The Laboratory plan for

2nd International Piezoresponse Force Microscopy Workshop

EPFL, Switzerland

Organizers: Nava Setter (EPFL) and Sergei V. Kalinin (ORNL)

Available equipment:

Agilent Technologies: 5500AFM system with PFM capabilities

Asylum Research: 4 MFP-3D units with HV PFM moduli,

Nanonis Gmbh: 1 controller (to be combined with EPFL MultiMode platform)

Veeco Instruments: Multimode-V and Nanoman-V

Personnel:

Agilent Technologies: Shuji Wu,

Asylum Research: Roger Proksch, Amir Moshar, Rolan Goschke, Ludger Weiser, Stephan Vinzelberg

Nanonis Gmbh: Romain Stomp, Anisoara Socoliuc

Veeco Instruments: Patrick Markus, Bede Pittenger

Attendees: 40

Foreword:

This lab course aims to provide a general experimental overview of Piezoresponse Force Microscopy and other SPM techniques for characterization of ferroelectric materials. As it is the case for all experimental techniques, the true mastery of PFM comes only after many hours spent in the lab, trying to make the recalcitrant sample work or peering at the image filled with mysterious squiggles and patches. Hence, it is impossible to learn everything within several short lectures. However, it is entirely possible to learn what to learn.

The purpose of this lab is three fold. One is to show the PFM in action and give the opportunity to turn the knobs on operational microscope and see the concepts discussed during the lectures unfold in real life. The second is have a broad overview of the field to gain the general understanding for novice in PFM, and get exposed to some of the advanced concepts complementary to one's experience for avis PFM practitioners. The final one is to get exposed to other PFMers and SPM manufacturers, share experience, and learn how PFM can further your research.

Finally, the control questions in the end of each lab are intended to be open ended and thought provoking, rather then require some formal answer. Some of these questions can be answered only by the end of the course. Some of them do not have a unique answer. For some of them, answers come only from experience, and we do not necessarily understand the reasons for the observed behaviors yet. Finally, many are the active field of research.

Enjoy the journey!

Lab I: Low-frequency PFM Imaging and Lithography

Goal: demonstrate basic PFM operation and polarization patterning.

Duration: 120 minutes

Materials:

Imaging: any (can be calibration sample from microscope manufacturer)

Writing: sol-gel or sputter PZT films

Suggested plan:

1. Demonstrate microscope operation in the contact mode
2. PFM imaging.
    a. The effect of Vac on contrast. What happens at 10 mV, 100 mV, 1,3,5, 10 V?
    b. The effect of driving frequency on contrast in vertical PFM. What happens at 100 Hz, 1 kHz, 3, 10, 50, 100, 300 kHz?
    c. The effect of driving frequency on contrast in lateral PFM. What happens at 100 Hz, 1 kHz, 3, 10, 50, 100, 300 kHz?
    d. Cantilever tune in contact: what happens at or away from the resonance?
    e. The effect of lock-in time constant on contrast: τ << pixel time, τ = pixel time, τ >> pixel time
3. Quantitative PFM
    a. Calibration. Quantify absolute response signal (from measured signal to d33) using standard calibration procedure
    b. Resolution. Zoom in on domain wall and determine width in amplitude and phase images.
    c. (optional) Pole the sample with 10 Vdc to achieve stationary domain structure [or use high coactivity sample], and compare PFM images at 3 Vpp and Vdc of 0 V and 10 V.
4. PFM lithography
    a. Write a pattern on materials surface (square, single pulse switching, or image using bit or vector lithography)
    b. Image the pattern in a standard PFM mode (by default, 50 kHz, 3 Vpp, or using optimal conditions determined in I.2)
    c. Examine the edges of the pattern: are they smooth, ragged, related to topography?
    d. Try to image pattern with 10 Vpp and see if it is stable.

