Surface analysis

Lecture 3: functional AFM/SFM

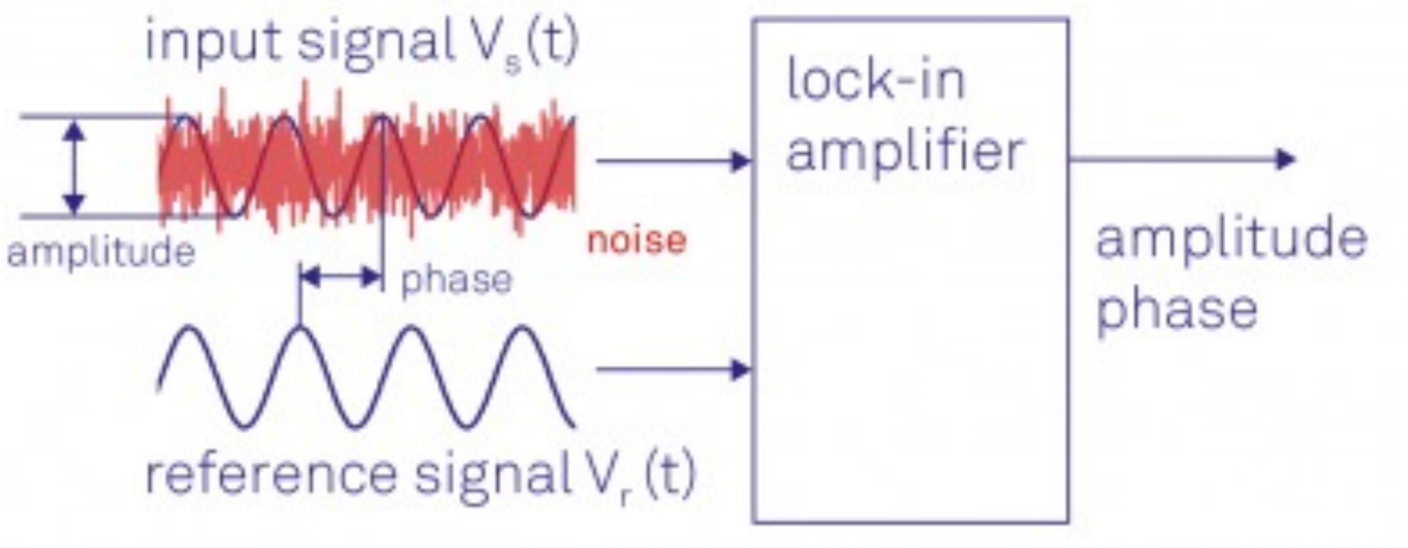
AFM techniques for probing functional properties - electromechanic interactions and piezoelectric force microscopy (PFM)

technical note:

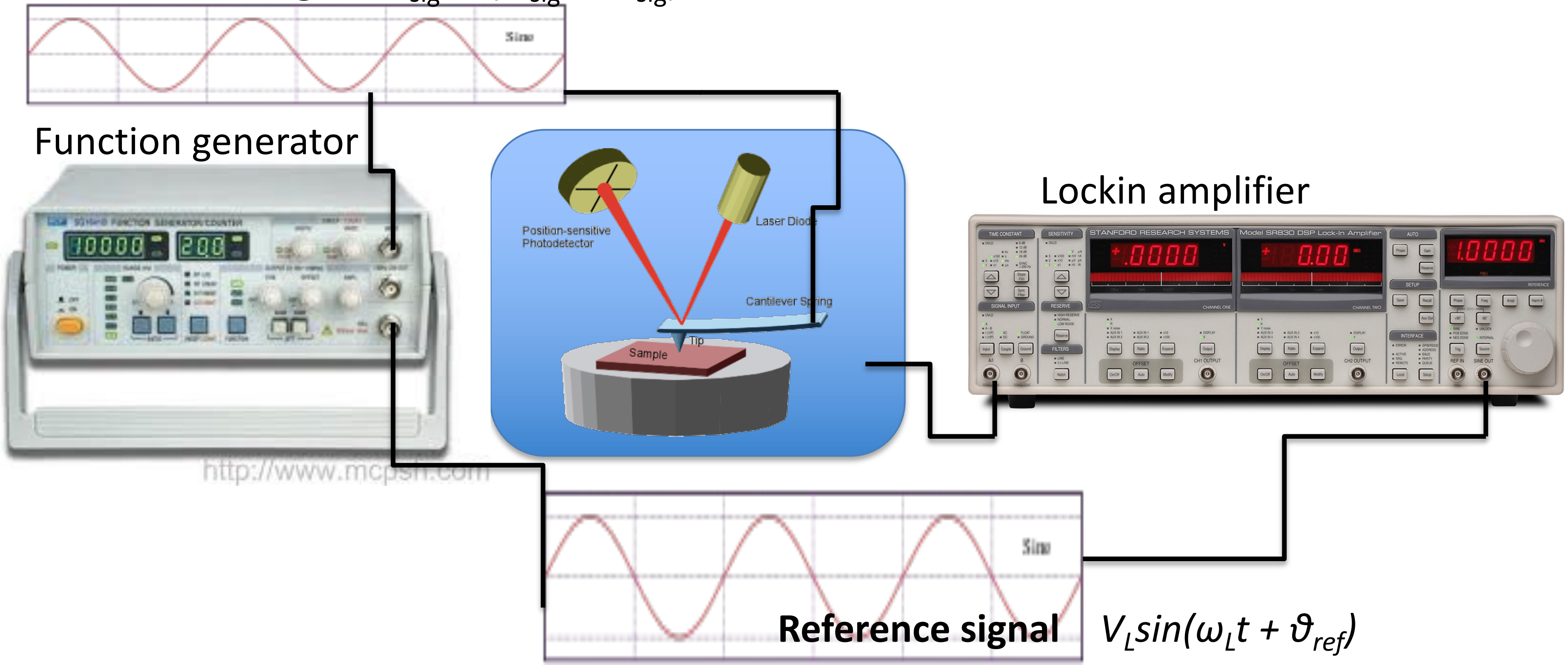
Lock-in amplifiers: essential hardware for different functional AFM / STM modes

- Many methods rely on sample excitation at a chosen frequency and extracting the response at the same frequency (or superior harmonics)

- A lock-in amplifier can be considered as an extremely sensitive filter capable of extracting an AC signal at given frequency even if this signal is masked by a noise, which is orders of magnitude stronger than the signal



Hardware for functional AFM modes: Lock-in amplifiers



excitation signal $V_{sig}\sin(\omega_{sig}t + \theta_{sig})$

Function generator

Lockin amplifier

Reference signal $V_L sin(\omega_L t + \vartheta_{ref})$

The Lock-in amplifier implements phase-sensitive detection (PSD). The output of PSD is the product of two sine waves:

$$V_{psd} = V_{sig}\sin(\omega_{sig}t + \theta_{sig})\ \text{x}\ V_L\sin(\omega_L t + \theta_{ref}) =$$

$$= 1/2V_{sig}V_L\cos([\omega_{sig} - \omega_L]t + \theta_{sig} - \theta_{ref}) - 1/2V_{sig}V_L\cos([\omega_{sig} + \omega_L]t + \theta_{sig} + \theta_{ref})$$

Hence the output of PSD consists of two AC signals: one is proportional to cos **$[\omega_{sig} - \omega_L]$** and the other is proportional to cos **$[\omega_{sig} + \omega_L]$**

Lock-in amplifiers: concept of measurements

- The output of PSD consists of two AC signals: one is proportional to cos [$\omega_{sig} - \omega_L$] and the other is proportional to cos [$\omega_{sig} + \omega_L$]

- If the PSD output is passed through a low pass filter, the AC signals are removed. What will be left? In the general case, nothing. However, if ω_{sig} equals ω_L, the difference frequency component will be a DC signal. In this case, the filtered PSD output will be:

$V_{psd} = 1/2 V_{sig} V_L \cos(\theta_{sig} - \theta_{ref})$

This is a DC signal proportional amplitude of the signal that we need to detect.

- In general case instead of a pure sine wave, the input is made up of signal plus noise. The PSD and low pass filter only detect the signal with frequencies very close to the lock-in reference frequency. Noise signals, at frequencies far from the reference, are attenuated at the PSD output by the low pass filter
- Noise at almost same frequency as the reference will result in very low frequency AC outputs from the PSD ($\omega_{noise} - \omega_{ref}$) is small). Their attenuation depends upon the low pass filter bandwidth (a trade-off between the speed and sensitivity)

- The phase dependence of the detected signal can be eliminated by adding a second PSD. If the second PSD multiplies the signal with the reference oscillator shifted by 90°. From these two outputs the amplitude and phase of detected signal can be extracted.

Lock-in amplifiers: concept of measurements - summary

- A lock-in amplifier, because it multiplies the signal with a pure sine wave, measures the single Fourier (sine) component of the signal at the reference frequency.

- A lock-in amplifier can be considered as an extremely sensitive filter capable of extracting an AC signal at given frequency even if this signal is masked by a noise, which is orders of magnitude stronger than the signal

- A lock-in is a very powerful tool that allows detection of very low-amplitude signals. Its use relies on excitation of the system with AC signal (or just periodic signal) at given frequency and use this frequency as a reference

technical note end

Density of states measured by STM - a lock-in technique

The DOS is a very useful quantity to be able to measure since it can be used to derive a wealth of information about the crystal's properties.
The DOS can vary as a function of position in the crystal which means that one can define a local density of states (LDOS). LDOS is then a quantity which depends on both energy and on position, LDOS(*x*, *y*, *E*).

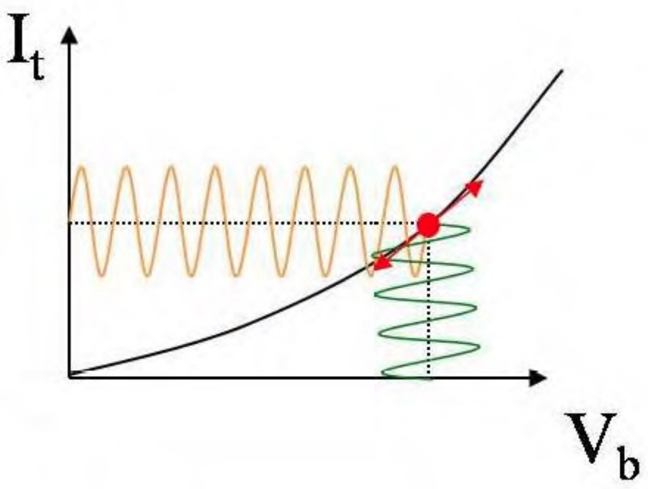
$$I = I_0 \int_{-eV}^{0} \rho_s(\varepsilon)\, d\varepsilon$$

For a negative bias voltage on the sample, the electrons are tunneling from sample to tip, and we are measuring the integrated density of full states below the Fermi level in the sample.

