtered PZT, thick. 0.3 μm, (111) orientation

- In rhombohedral films non-180° domains may contribute to electromechanical strain under high ac-field
Intrinsic vs. Extrinsic effect

Linearized electrostriction equation
\[ d_{33} = 2Q_{11} \varepsilon_0 \varepsilon P_r \]

- \( Q \approx 0.015-0.02 \text{ m}^4/\text{C}^2 \) for rhombohedral compositions
- \( d_{33} \) is relatively high in tetragonal films due to non-switchable self-polarization
**Effect of orientation**

**tetragonal (45/55)**

\[ \frac{dS}{dE} = 55 \text{ pm/V} \]

\[ \frac{dS}{dE} \approx d_{33} \]

**rhombohedral (70/30)**

\[ \frac{dS}{dE} = 115 \text{ pm/V} \]

\[ \frac{dS}{dE} >> d_{33} \]
Piezoelectric non-linearity

- 90° domains are almost inactive in tetragonal films
- Domain wall contribution is evident in MPB and rhombohedral films
Effect of orientation

[Graph showing the effect of Zr/Ti ratio on the effective $d_{33}$ for (111) and (100) orientations.]

$\text{Effect} \quad \text{of} \quad \text{orientation}$

Effective $d_{33}$ (pm/V)

PZT/Pt/TiO$_2$/SiO$_2$/Si

Zr/Ti ratio
Comparison with calculations

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Composition</th>
<th>Orientation</th>
<th>$d_{33}$ (free)</th>
<th>$d_{33}$ (clamped)</th>
<th>$\alpha$</th>
<th>$d_{33}$ (exp)</th>
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</thead>
<tbody>
<tr>
<td>tetragonal</td>
<td>45/55</td>
<td>[111]</td>
<td>161</td>
<td><strong>58</strong></td>
<td>0.64</td>
<td><strong>62</strong></td>
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<tr>
<td>rhombohedral</td>
<td>70/30</td>
<td>[001]</td>
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<td>71</td>
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<td>[011]</td>
<td>88</td>
<td>42</td>
<td>0.52</td>
<td></td>
</tr>
</tbody>
</table>

*All thermodynamical coefficients are taken from Haun et al., Ferroelectrics 99, 63 (1989)*
Dielectric vs. Piezoelectric nonlinearity

tetragonal (45/55) <111> orientation

90° domains contribute only to dielectric constant

MPB (53/47) random orientation

non 180° domains contribute to both dielectric constant and $d_{33}$
Evidence of domain wall contribution

I - reversible domain wall motion
II - irreversible domain motion
III - depoling and switching

Effective $d_{33}$ (pm/V) vs. ac-field (kV/cm)

PZT (53/47) 7 µm thick

I - reversed domain wall motion
II - irreversible domain motion
III - depoling and switching
Bulk ceramics vs. thin/thick films

- non-linear piezoelectric properties are similar in thick films and hard PZT
- threshold field for irreversible domain wall motion is very high in thin films ($\approx 0.1E_c$)

Onset of non-linearity at $\sim 0.2\text{-}0.3 \text{kV/cm}$

- Quasi-linear response at higher fields
- Sub-linear behaviour at $E>2.5 \text{kV/cm}$ (depoling)
- Switching at $E>6 \text{kV/cm}$

Non-linearity in thick films

\begin{figure}
\centering
\includegraphics[width=\textwidth]{pzt_diagram.png}
\caption{PZT(53/47)/Pt/TiO$_2$/SiO$_2$/Si thick. 7 $\mu$m}
\end{figure}
Modelling of piezoresponse

- Poor fit for Rayleigh law
- Non-linearity is better described by the empirical fit with $\alpha=1.2$
Dielectric constant, $d_{33}$ (norm.)

PZT(53/47) thick. 300 nm

- frequency dispersion of $d_{33}$ is close to dispersion of dielectric constant
- piezoelectric loss is close to dielectric loss
• two stages of $d_{33}$ relaxation: fast depoling and slow logarithmic decrease
• aging rates $\approx 2\div5$ %/dec depending on poling time

A.Kholkin et al., Inegr. Ferroelectr. (1997)
• $d_{33}$ decays much faster than dielectric constant in PZT films
• aging of dielectric constant is comparable in films and ceramics
• aging of $d_{33}$ is close to the reduction of $P_r$ with time (retention)
• aging of $d_{33}$ is due to depoling of PZT films rather than to the reduction of domain wall contribution

$$d_{33}(t) = 2Q_{11} \varepsilon_0 \varepsilon(t)P_r(t)$$
Case study: PbTiO$_3$:Ca