Control questions:

1. What are the optimal conditions for PFM imaging? How do we choose driving voltage and driving frequency?
2. What can we expect to happen if the driving frequency is 100 Hz? 3 kHz? 100 kHz?
3. What happens close to the resonances? What are the arguments for and against PFM imaging close to the resonance?
4. Does the topography affect PFM imaging, and when is this effect important?
5. What is the dc bias offset on PFM imaging?
6. How do we choose the time constant on the lock-in?
7. Why is the width of domain wall in phase image is much smaller then amplitude or mixed? Is phase imaging superior?
8. What would you do if the PFM stops working (assume that you have PFM enabled on the microscope level, so you do not need to worry about setting up your own system)?
9. How would you choose the tip for a PFM experiment on (a) 10 nm epitaxial PZT film, (b) 1 micron sol-gel PZT film, (c) PZT ceramics, (d) tooth dentin, (e) ferroelectric polymer film. Consider (a) optimal spring constant [e.g. from 0.01, 0.03, 0.1, 0.3, 1, 3, 10, 40 N/m] and (b) type of conductive coating [Au, Pt, Co-Cr, diamond, TiN, W2C].
10. Why PFM domain imaging and writing are of interest (a) for basic research, (b) for applied research and industry, (c) for you?

Suggested reading:

Reviews and Books:

1. Sergei V. Kalinin, A. Rar, and S. Jesse, *A Decade of Piezoresponse Force Microscopy: Progress, Challenges, and Opportunities*, IEEE Transactions on Ultrasonics and Ferroelectric Materials **53**, 2226 (2006).
2. "*Scanning Probe Microscopy of Electrical and Electromechanical Phenomena at the Nanoscale*", edited by S.V. Kalinin and A. Gruverman (Springer, 2006).
3. "*Ferroelectrics at Nanoscale: Scanning Probe Microscopy Approach*", edited by M. Alexe and A.Gruverman (Springer, 2004).
4. “*NanoScale Phenomena in Ferroelectric Thin Films*”, edited by S. Hong (Kluwer Academic Publishers, Boston, 2004).

Resolution:

5. A.N. Morozovska, S.L. Bravina, E.A. Eliseev, and Sergei V. Kalinin, *Resolution-function theory in piezoresponse force microscopy: Wall imaging, spectroscopy, and lateral resolution*, Phys. Rev. **B 75**, 174109 (2007)

6. Sergei V. Kalinin, S. Jesse, B.J. Rodriguez, E.A. Eliseev and A.N. Morozovska, *Quantitative Determination of Tip Parameters in Piezoresponse Force Microscopy*, Appl. Phys. Lett. **90**, 212905 (2007)
7. S. V. Kalinin, S. Jesse, J. Shin, A.P. Baddorf, H.N. Lee, A. Borisevich, and S.J. Pennycook, *Resolution, Information Limit, and Contrast Transfer in Piezoresponse Force Microscopy*, Nanotechnology **17**, 3400 (2006).

Frequency effects:

8. S. Jesse, A.P. Baddorf, and Sergei V. Kalinin, *Dynamic Effects in Electromechanical Scanning Probe Microscopies*, Nanotechnology **17**, 1615 (2006).
9. C. Harnagea, M. Alexe, D. Hesse et al. *Contact resonances in voltage-modulated force microscopy*, Appl. Phys. Lett. 83, 338 (2003).
10. B. Mirman and S.V. Kalinin, *Resonance Frequency Analysis for Surface-Coupled AFM Cantilever in Ambient and Liquid Environments*, Appl. Phys. Lett. **92**, 083102 (2008)

Calibration:

11. M.J. Higgins, R. Proksch, J.E. Sader et al. *Noninvasive determination of optical lever sensitivity in atomic force microscopy*, Rev. Sci. Instr. 77, 013701 (2006).

Lab II: PFM of capacitor structures

Goal: demonstrate imaging and polarization switching in capacitor structures

Duration: 120 minutes

Suggested plan:

1. Demonstrate microscope operation in the contact mode, and image capacitor structure. Identify the primary elements of a capacitor structure.
2. PFM imaging of capacitor structure.
    a. Acquire vertical and lateral PFM image of a capacitor
    a. Zoom in on domain wall and determine width in amplitude and phase images.
3. Polarization switching in a capacitor
    a. Pole capacitor with a strong (10V) bias pulse and examine the changes in domain structure.
    b. Apply a small (1,2,3 V) pulse of opposite polarity and examine changes in domain structure and distribution.
    c. Pole a capacitor with a strong (10V) pulse and image at increasing Vac amplitudes.