How to get DOS (rather than integrated DOS)? By taking derivative numerically one gets a lot of noise. However derivative can be measured directly by modulating bias voltage.

$$\frac{dI}{dV} \propto DOS$$

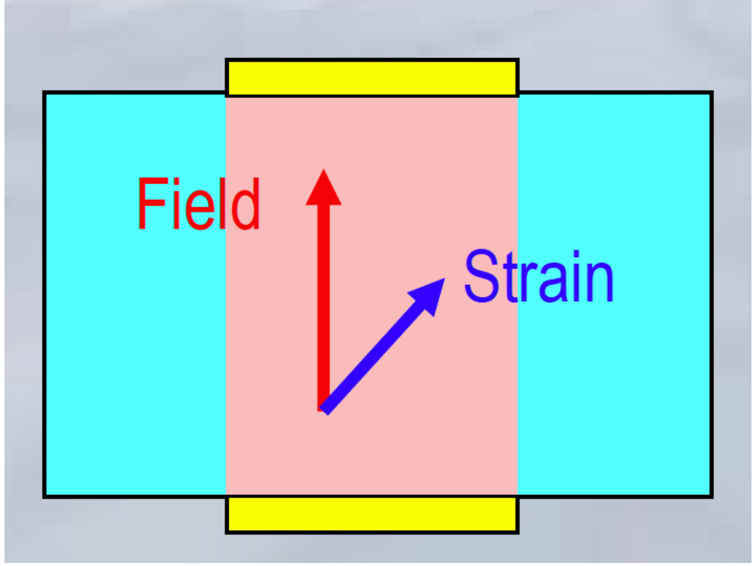
To measure DOS one has to modulate the bias voltage by ***dV*** and measure current modulation ***dI***
Technically this in done using ***lock-in amplifier***, which is a very sensitive tool that permits to extract a signal at a given frequency and filter out noise that can be much (orders of magnitude) stronger than the signal.



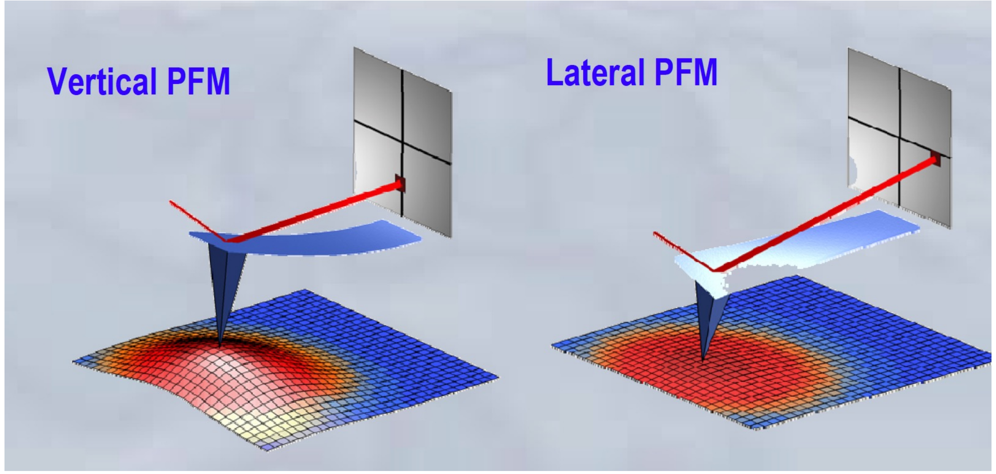
The resolution of DOS measurements is determined by ***dV***. The resolution limit is imposed by the amplitude of thermal wiggle (when the modulation becomes less than K_BT = 0.36 meV at T = 4.2 K). However in real experiments the modulation can be as small as 2-3mV

Probing nanoelectromechanics
Piezoelectric response force microscopy (PFM)

In macroscopic systems, we measure response to the uniform external field (e.g. by interferometry)



Interpretation:
In general case the strain ***x*** is linked to the polarization ***P*** through the equation $x=QP^2$



Piezoresponse Force Microscopy:
electromechanics can be probed locally

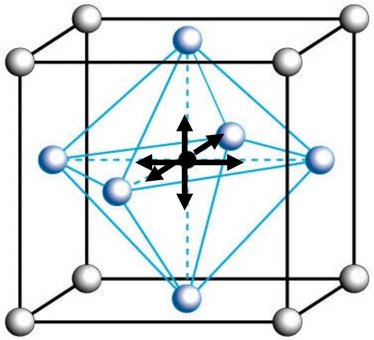
Application of AC + DC bias to the tip

$V_{tip} = V_{dc}+V_{ac}\cos(\omega t)$

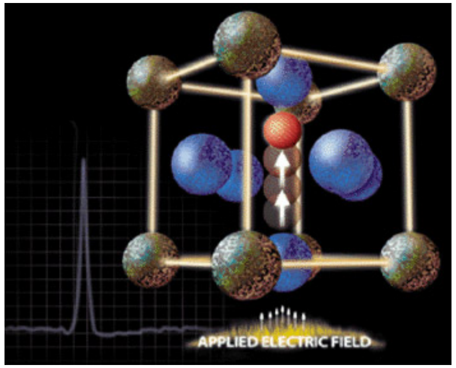
$d = d_0+A(\omega,V_{dc})V_{ac}\cos(\omega t+\varphi)$

Ferroelectric materials: a strong electromechanical response

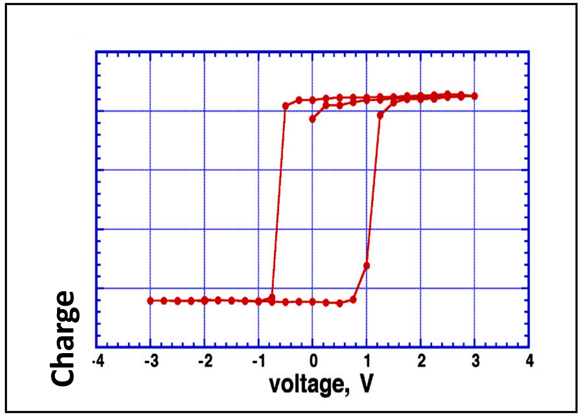
Possible polarization directions in a perovskite ferroelectric in tetragonal phase



Control of polarization direction by an external electric field



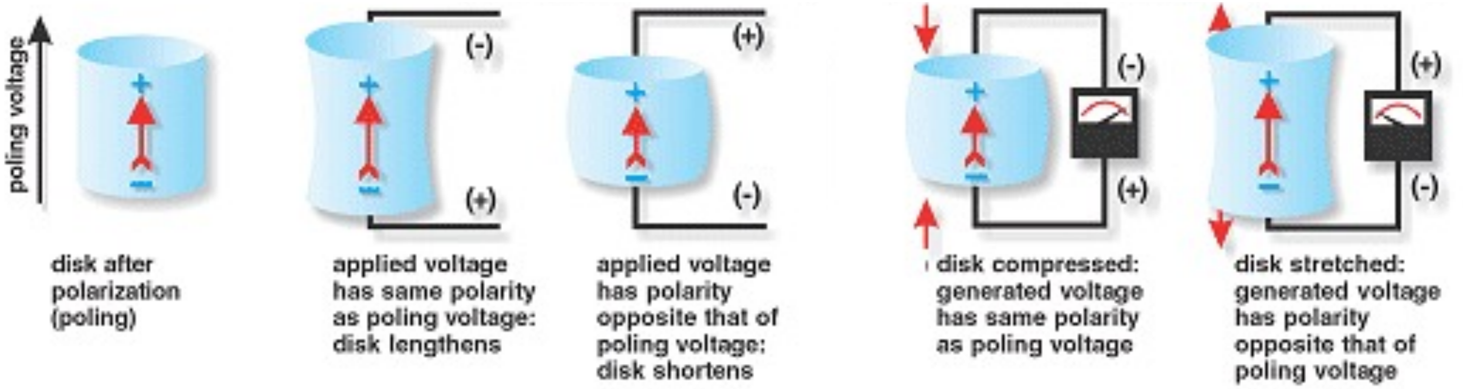
Hysteresis of polarization



Piezoelectric effect

Converse piezoelectric effect

Direct piezoelectric effect



$\Delta d = d_{33}V$, for PZT ceramics d_{33}=500pm/V , e.g. by applying 1V you can get a displacement of 5Å

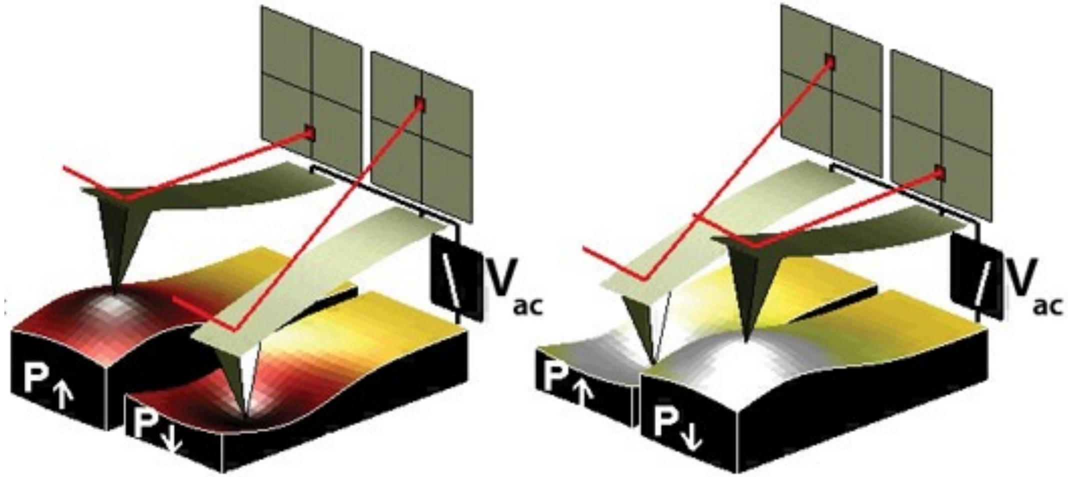
Piezoelectric response force microscopy (PFM)

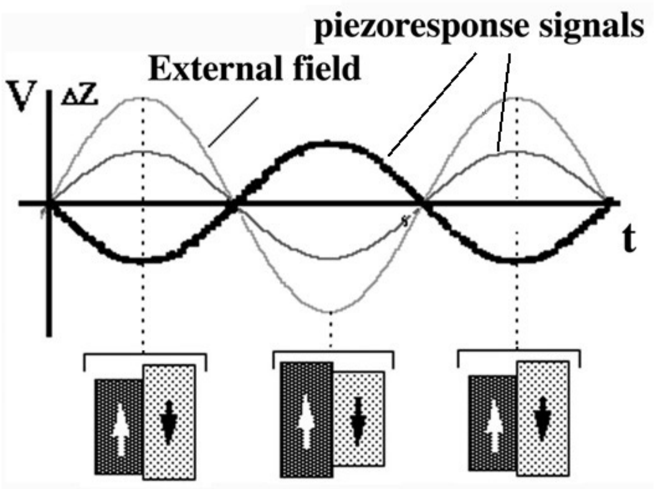
Measurements of strain in dc mode are often very difficult, PFM is much more practical

- The most efficient way to probe local piezoelectric response is to drive the conductive tip with a small ac voltage $\boldsymbol{V_{ac} = V_0 \sin(\omega t)}$
The mechanical displacement at the same frequency (both amplitude and phase) is detected – ***lock-in***