- simple tetragonal structure
- decrease of tetragonality with Ca addition
- high $g_{33}$ coefficients
- high piezoelectric anisotropy for low Ca content
- High breakdown field results in a giant strain at 1 MV/cm (≈1 %)
- At high field strain is linear with the amplitude of ac-field
**SBT films: absence of extrinsic strain**

- \((d_{33})_{\text{max}}\) is about 75% of bulk ceramics value
- \(d_{33} \approx \frac{dS}{dE}\) in contrast to PZT films
SBT films: absence of extrinsic strain

\[ S = Q_{11} P^2 \]

- pure electrostrictive strain behavior at \( T \ll T_c \) (\( Q_{11} \approx 0.1 \, \text{m}^4/\text{C}^2 \))
Domain pinning and voltage offset

- electrons generated by UV light compensate polarization charge at the film-electrode interfaces
- voltage offset is due to the space-charge internal field
Piezoelectric fatigue: evidence of domain pinning

Fatigue of polarization

Fatigue of $d_{33}$

Polarization offset as a function of fatigue

$$P_{bi} = \frac{d_{33}}{2Q_{\text{eff}}\varepsilon_0\varepsilon}$$

A.Kholkin et al., APL (1996)
UV-induced poling

\[ d_{33} = 2Q_{\text{eff}} \varepsilon_0 \varepsilon P_{\text{bi}} \]

\( d_{33} \text{ loop of virgin film} \)

\( d_{33} \text{ loop of illuminated film} \)

Photoinduced poling effect

Downscaling of actuators

Piezoresponse Force Microscopy

optical methods

$\text{d}_{33}$ meter

characteristic lengths (log scale)
Local characterization:
Piezoresponse Force Microscopy
PFM vs. EFM

Contact - Piezoresponse

Non-Contact - EFM

Topography  z - Piezoresponse  EFM-Surface charge
KFM and EFM for domain imaging

Kalinin & Bonnell PRB (2001)
Advantages/disadvantages of PFM

• Much higher resolution: limited by tip diameter
• Control of polar state: new applications of ferroelectrics: e.g., nanolithography and self-assembly routines
• Local domain engineering and interaction with defects
• Visualization of small domains impossible in the past
• Multiferroics and magnetoelectric interaction on the nanoscale
• Slow acquisition
• Difficult to get reliable absolute values of $d_{33}$
• Not easy interpretation: electrostatics
Potential distribution and effective $d_{33}$

BaTiO$_3$ ($V_{\text{appl}}=1$ V)

$\Psi_m$, $a=3$ nm

Influence of interface layer

PZT6b

$\delta$

$\varepsilon_{11}$

$\varepsilon_{33}$

$d_{33}$ contribution

$d_{15}$ contribution

$E_3$

$-E_1$

$A_{1\omega}$

$(d_{33})_{\text{eff}} \propto \frac{A_{1\omega}}{V_{ac}} = \frac{A_{1\omega}}{1 + \frac{\delta \varepsilon}{d \varepsilon}}$

**Effect of tip-surface interaction**

**Weak indentation**
- Small contact area $<< R$.
- Electrostatic signal dominates electromechanical one. $F = \frac{V^2}{2} \frac{\partial C}{\partial z}$
- Distribution of E-field can be calculated using image charge models.

**Strong indentation**
- Medium contact area $a \leq R$.
- Electromechanical signal dominates electrostatic (Maxwell stress).
- Coupled electrostatic + elastic + electroelastic problems should be solved!
**Local vs. macroscopic measurements**

**Macroscopic**

\[ V = V_{dc} + V_o \sin(\omega t) \]

**Local**

\[ V = V_{dc} + V_o \sin(\omega t) \]

Probing beam of interferometer

To photodetector

Probing laser beam

PFM tip

low-dielectric-permittivity layer

\[ d \]

\[ \delta \]
Piezoelectric hysteresis

Strain in monodomain ferroelectric with centrosymmetric paraelectric phase

\[ S = QP^2(E) = Q[P_s + P_{ind}(E)]^2 = QP_s^2 + 2Q\varepsilon_o\varepsilon P_s E + QP_{ind}^2 \]

For small ac-field

\[ E = E_{dc} + E_o \sin(\omega t) \]

1st harmonics of ac-strain

\[ S_{1\omega} = 2Q\varepsilon_o\varepsilon P_s E_o \sin(\omega t) \]

If polarization is changed by \( E_{dc} \), \( d_{33} = f(E_{dc}) \) and can be formally rewritten as

\[ d_{33}(E_{dc}) = 2Q\varepsilon_o\varepsilon(E_{dc}) P(E_{dc}) \]
P(E) reconstruction