Control questions:

1. What are the differences in PFM imaging mechanism in a capacitor structure and on a bare surface? Compare electric field distribution, strain field distribution, and signal generation volume.
2. What determines the resolution in a capacitor experiment?
3. Why we can use tip bias for small capacitors and thick films, but not for large capacitors and thin films? Can you estimate the limit on the experimentally-accessible sizes? What strategies can we use if tip-electrode approach fails?
4. Experimentally, we observed a ~10 nm feature in a 100 nm epitaxial PZT capacitor with 1 micron top electrode. Is it real domain wall, or artifact? What if (a) top electrode thickness is 10 nm or (b) film is columnar sol-gel? What can be the origins of observed artifact, and how would one verify them?
5. How does switching occur in capacitor structures? Can we pattern an image in capacitor?
6. Compare the PFM imaging on free surfaces and tip-electrode and wire-electrode set-up for capacitor imaging in terms of experimental difficulties.
7. How would you choose the experimental set-up for a PFM experiment on (a) 10 nm thin, 50 nm size epitaxial PZT capacitor, (b) 1 micron thick, 300 micron wide sol-gel

PZT capacitor, (c) PZT ceramics actuator, Consider (a) optimal spring constant [e.g. from 0.01, 0.03, 0.1, 0.3, 1, 3, 10, 40 N/m] and (b) type of conductive coating [Au, Pt, Co-Cr, diamond, TiN, W2C], and (c) optimal set-up (tip or wire)

8. Why PFM domain imaging and polarization switching in capacitors is of interest (a) for basic research, (b) for applied research and industry, (c) for you?

Suggested reading:

1. A. Gruverman, D. Wu, and J.F. Scott, *Piezoresponse Force Microscopy Studies of Switching Behavior of Ferroelectric Capacitors on a 100-ns Timescale*, Phys. Rev. Lett. **100**, 097601-604 (2008).
2. C.Dehoff, B.J.Rodriguez, A.I.Kingon, R.J.Nemanich, A.Gruverman, and J.S.Cross, *AFM-Based Experimental Setup for Studying Domain Switching Dynamics in Ferroelectric Capacitors*, Rev. Sci. Instrum. **76**, 023708 (2005).
3. A.Gruverman, B.J.Rodriguez, R.J.Nemanich, A.I.Kingon, A.Tagantsev, J.S.Cross and M.Tsukada *Mechanical Stress Effect on Imprint Behavior of Integrated Ferroelectric Capacitors*, Appl. Phys. Lett. **83**, 728-730 (2003).
4. A.Gruverman, B.J.Rodriguez, R.J.Nemanich, A.I.Kingon, J.S.Cross and M.Tsukada *Spatial Inhomogeneity of Imprint and Switching Behavior in Integrated Ferroelectric Capacitors*, Appl. Phys. Lett. **82**, 3071-3073 (2003).
5. R. Gysel, A. K. Tagantsev, I. Stolichnov, N. Setter, and M. Pavius, *Ferroelectric film switching via oblique domain growth observed by cross-sectional nanoscale imaging*, Appl. Phys. Lett. **89**, 082906 (2006).
6. I. Stolichnov, L. Malin, E. Colla, A.K. Tagantsev, and N. Setter, *Microscopic aspects of the region-by-region polarization reversal kinetics of polycrystalline ferroelectric* $Pb(Zr,Ti)O_3$ *films*, Appl. Phys. Lett. **86**, 012902 (2005).
7. I. Stolichnov, E. Colla, A. Tagantsev, S. S. N. Bharadwaja, S. Hong, N. Setter, J. S. Cross, and M. Tsukada, *Unusual size effect on the polarization patterns in micron-size* $Pb(Zr,Ti)O_3$ *film capacitors*, Applied Physics Letters, Vol. **80**, 4804–4806 (2002).
8. Sergei V. Kalinin, B.J. Rodriguez, S.H. Kim, S.K. Hong, A. Gruverman, and E.A. Eliseev *Imaging Mechanism of Piezoresponse Force Microscopy in Capacitor Structures*, Appl. Phys. Lett. **92**, 152906 (2008).

Lab III: Polarization Dynamics and Piezoresponse Spectroscopy in Films

Goal: demonstrate Piezoresponse Force Spectroscopy and Switching Spectroscopy mapping.