- in many materials typical piezoelectric response is of order of magnitude of d_{33}=10 pm/V. The driving ac voltage for thin films and nanostructures is typically kept below 1V in order to avoid polarization switching, high conduction and other undesired effect. Hence the expected response amplitude may be below 10 pm (<0.1Å)

- lock-in technique permits filtering out such a small response even if the high-nose environment





- If the material consists of polarization domains (regions where the polarization points in different directions), which is typically observed in ferroelectrics the map of phase of local piezoelectric response corresponds to the map of ferroelectric domains

Piezoelectric response force microscopy (PFM)

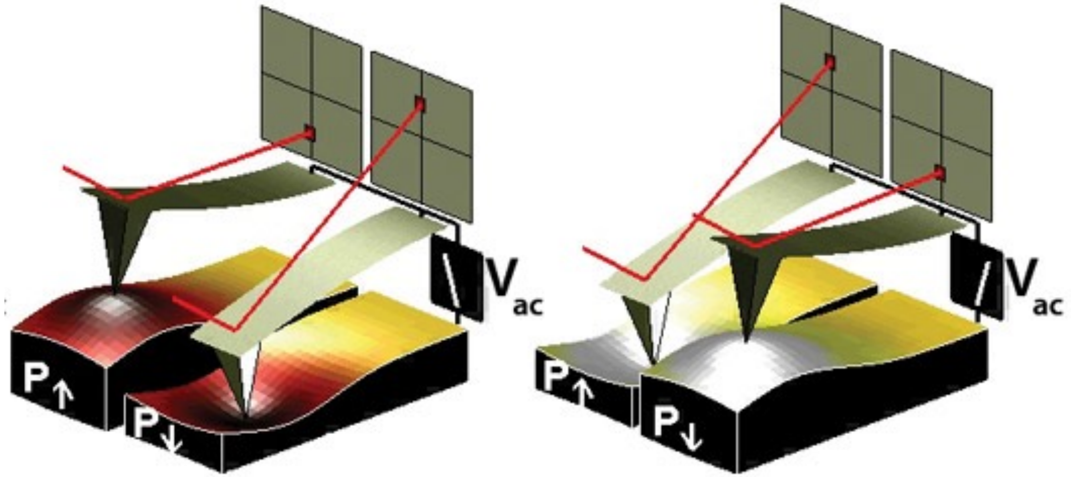
PFM background: where does the linear piezoresponse come from?

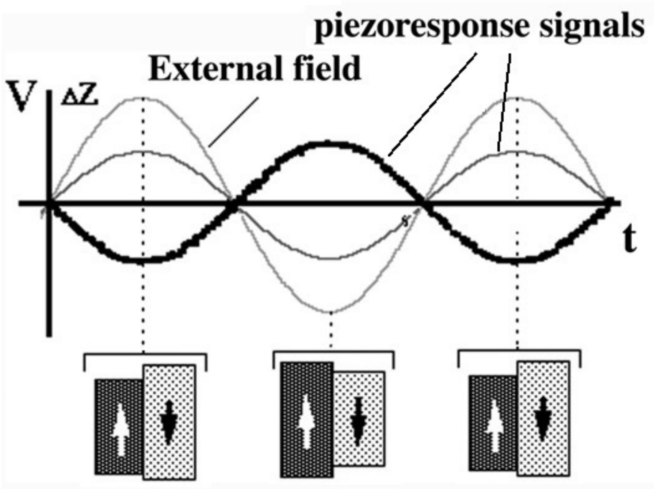
In most general case the strain ***x*** is linked to the polarization ***P*** through the equation $x=QP^2$, where Q is the electrostrictive coefficient. In presence of spontaneous polarization ***P*** slightly modified by a small external AC signal $P\pm\delta P$ we get for strain :

$$x = Q(P\pm\delta P)^2 = QP^2+ 2QP\delta P + \cancel{Q\delta P^2} = QP^2+ 2QP\varepsilon\varepsilon_0 E$$ ***, where E is small ac electric field***

$2QP\varepsilon\varepsilon_0$ ***is a piezoelectric coefficient (m/V), realistic values for ferroelectrics are 10-100 pm/V***

Thus a small AC signal linearizes the electromechanical response, so the phase of the response shows the polarization direction





- If the material consists of polarization domains (regions where the polarization points in different directions), which is typically observed in ferroelectrics the map of phase of local piezoelectric response corresponds to the map of ferroelectric domains

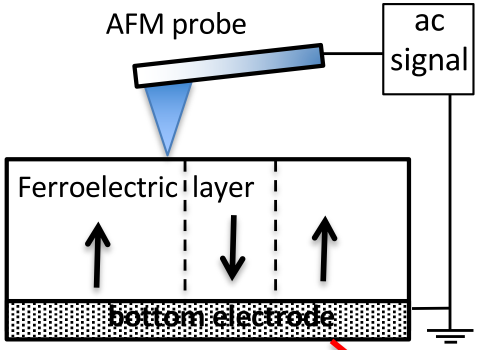
PFM: principles

- Drive: Eac of Eac+Edc, detect mechanical displacement (x or Z)
- E_{ac} must be small (does not switch or destroy – just probe)
- Contact technique, conductive probe
- Lock-in technique – signal is normally hidden by noise (pm range)
- DC-deformation is difficult to measure, ac displacement – pm resolution
- Displacement can be quantified – measure piezoelectric coefficient

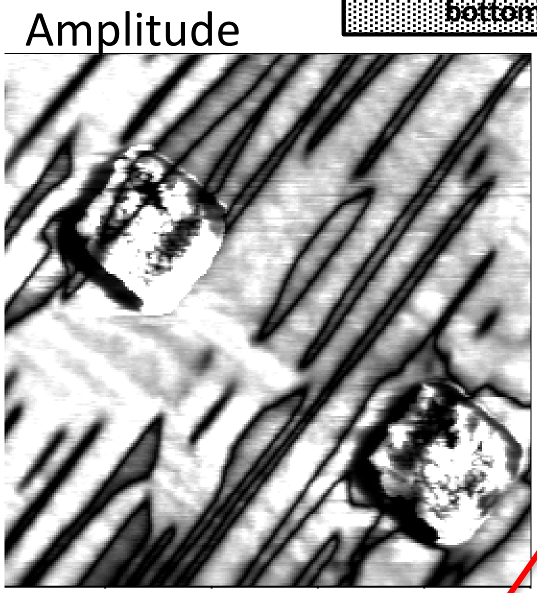
Useful for:

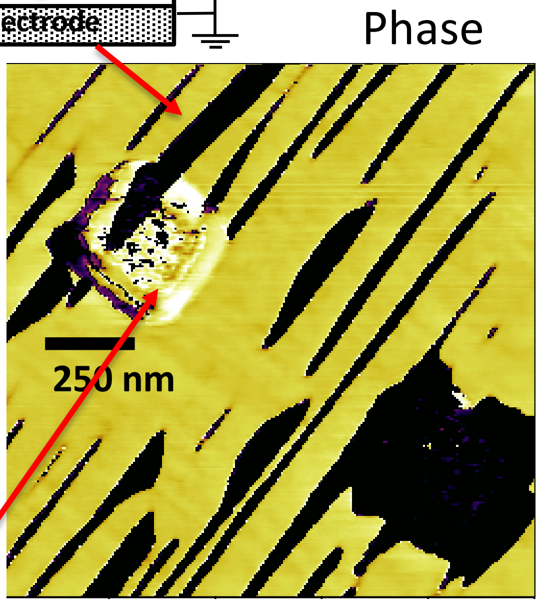
- Polar materials, in particular materials with polarization domains
- Materials with induced polarizations (mechanically, chemically, electrically)
- Useful for functional dielectrics, ionic materials (batteries), biomaterials…

Piezoelectric response mapping, through-electrode imaging



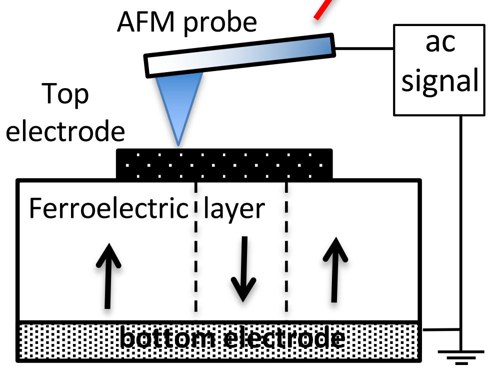
This example shows amplitude and phase of local piezoresponse measured on a thin (50 nm) film of ferroelectric bismuth ferrite ($BiFeO_3$).





In the phase image the domains with the spontaneous polarization pointing up are represented by bright color while the domains with polarization pointing down are black.

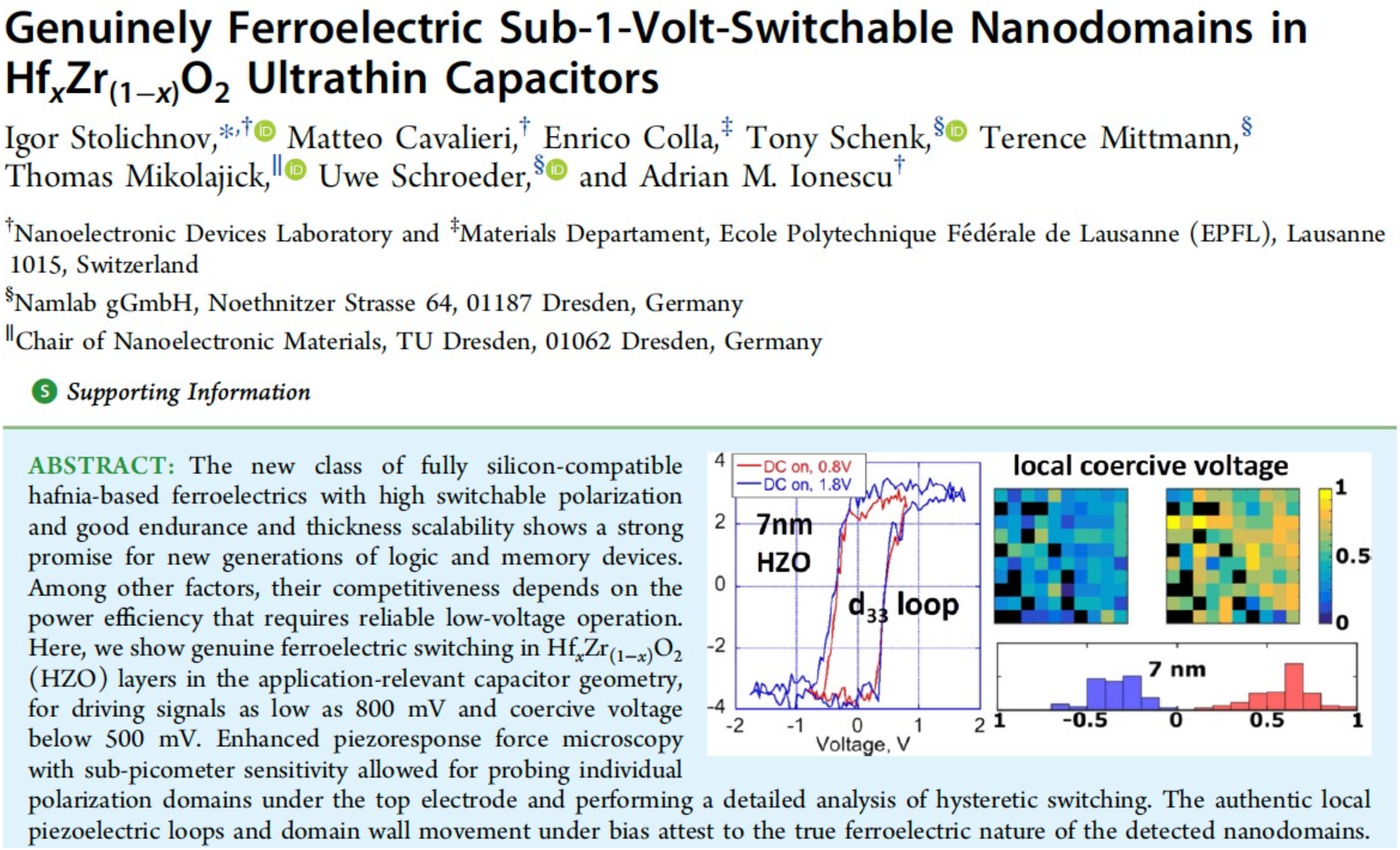
In the amplitude image the boundaries of domains are black (zero amplitude)