Simultaneous measurements of $d_{33}(E)$ and $\varepsilon(E)$

Comparison of P(E) and reconstructed from $d_{33}/\varepsilon$

- Polarization hysteresis is close to $d_{33}/\varepsilon(E)$ hysteresis
- $d_{33}(E)$ shape is determined by both $\varepsilon(E)$ and P(E)

Kholkin et al, JAP 89, 2001
**Influence of electrostatics**

Two modes of voltage application

**Step mode**

\[ V(t) \]

**Pulse mode**

\[ A \cos \varphi = -\frac{K}{k_{lever}} \frac{\partial C}{\partial z} (V_{dc} + V_k) \pm d_{33} V_o \]

Electrostatic term

- Electrostatic interaction distorts the shape of the hysteresis in step mode and simulates polarization offset if \( V_k \neq 0 \)

Hong et al., JAP (2001)
Origin of piezosignal

\[ \Delta l = d_{33} \int_0^d E(z)dz - d_{33} \int_0^{z_1} E(z)dz - d_{33} \int_{z_1}^d E(z)dz = d_{33} \{ \varphi(0) - 2\varphi(z_1) + \varphi(d) \} = d_{33} \{ U - 2(\varphi(z_1) - \varphi(d)) \} \]

\[ \Delta l = (d_{33})_{\text{eff}} U \Rightarrow (d_{33})_{\text{eff}} = d_{33} \left\{ 1 - \frac{2(\varphi(z_1) - \varphi(d))}{U} \right\} \]

Wu et al., Nanotechnology 16 (2005)

\[ E_c \text{ at } \varphi(z_1) = \frac{\varphi(0) + \varphi(d)}{2} \]

\[ d_{\text{eff}} \propto \alpha d_{33} \left[ 1 - \frac{2R}{R + P_S U_{dc} \ln(\varepsilon)/\varepsilon \sigma_W} \right] \]
Hysteresis in PZT films

\[
d_{33} \text{ (a.u.)}
\]

\[
U_{dc} \text{ (Volts)}
\]
**Vertical vs. horizontal hysteresis**

Piezoresponse vs. $V_{dc}$

Domain size vs. $V_{dc}$

\[ V_{out} = \alpha d_{33} V_{ac} f[I(V_{dc})] \]

\[ r(V_{dc}) = [S(V_{dc})/\pi]^{1/2} \]
Effect of PZT composition

PZT films
1 µm, sol-gel INOSTEK

Bdikin et al, J. Electroceram. (in press)
Effect of dielectric constant

Local $d_{33}$ is inversely proportional to dielectric constant

$$\left(d_{33}\right)_{\text{eff}} \propto \frac{A_{1\omega}}{V_{ac}} = \frac{A_{1\omega}}{1 + \frac{\delta\varepsilon}{d\varepsilon}}$$
Effect of topography

Macroscopic loop

Nanoscale loops

PbTiO$_3$: 24%Ca

Shvartsman et al., Ferroelectrics (2003)
Domains in Airvillius-type materials

Phase diagram of PZN-PT

The diagram shows the phase transition between Rhombohedral (R) and Tetragonal (T) phases in a PZN-PT system. The diagram includes a plot of $a_{33}(PC/N)$ against the concentration of $n_{1/3}Nb_{2/3}O_3$ and the percentage of PbTiO$_3$. The phase boundary is indicated by a line dividing the Rhombohedral and Tetragonal regions. The concentration of 4.5% PbTiO$_3$ is marked with an arrow.
Polar nanodomains

Poling by the tip

- Poling does not remove nanodomains
- “Normal” micron-sized domains can be written

• Local properties are comparable giant piezoresponse is related to nanodomains
Mechanical stress effect on hysteresis

- Compressive strain (||P) results in depoling (soft PZT) through ferroelastic domain wall motion

Fang & Li, J. Mater. Sci. 34, 4001 (1999)
Stress by PFM: PbTiO$_3$-La films

- Sol-gel spin-on technique
- Thickness $\approx$ 340 nm
- (001)/(100) preferred orientation
- Grain size 50-150 nm
- High piezoelectric anisotropy

$d_{33}$ of bright domain vs. force

Hysteresis suppression

- $d_{33}$ suppression depends on the initial contrast
- Hysteresis is suppressed with strong polarization offset