Duration: 120 minutes

Suggested plan:

1. Acquire the standard PFM image and explore the sample structure. Identify regions of interest (grains with different response, grain boundaries, topographic defects)
2. Acquire PFS loop at a single location
   a. Explore the probing waveform for PFS.
   b. Acquire several hysteresis loops. Identify the local nucleation and coercive biases and remanent response. Are the loops stationary, or change between the cycles?
   c. Determine the effect of Vac on the loop shape. What happens at 10 mV, 100 1, 10 Vpp? What happens iv Vac is 0.1, 0.5, 0.9, and 1.2 of coercive bias?
   d. (optional) Compare the in-field and remanent loops
   e. (optional) Compare the loops at and away from the cantilever resonance
   f. Acquire the PFM imaging after the PFS experiment
3. Spatially resolved PFS and SSPFM
   a. Acquire hysteresis loops at different locations (grain center, boundary between two grains, topographic defect), and compare them
   b. (optional) Acquire sparse and dense SSPFM maps of the system using known affected volume
   c. Compare PFM images before and after the SSPFM experiment

Control questions:

1. What are the conditions for successful PFS experiment (sample properties, cantilever choice, driving frequency and voltage amplitude)?
2. Compare the hysteresis loops acquired in-field and out of field (remanent)? What is the role of (a) polarization dynamics, (b) electrostatic tip-surface interactions.
3. Compare to the mechanism of local PFM hysteresis loops, PFM loops in capacitor structures, and macroscopic loops. Consider (a) the field structure, (b) localization of nucleation sites, (c) nature of response, and (d) measured properties.
4. What information can be extracted from local PFM hysteresis loop? SS-PFM maps in dense and sparse regimes?

5. The macroscopic P-E hysteresis loops are always clock-wise as a consequence of 2nd law of thermodynamics. Does this limitation apply to PFM loops?
6. What are the factors determining the quantitativeness of PFM loops? Consider the ideal square hysteresis loop, and discuss possible contributions that can expand and shift it along (a) voltage axis and (b) response axis
7. What are the criteria for choice of Vac in PFS experiment? Consider signal to noise ratio and polarization switching. Which strategies can you think of to improve signal to noise ratio?
8. Why PFM spectroscopy are of interest (a) for basic research, (b) for applied research and industry, and (c) would you ever want to do it for living?

Suggested reading:

Piezoresponse Force Spectroscopy and 3D-PFM Imaging:

1. U. Roelofs, U. Bottger, R. Waser, F. Schlaphof, S. Trogisch, and L.M. Eng, *Differentiating 180 degrees and 90 degrees switching of ferroelectric domains with three-dimensional piezoresponse force microscopy*, Appl. Phys. Lett. **77**, 3444 (2000)
2. H.Y. Guo, J.B. Xu, I.H. Wilson, Z. Xie, E.Z. Luo, S.B. Hong, H. Yan, *Study of domain stability* on (Pb0.76Ca0.24)TiO3 *thin films using piezoresponse microscopy*, Appl. Phys. Lett. **81**, 715 (2002)
3. B.J.Rodriguez, A.Gruverman, A.I.Kingon, R.J.Nemanich, and J.S.Cross, "Three-Dimensional High-Resolution Reconstruction of Polarization In Ferroelectric Capacitors by Piezoresponse Force Microscopy", J. Appl. Phys. **95**, 1958-1963 (2004).
4. S.V.Kalinin, B.J.Rodriguez, S.Jesse, J.Shin, A.P.Baddorf, P.Gupta, H. Jain, D.B.Williams, and A.Gruverman, “Vector Piezoresponse Force Microscopy”, Microscopy and Microanalysis **12**, 206-220 (2006).

Switching Spectroscopy PFM

1. S. Jesse, H.N. Lee, and Sergei V. Kalinin, *Quantitative Mapping of Switching Behavior in Piezoresponse Force Microscopy*, Rev. Sci. Instr. **77**, 073702 (2006).
2. Sergei V. Kalinin, B.J. Rodriguez, S. Jesse, Y.H. Chu, T. Zhao, R. Ramesh, E.A. Eliseev, and A.N. Morozovska, *Intrinsic Single Domain Switching in Ferroelectric Materials on a Nearly-Ideal Surface*, PNAS **104**, 20204 (2007).
3. Stephen Jesse, B.J. Rodriguez, A.P. Baddorf, I. Vrejoiu, D. Hesse, M. Alexe, E.A. Eliseev, A.N. Morozovska, and Sergei V. Kalinin, *Direct imaging of Spatial and Energy distribution of Nucleation Centers in Ferroelectric Materials*, Nature Materials **7**, 209 (2008).
4. Sergei V. Kalinin, S. Jesse, B.J. Rodriguez, Y.H. Chu, R. Ramesh, E.A. Eliseev and A.N. Morozovska, *Probing the role of single defects on the thermodynamics of electric-field induced phase transitions*, Phys. Rev. Lett. accepted