Rectangular Au electrodes are deposited on the film surface for electrical measurements.
Remarkably the domains can be sensed through the thick (50 nm) gold layer. Lower image shows a sketch of the electrical configuration used for probing piezoelectric response through the electrode

Another rectangular electrode have been poled and then mechanically removed by the probe. The area underneath is fully poled (big black spot)

PFM: ultimate limit of sensitivity: fractions of pm



Genuinely Ferroelectric Sub-1-Volt-Switchable Nanodomains in $Hf_xZr_{(1-x)}O_2$ Ultrathin Capacitors

Igor Stolichnov,*,[†] Matteo Cavalieri,[†] Enrico Colla,[‡] Tony Schenk,[§] Terence Mittmann,[§]
Thomas Mikolajick,[‖] Uwe Schroeder,[§] and Adrian M. Ionescu[†]

[†]Nanoelectronic Devices Laboratory and [‡]Materials Departament, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne 1015, Switzerland

[§]Namlab gGmbH, Noethnitzer Strasse 64, 01187 Dresden, Germany

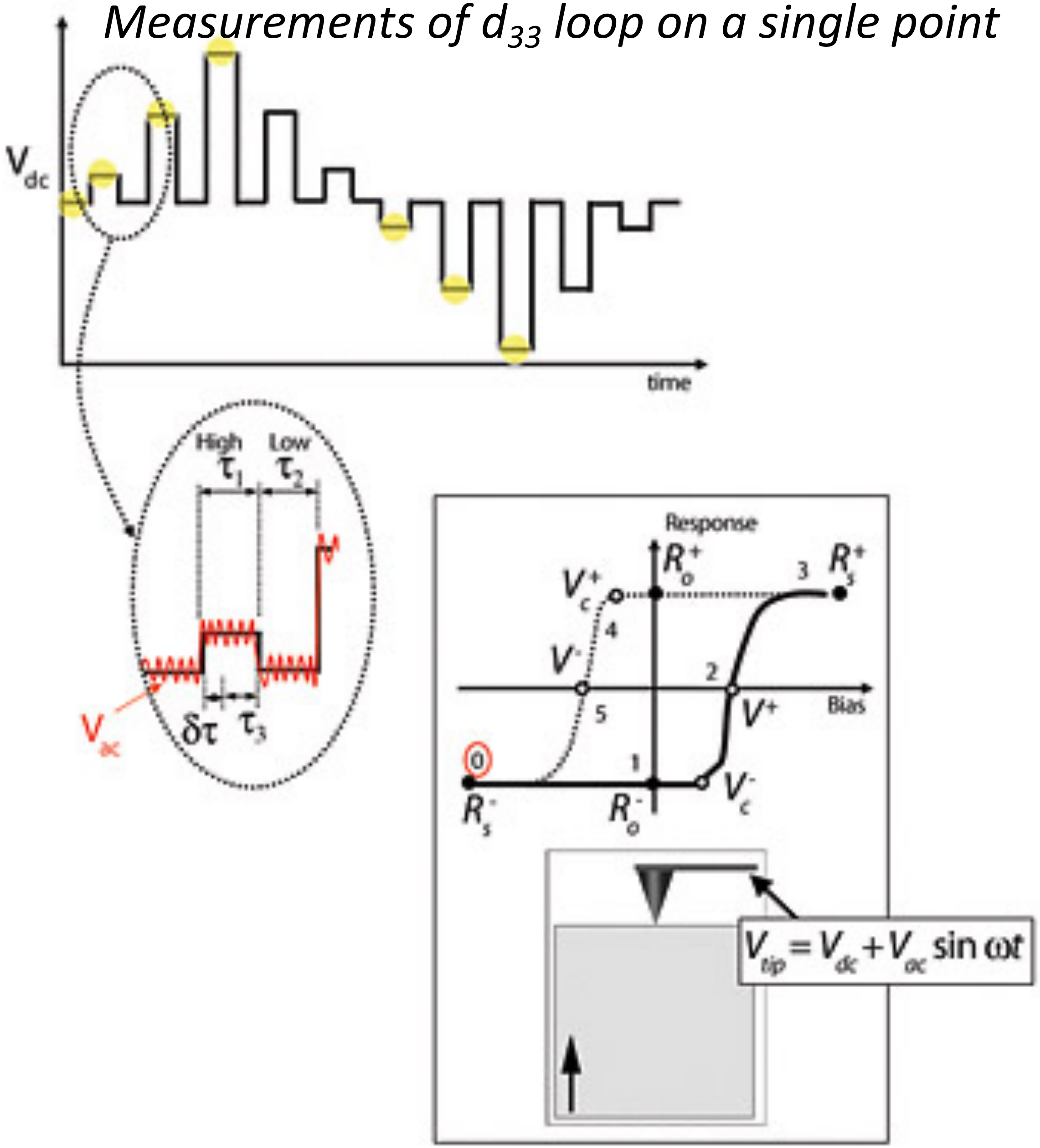
[‖]Chair of Nanoelectronic Materials, TU Dresden, 01062 Dresden, Germany

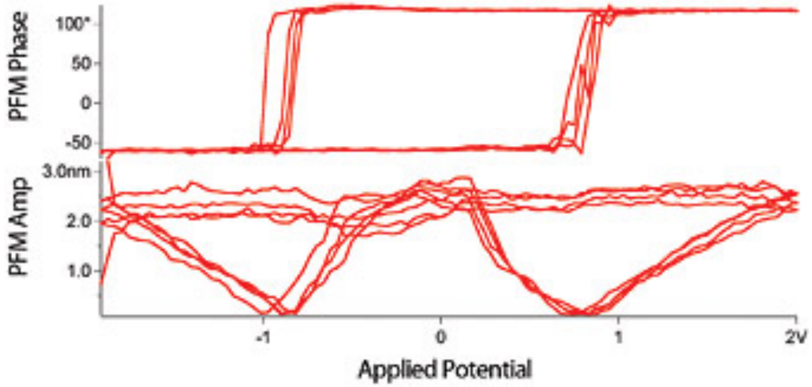
Supporting Information

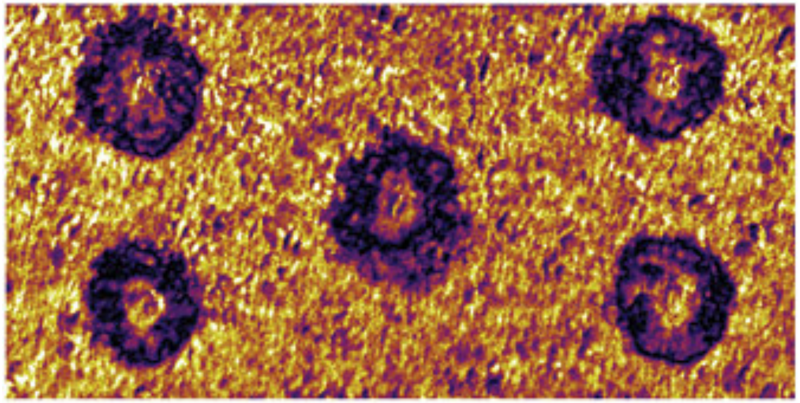
ABSTRACT: The new class of fully silicon-compatible hafnia-based ferroelectrics with high switchable polarization and good endurance and thickness scalability shows a strong promise for new generations of logic and memory devices. Among other factors, their competitiveness depends on the power efficiency that requires reliable low-voltage operation. Here, we show genuine ferroelectric switching in $Hf_xZr_{(1-x)}O_2$ (HZO) layers in the application-relevant capacitor geometry, for driving signals as low as 800 mV and coercive voltage below 500 mV. Enhanced piezoresponse force microscopy with sub-picometer sensitivity allowed for probing individual polarization domains under the top electrode and performing a detailed analysis of hysteretic switching. The authentic local piezoelectric loops and domain wall movement under bias attest to the true ferroelectric nature of the detected nanodomains.

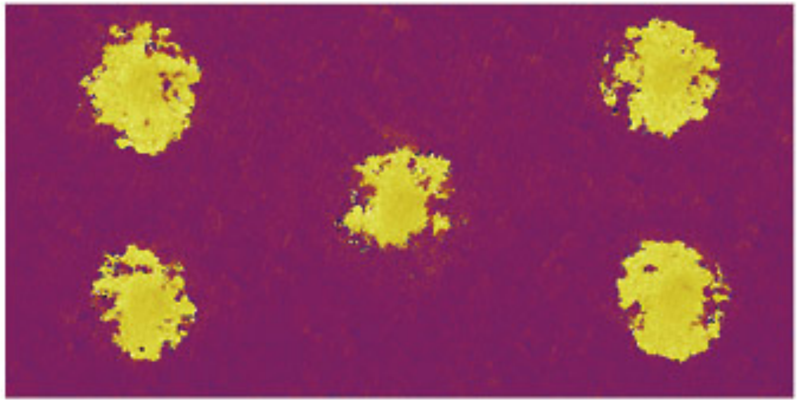
Piezoelectric response force (PFM) spectroscopy