Non-linear thermodynamic approach

\[ G = G + S_1 \sigma_1 + S_2 \sigma_2 + S_6 \sigma_6 \]

\[ \tilde{G} = \frac{(S_m - s_{12} \sigma_3)^2}{s_{11} + s_{12}} - \frac{1}{2} s_{11} \sigma_3^2 + a_1^* (P_1^2 + P_2^2) + a_3^* P_3^2 \]

\[ + a_{11}^* (P_1^4 + P_2^4) + a_{12}^* P_1^2 P_2 + a_{13}^* (P_1^2 + P_2^2) P_3^2 + a_{33}^* P_3^4 \]

\[ + a_{111} (P_1^6 + P_2^6 + P_3^6) + a_{112} [P_1^4 (P_2^2 + P_3^2) + P_2^4 (P_1^2 + P_3^2) + P_3^4 P_1^2 P_2 P_3^2] \]

where \( a_{1}^*, a_{ij}^*, a_{ijk}^* \) are dielectric stiffnesses at constant stress.

e.g.

\[ a_1^* = a_1 - \frac{Q_{11} + Q_{12}}{s_{11} + s_{12}} S_m + \frac{Q_{11}s_{12} - Q_{12}s_{11}}{s_{11} + s_{12}} \sigma_3 \]

\[ S_m^\sigma = S_m - (s_{11} + 2s_{12}) \sigma_3, \]

\[ T_\sigma = T - 2 \varepsilon_0 C (Q_{11} + 2 Q_{12}) \sigma_3. \]
Phase diagrams under stress

- Phase transition into r- and aa-phases is possible under high compressive stress

Proper stress design of microdevices may enhance materials properties near stress-induced phase transitions.

Tentative explanation of asymmetry

- Electrode + Substrate
- Built-in layer
- Bright grain
- Film
- Rotated volume

Tip a

Currents c
**Mesoscopic disorder in relaxors**

<table>
<thead>
<tr>
<th>Normal Ferroelectric</th>
<th>Relaxors</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
</tr>
<tr>
<td>* Macro-size FE domains</td>
<td>* Nano-size polar domains</td>
</tr>
<tr>
<td><img src="image3.png" alt="Diagram" /></td>
<td><img src="image4.png" alt="Diagram" /></td>
</tr>
<tr>
<td>* No polar domains above $T_c$</td>
<td>* Nano-size polar domains persist well above $T_m$</td>
</tr>
</tbody>
</table>

| ![Diagram](image5.png) | ![Diagram](image6.png) |
| ![Diagram](image7.png) | ![Diagram](image8.png) |

AFM tip

Polar clusters (nanodomains) $d=5-50$ nm
Relaxor “ergodic” cubic phase at room temperature

No piezoelectric activity at large scale
Domains in virgin ceramics

vertical piezoresponse  lateral piezoresponse  reconstructed domains
Threshold-like increase of piezoresponse signifies bias-induced phase transition.

Further hysteresis is due to evolution of ferroelectric phase.

Kholkin et al, APL (2005)
Polar nanoclusters in PMN-10%PT

piezoresponse

autocorrelation image of $d_{33}$

$C(r_1, r_2) = \sum_{x,y} D(x, y)D(x + r_1, y + r_2)$

Averaged autocorrelation function vs. distance

average cluster size
Aging in ferroelectrics

Mason (1954)

Jonker (1972)

Bradt & Ansell (1968)

Formation of new 90° domain walls

Robels & Arlt (1992)

Stabilization of existing walls by polar defects
Piezorelaxation at the nanoscale

5 min after dc

20 min

90 min

250 nm
Piezorelaxation vs. grain size

- Stretched exponential dependence is typical for systems with the broad spectrum of relaxation times
Bipolar fatigue in piezoceramics

- Strain asymmetry as a result of fatigue-induced polarization offset
Fatigued vs. virgin piezoceramics (PIC151)
Effect of annealing

After annealing ($T=700 \, ^\circ\text{C}$, $10 \, \text{h}$) the initial ratio between $180^\circ$ and ferroelastic domains is restored along with the rejuvenation of switchable polarization.
Concentration of stripe domains vs. depth

- Concentration of stripe domains decreases with the distance from the electrode.
- A maximum at about 80-100 μm below the electrode.
In fatigued areas the domain histogram is highly asymmetrical demonstrating a preference of polarization state (domain head at electrode). The symmetrical domain distribution is restored with depth.
Local polarization switching vs. fatigue

- Local poling is different for both directions of poling field
- Pinning mechanism might be applicable for fatigue in ceramics
Conclusions:

• Miniaturization requires integration of piezoelectric/ferroelectric materials using Si-based technology

• Laser interferometry is an indispensable technique for the piezoelectric measurements in thin films down to nm thickness

• Piezoresponse Force Microscopy (PFM) can be used for integrated piezoelectrics provided the mechanism of the tip-surface interaction is understood

• PFM is suitable for the local study of polarization reversal, aging and fatigue in ferroelectrics including relaxors