Lab IV: Dynamics PFM modes

Goal: Demonstrate frequency-dependent PFM operation

Duration: 120 minutes

Suggested plan:

1. Acquire low frequency PFM image of the sample (PPLN or PZT sol-gel film)
2. Explore the high-frequency PFM operation
    a. Tune the cantilever in contact with the surface for several different set-point
    b. Tune the cantilever at different locations on the surface (e.g. grain center and grain boundary). Compare the resonance frequency shift and peak width.
    c. Acquire images well below the first resonance and at frequencies close to resonance (e.g. at half height, and at resonance). Compare the observed contrast (positive and negative regions in phase images, phase difference between the positive and negative domains, relationship between amplitude maxima and topography).
3. Frequency tracking PFM
    a. Acquire resonance-tracking PFM image using DRFT or BE.
    b. (optional) Acquire piezoresponse force spectrum with resonant tracking

Control questions:

1. What are the advantages and disadvantages of resonance-enhanced PFM? Consider the signal to noise ratio and topographic cross-talk. Does the importance of these factors depend on material?
2. Does the resonance enhancement reduce contribution of thermomechanical noise, electronic noise, or laser shot noise?
3. Discuss the strategies for resonance-frequency tracking in PFM.

Suggested reading:

Dual AC:

1. R. Proksch, *Multifrequency, repulsive-mode amplitude-modulated atomic force microscopy*, Appl. Phys. Lett. **89**, 113121 (2006).
2. N.F. Martinez, S. Patil, J.R. Lozano, and R. Garcia, *Enhanced compositional sensitivity in atomic force microscopy by the excitation of the first two flexural modes*, Appl. Phys. Lett. **89**, 153115 (2006)

3. J.R. Lozano and R. Garcia, *Theory of multifrequency atomic force microscopy*, Phys. Rev. Lett. **100**, 076102 (2008).

DRFT:

1. B.J. Rodriguez, C. Callahan, S.V. Kalinin, and R. Proksch, *Dual-Frequency Resonance-Tracking Atomic Force Microscopy*, Nanotechnology **18**, 475504 (2007).

Band Excitation:

1. Stephen Jesse, Sergei V. Kalinin, R. Proksch, A.P. Baddorf, and B.J. Rodriguez, *Energy Dissipation Measurements on the Nanoscale: Band Excitation Method in Scanning Probe Microscopy*, Nanotechnology **18**, 435503 (2007),

Lab V: Other Modes of Characterization of Ferroelectric Films - I

Goal: Probing electrical functionality - conductive SPM imaging and Scanning Capacitance Microscopy of ferroelectric films

Suggested plan:

1. Acquire topography and low frequency PFM image of the sample (PZT sol-gel film)
2. Explore the conductance image of film.
   a. Acquire I-V curves at specific location – e.g. in the center of grains and at grain boundaries. Compare the reproducibility of the I-V curves at different locations and between locations.
   b. Acquire the conductance images at different voltages. Analyze the relationship between the microstructure and conductivity.
3. Scanning capacitance imaging
   a. Acquire SCM image on the film. Is there domain related contrast?.
   b. Write the parallel positively and negatively polarized lines and image the resulting pattern with SCM

Control questions:

1. What information SSRM and SCM provides about material?
2. Why are these methods of interest (a) for basic research, (b) for applied research and industry, and (c) for you?

Suggested reading:

A.Gruverman, "Ferroelectric Nanodomains", in *Encyclopedia of Nanoscience and Nanotechnology*, edited by H. S. Nalwa (American Scientific Publishers, Los Angeles, 2004), Vol. 3

Lab VI: Other Modes of Characterization of Ferroelectric Films - II

Goal: Mechanical and electrostatic property characterization by dynamic SPM modes:

- HarmoniX (Veeco)
- DualAC (Asylum)
- DualFrequency KPFM (Nanonis)
- Kelvin Probe Force Microscopy (Agilent)
- Piezoelectric Nanoindentation (Asylum)
- … and more