Measurements of d_{33} loop on a single point







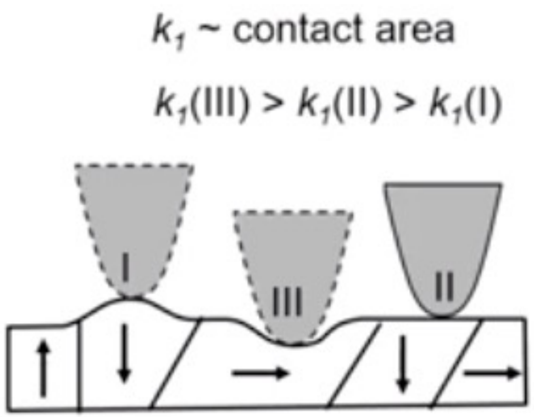


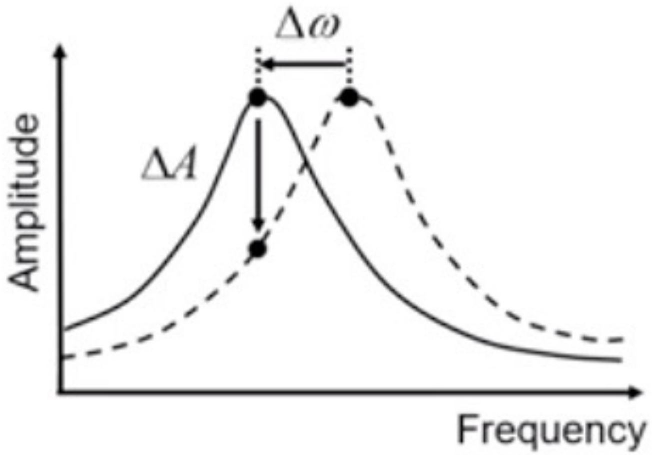
Loop measurement: the tip position is fixed, dc voltage is applied by steps; ac signal is permanently applied, the amplitude and phase of the mechanical response is plotted vs. V_{DC}

Cantilever resonance and frequency effects in PFM

- In PFM measurements the use of frequencies close to the tip resonance is very attractive – you can amplify the mechanical response by order(s) of magnitude

- There are difficulties – the resonance frequency may shift , this causes artifacts!
- The resonance frequency needs to be tracked and adjusted during PFM





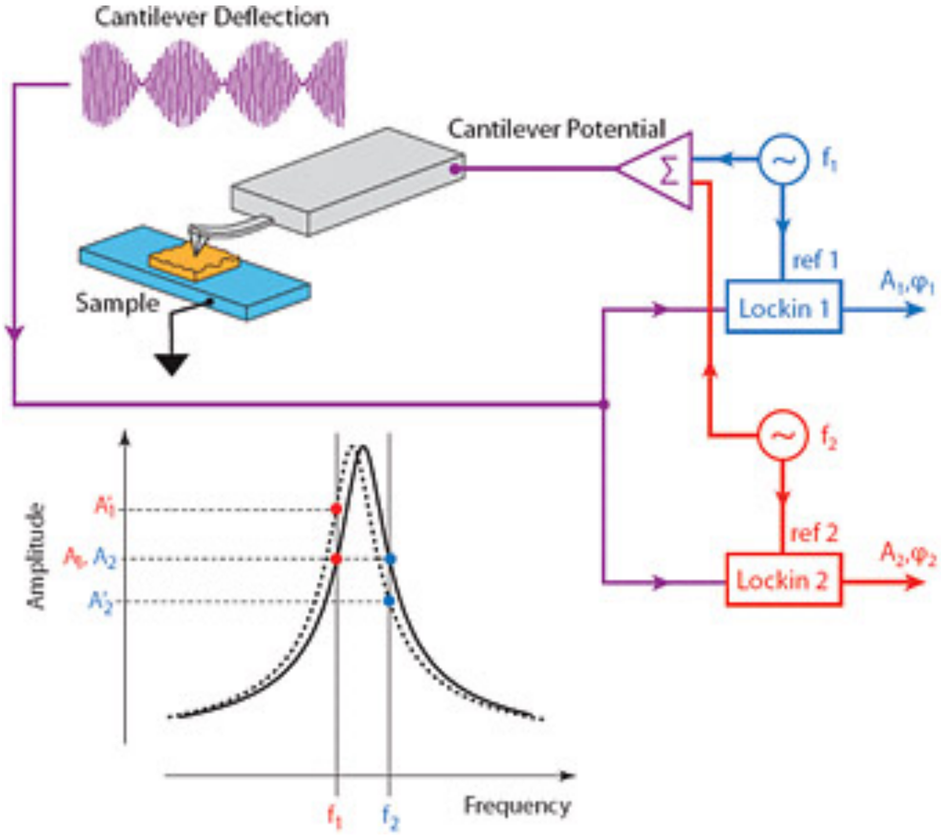
Problem 1: Resonance frequency depends on the topography (and not on the electromechanical response)

Problem 2: Standard PLL frequency tracking loops are unstable

Piezoelectric response force microscopy (PFM):

Enhancing sensitivity by using cantilever resonances

Dual AC Resonance Tracking (DART)



- Driving cantilever with ac voltage at resonance frequency enhances sensitivity by an order of magnitude

- How to maintain the resonance while scanning the surface?

- the most common kind of resonance-tracking feedback loop is called a phase-locked loop (PLL) – does not work (phase changes)

By measuring the amplitudes at two frequencies, it is possible to measure changes in the resonance behavior and track the resonant frequency. Specifically, by driving at one frequency below resonance (A1), and another above (A2), A2-A1 gives an error signal used as a feedback

A powerful technique to track resonance: band excitation

Instead of tracking the resonance frequency like DART, a band of frequencies is generated in order to characterize the resonance peak at each point

Application note from Asylum research says:

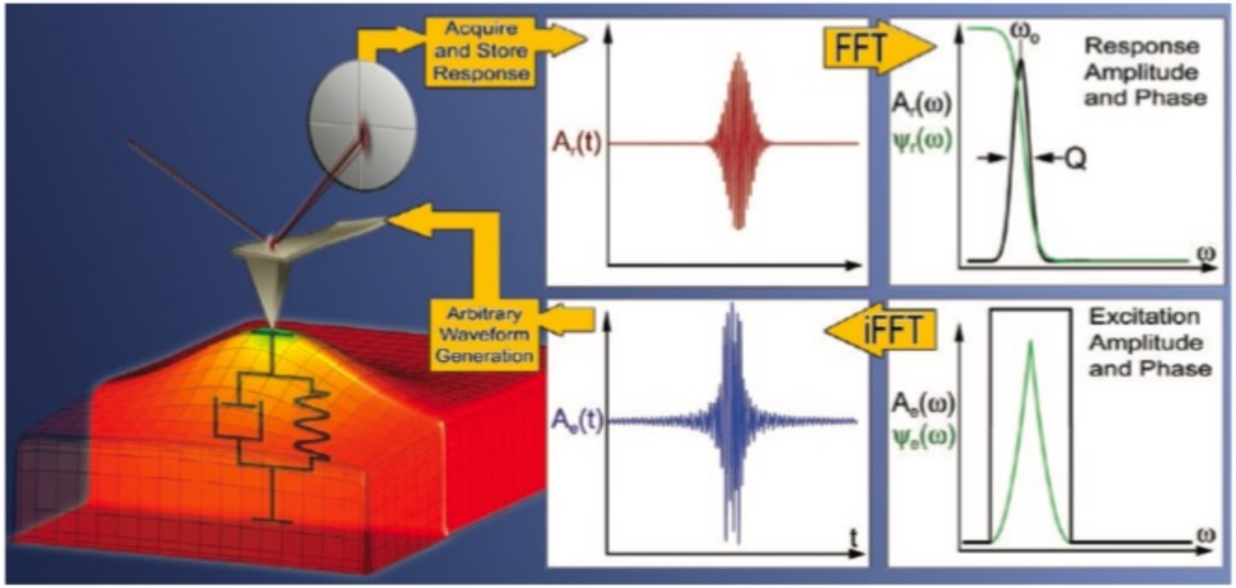
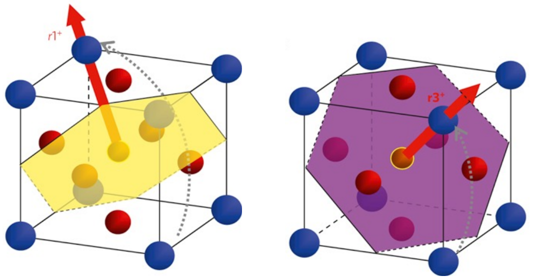


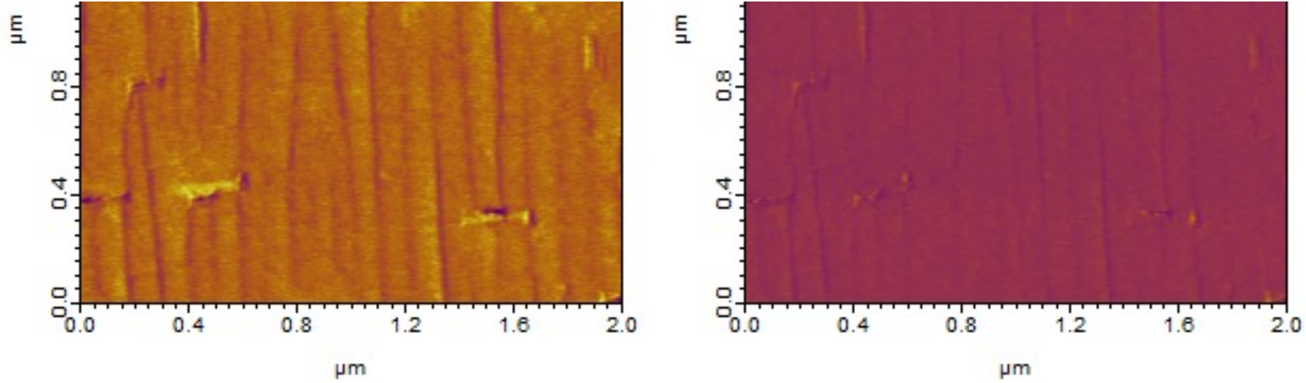
Figure 1: Principle of BE SPM. The excitation signal is digitally synthesized to have a predefined amplitude and phase in the given frequency window. The cantilever response is detected and Fourier transformed at each pixel in an image. The ratio of the fast Fourier transforms of response and excitation signals yields the cantilever response (sometimes also called the "transfer function"). Fitting the response to the simple harmonic oscillator yields amplitude, phase, resonance frequency, and Q-factor, plotted as 2D images or used as feedback signals.

Lateral PFM

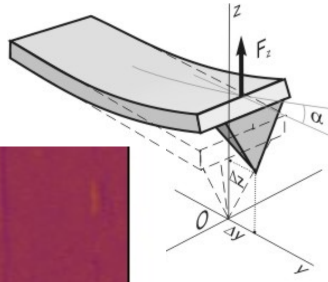


domain structures with unchanged vertical component of polarization do not show any contrast in standard (vertical) PFM images. However lateral PFM response shows clear amplitude and phase contrast

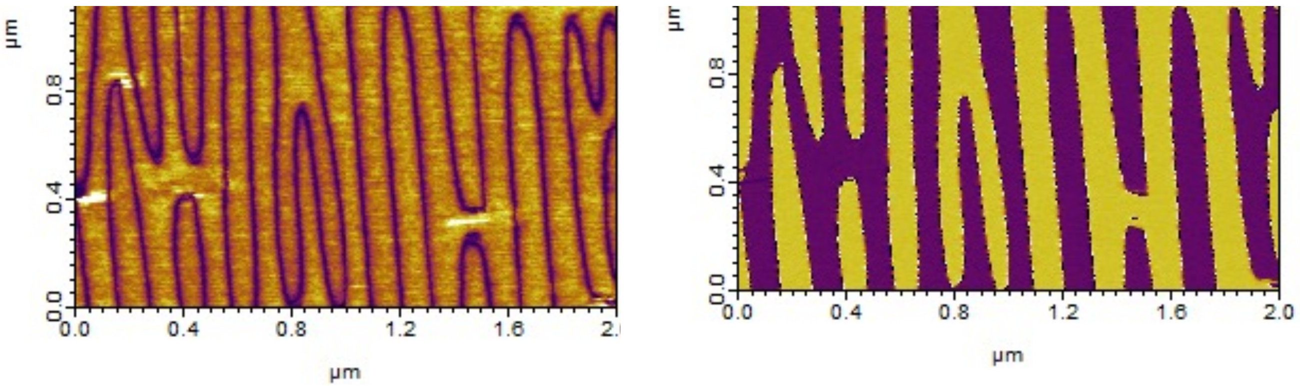
Vertical PFM


amplitude

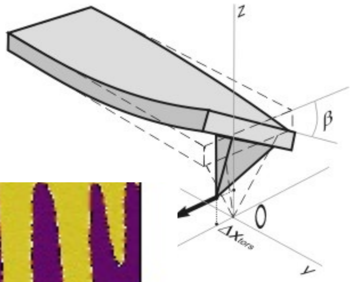
phase



Lateral PFM


amplitude

phase



-Substrate: DSO/SRO(5nm)

-Thickness 60 nm

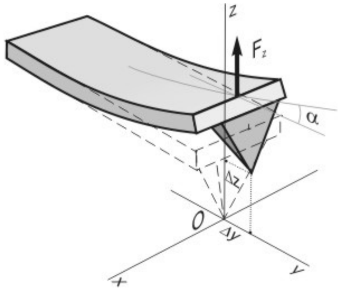
-Very smooth $BiFeO_3$ ferroelectric film (regular monolayer terraces)

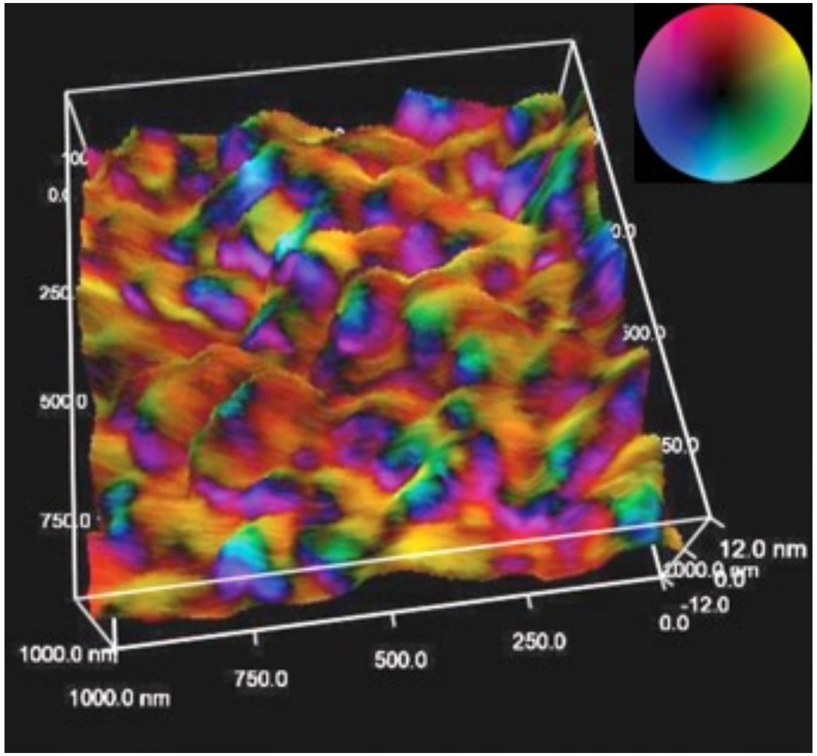
-Arrays of regular domains with 71° DWs
(vertical polarization component unchanged)

Vector PFM

In vector PFM, the real space reconstruction of polarization orientation comes from three components of piezoresponse: vertical PFM plus at least two orthogonal lateral PFM. The picture shows an example of a vector PFM image of a barium strontium titanate film (BST), permitting qualitative inspection of the correlation of grain size, shape and location with local polarization orientation. Here, the color wheel permits identification of the local orientation of the polarization. Regions colored as cyan (darker blue/green) possess polarizations which are oriented predominantly normal to the plane of the film, whereas regions that appear magenta-blue or light green possess polarizations which are oriented predominantly within the plane of the film. The intensity denotes the magnitude of the response.

Vertical PFM





Lateral PFM

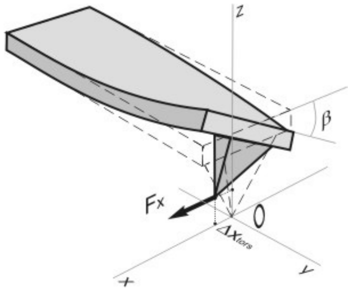
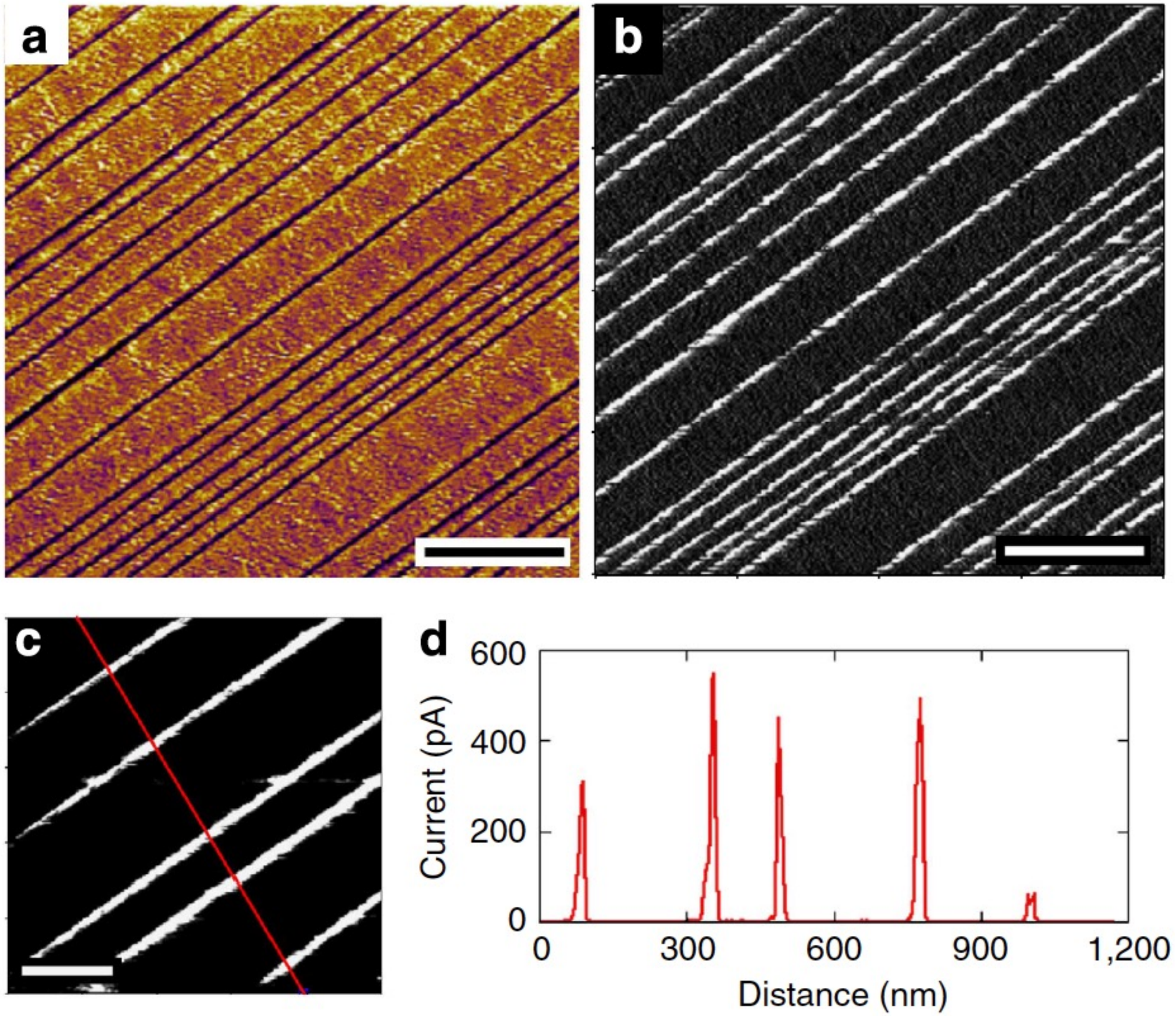


Image from Asylum Research website

Multi-functional AFM: combination of PFM and Conductive AFM (c-AFM)

PZT film with 1D array of ferroelectric domains (90° domains)
Combination of PFM and c-AFM: narrow 90° domains provide conductive channels



Nature Communications 5, 4677 (2014)

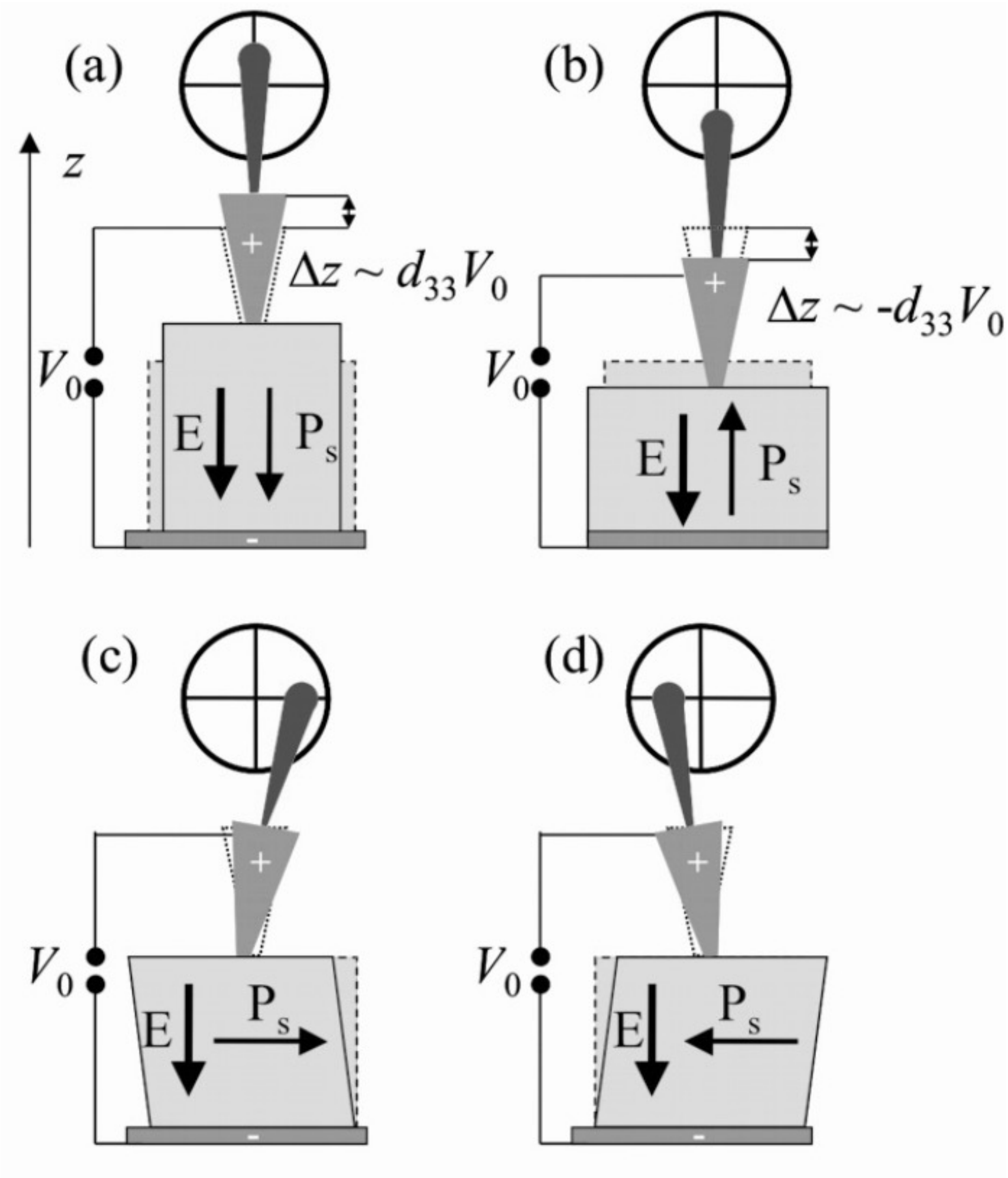
a) PFM amplitude, 4x4 μm scan

b) c-AFM, constant V=4V, same area

c) Zoom in: 1x1 μm c-AFM

d) Current profile, cross-section

Is it possible to use PFM if the polarization is in-plane?



Vertical mode:
Piezo coefficient $d_{33} = d_{333}$

Shear mode:
Piezo coefficient $d_{15} = d_{113}$

Exercise

- Download from moodle the paper cited below and supplementary materials
- Analyze the PFM measurements presented in this work
- Make sure you understand how the PFM experiment has been carried out
- Answer why angle-resolved measurements have been undertaken
- Answer why both vertical and lateral PFM are used (and what way they complement each other)

COMMUNICATION

Flexible Electronics

ADVANCED MATERIALS

www.advmat.de

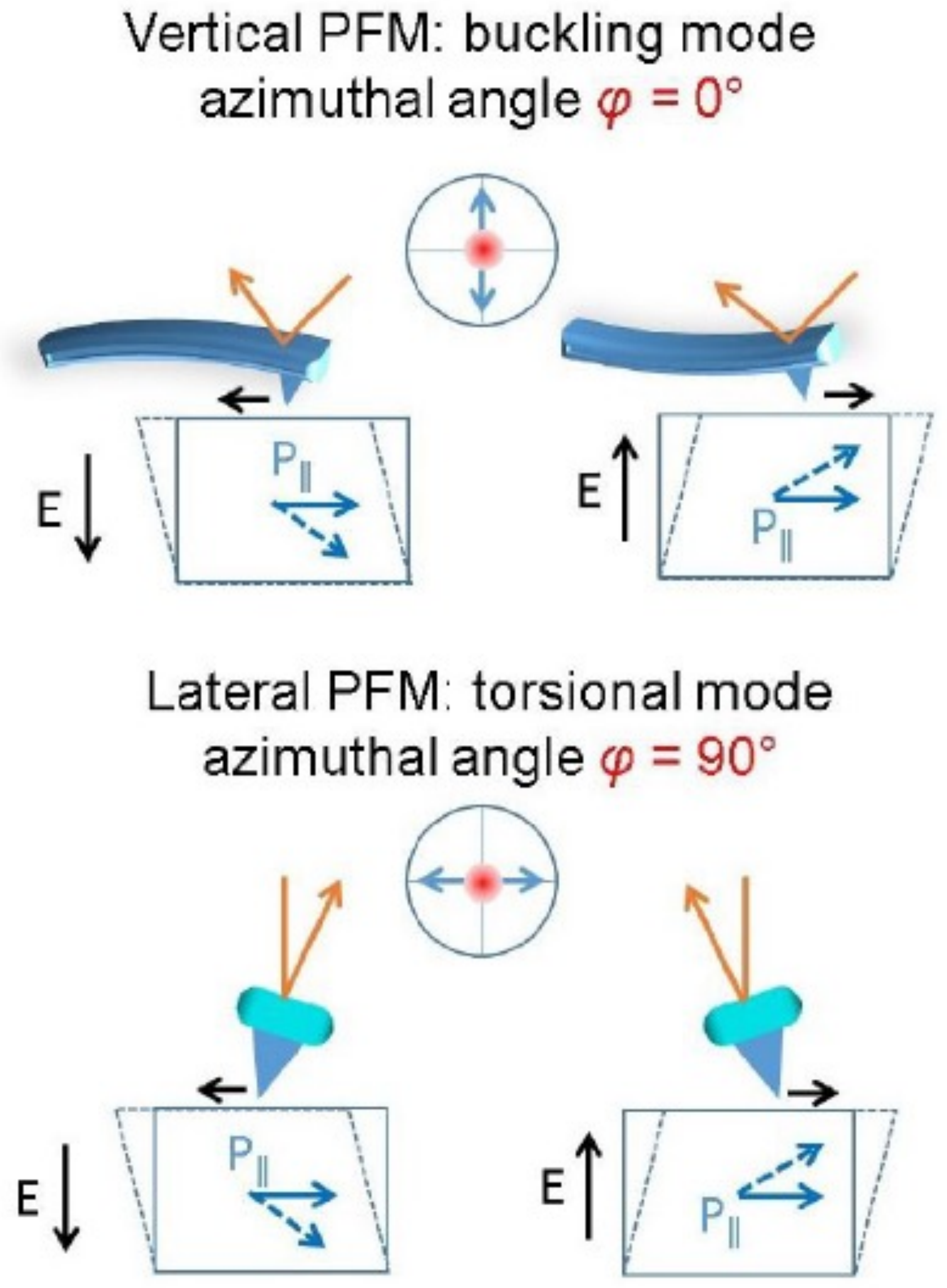
In-Plane Ferroelectricity in Thin Flakes of Van der Waals Hybrid Perovskite

Lu You, Fucai Liu, Hongsen Li, Yuzhong Hu, Shuang Zhou, Lei Chang, Yang Zhou, Qundong Fu, Guoliang Yuan, Shuai Dong, Hong Jin Fan, Alexei Gruverman, Zheng Liu, and Junling Wang**

Is it possible to use PFM if the polarization is in-plane?

Shear modes:

- signal is seen in both vertical and lateral PFM
- angle dependence: max of vertical PFM = min of lateral PFM



Shear piezocoefficient:

How to find deformation ε_{13}

$\varepsilon_n = d_{in}E_i$ – *inv. piezoeffect*

$\varepsilon_5 = \varepsilon_{13}$

$d_{15} = d_{113}$

$\varepsilon_{13} = d_{113}E_1$ *(E – electric field)*

Exercise

COMMUNICATION

Flexible Electronics

ADVANCED MATERIALS

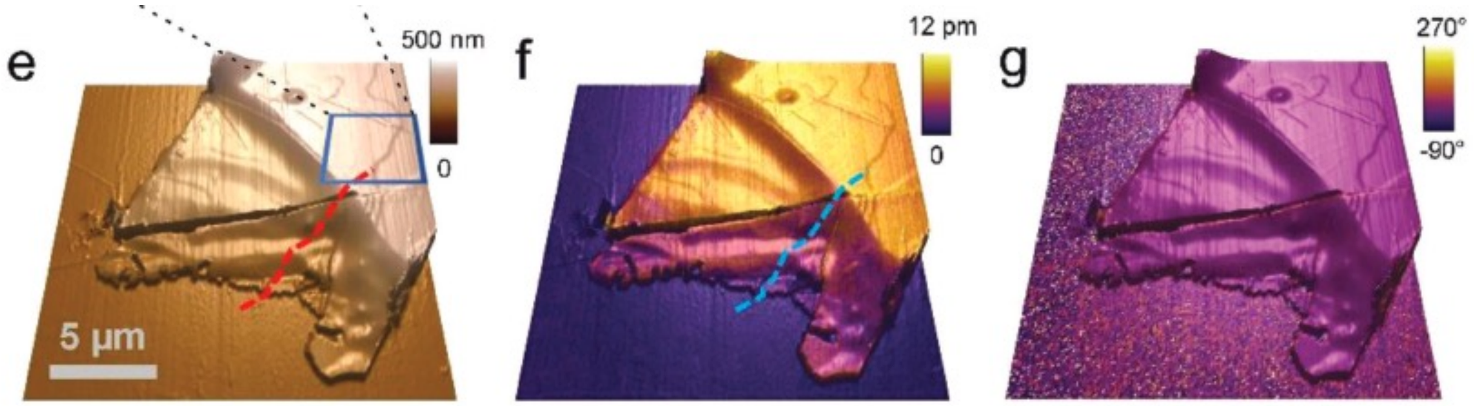
www.advmat.de

In-Plane Ferroelectricity in Thin Flakes of Van der Waals Hybrid Perovskite

Lu You, Fucai Liu, Hongsen Li, Yuzhong Hu, Shuang Zhou, Lei Chang, Yang Zhou, Qundong Fu, Guoliang Yuan, Shuai Dong, Hong Jin Fan, Alexei Gruverman, Zheng Liu, and Junling Wang**

- Study of ***in-plane ferroelectricity*** in bis(benzylammonium) lead tetrachloride (BA_2PbCl_4) down to one unit cell or two vdW layers
- Our purpose, understand how vertical PFM, lateral PFM and KPFM measurements in this study complement each other, what information could be extracted

Fig. 1 – topo (e), piezo response amplitude (f) and phase (g)



Exercise, continuation

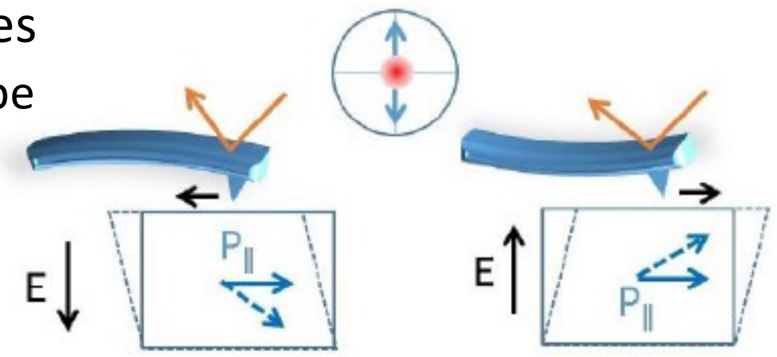
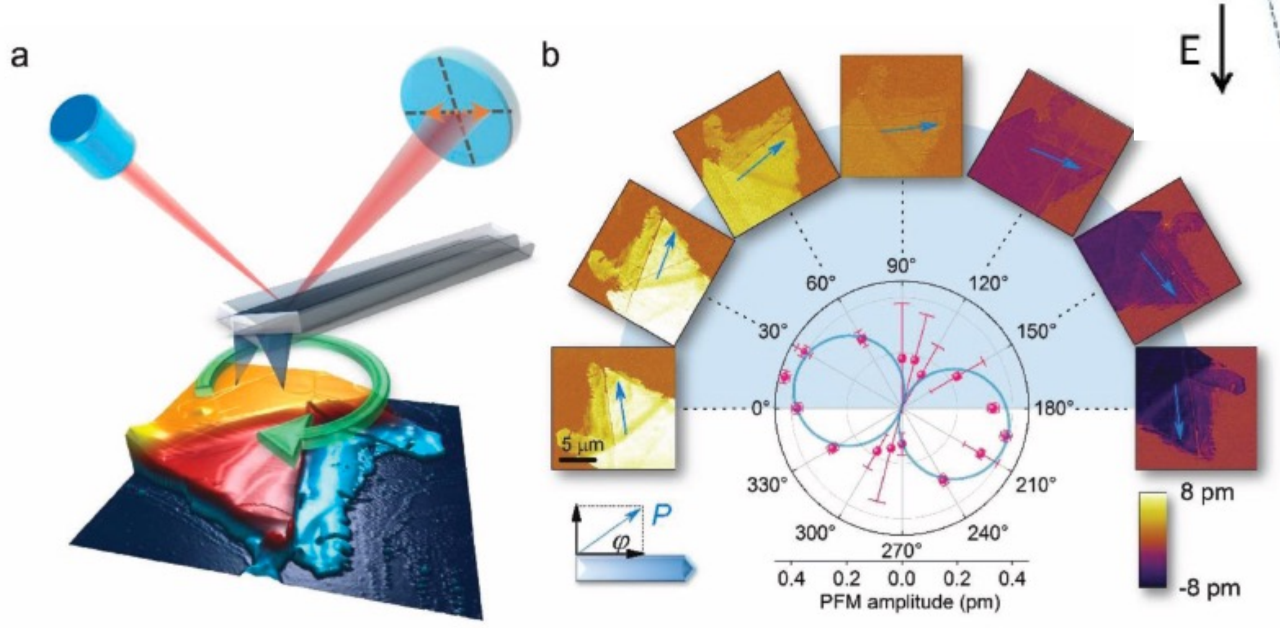

Vertical PFM: buckling mode
azimuthal angle $\varphi = 0°$

Fig. 2 Angular-resolved PFM study of BA2PbCl4 flakes
- physical rotation of the sample with respect to the probe
(just changing scan direction is not enough)



The effective piezoresponse data are plotted in polar coordinate. The blue arrow denotes the identified polarization vector.

- mixed amplitude/phase plot (weakest amplitude near 90°)
- This analysis confirms that the shear piezoresponse is being measured, and helps identifying the direction of polarization
- If instead of shear deformation, vertical expansion/contraction was measured (d_{33}), one should not expect such a strong angular dependence

Exercise, continuation

Vertical vs lateral PFM

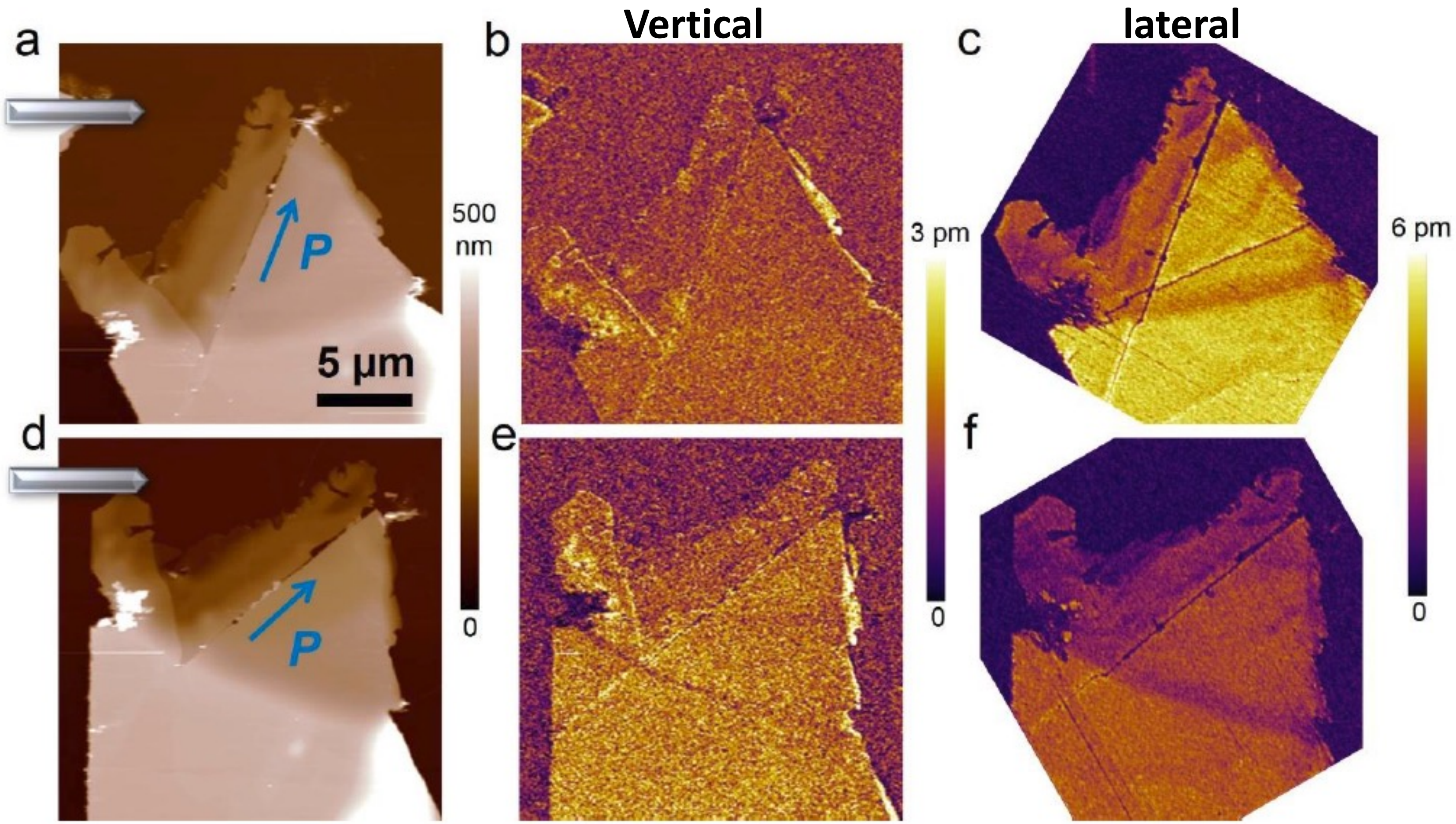


Figure S5. Vertical and lateral PFM comparison. a) Topographic, b) vertical PFM, c) lateral PFM images of the BA_2PbCl_4 flake at the azimuth angle of 30°. d) Topographic, e) vertical PFM, f) lateral PFM images of the BA_2PbCl_4 flake at the azimuth angle of 60°. When the polarization vector has a larger component along the cantilever axis, vertical PFM shows a higher response due to a stronger buckling effect, as described in Figure S2a. In the meantime, the response in lateral PFM reduces.

Higher signal in vertical PFM = lower signal in lateral PFM

Exercise, continuation

Lateral PFM images during the polarization switching using co-planar electrodes

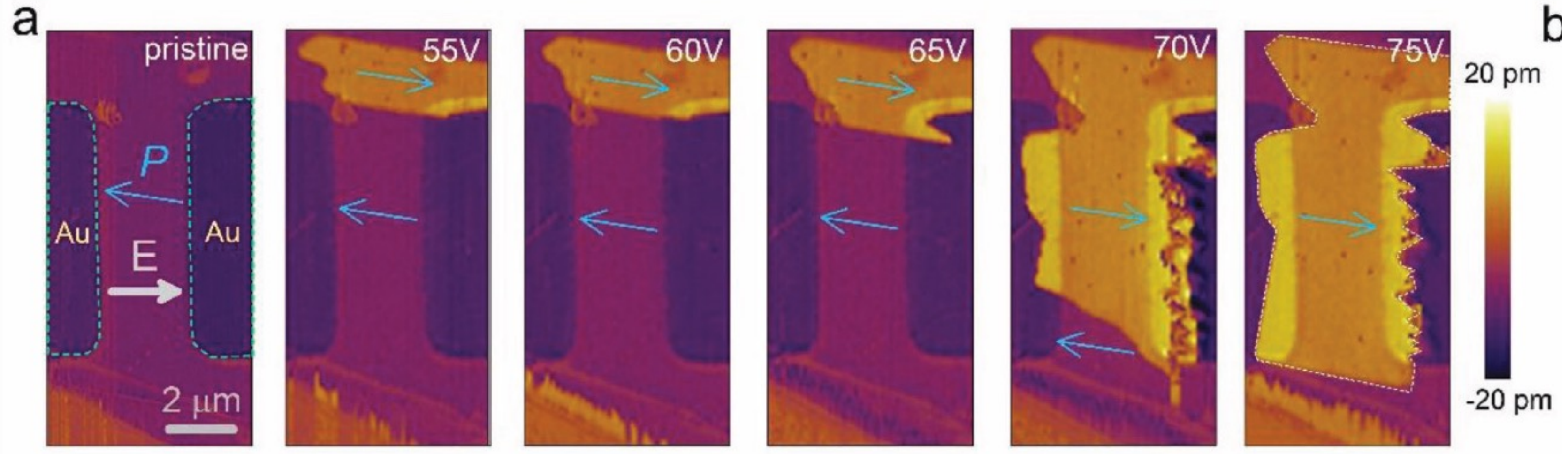


Fig. 4

- in-plane polarization reverses
- opposite domain boundaries have different roughness: insight into injection process
- The negatively charged wall is very flat and smooth, while the positively charged one is highly rough with zigzag pattern

- The positive charges can thus be understood as excessive holes injected from the electrode, which stabilize the negatively charged wall – smooth
- However, little electrons were injected from the other side, and there are no sufficient free electrons in the crystal. This makes the positively charged wall very energetic, which takes the zigzag form to minimize the electrostatic energy

Summary of the discussion

- Importance of understanding material (in the studied case – layered structure, in-plane polarization)

- PFM (unlike most of scanning probe techniques) studies tensorial properties, anisotropy is important, multiple measurements!

- In this case multiple vertical + multiple lateral PFM do the job
  - Identify type of electro-mechanical response (shear strain)
  - Determine orientation of in-plane polarization

- Based on this knowledge further analysis was possible
  - Study of switching domain nucleation/growth

  - analysis of charge injection from electrodes (predominant hole injection in this case)

Summary PFM

- Measurements of linear electromechanical response
- Drive with low ac signal – measure mechanical response at the same frequency (amplitude, phase)
- Contact technique, conductive probe (electric contact required)
- ac signal maybe combined with dc to study switching
- Very weak resonse (down to pm), maybe enhanced by cantilever resonpance
- Quantitative measurements of piezoelectric coefficient

- Polarization is a vector, piezoresponse – 3th rank tensor, full characterization involves vertical, lateral and angle-resolved measurements (PFM – tensorial SPM method)