

MICROSCOPY/IMAGE ANALYSIS

A Biased View of the Nanoworld: **Electromechanical Imaging By SPM**

Piezoresponse force microscopy has matured as a technique for probing electromechanical coupling.

Coupling between electrical and mechanical phenomena is one of the fundamental natural mechanisms manifested in materials and systems ranging from ferroelectrics and multiferroics to electroactive polymers and biological systems. Electromechanics refers to a broad class of phenomena in which mechanical deformation is induced by an external electric field, or, conversely, electric charge is generated by the application of an external force.

The study of electromechanical coupling has attracted rapidly increasing attention due to the emergence of ferroelectric non-volatile memories (FeRAMs) and data storage devices. Electromechanical coupling is ubiquitous in all polar inorganic materials (e.g. 20 out of 32 crystallographic point groups are piezoelectric). The very basis of functional biological systems is electromechanics—from nerve-controlled muscle contraction on the macroscale, to cardiac activity and hearing on the micron scale, to energy storage in mitochondria, voltage-controlled ion channels, and electromotor proteins on the nanoscale.

Finally, electromechanical coupling is a key component of virtually all electrochemical transformations, in which changes in the oxidation state are associated with changes in molecular shape and bond geometry. Electromechanical coupling is a nearly universal part of energy conversion and transport processes. It forms the basis for a multitude of device applications and is thus directly relevant to virtually all existing and emerging aspects of materials and nanoscience.

Recent years have witnessed a significant growth in interest towards electromechanics on the nanoscale, which originated independently in the ferroelectric, microelectromechanical systems (MEMS), biological, and organic chemistry communities. Many phenomena in nanophase materials and biological systems, for which single crystals are not available, can only be studied on the nanoscale, thus avoiding the limitations imposed by macroscopic averaging. Probing electromechanical coupling phenomena on the nanoscale brings the challenge of measuring electromechanical response with sensitivities on the order of 0.1-100 pm/V, or currents on the order of

several fA, over length scales of nanometers and below. Electromechanical measurements have become feasible with the advent of piezoresponse force microscopy (PFM), which combines high sensitivities (about 1 pm/V) with the high spatial resolution typical of scanning probe microscopes (SPMs).

Principles of PFM

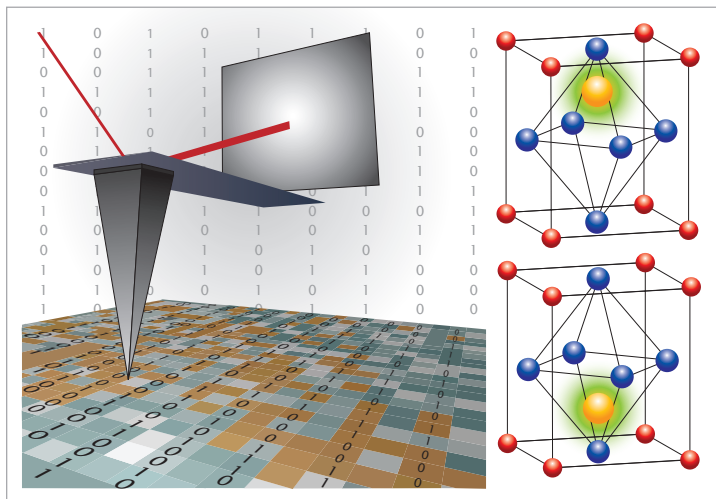
In PFM, a conductive tip traces surface topography using standard deflection-based feedback, also known as contact mode imaging. During the scanning, a bias with a sinusoidal component is applied to a conductive cantilever. The electromechanical response of the surface is detected as the first harmonic component of bias-induced tip deflection. The response amplitude provides a measure of the local electromechanical activity of the surface. The phase of the piezoresponse yields information on the polarization direction below the tip.

Typical driving frequencies are chosen to be above the bandwidth of the topographic feedback loop (greater than 1-3 kHz) so that the feedback loop does not compensate for the voltage-induced surface deformations. In low frequency PFM, imaging is performed well below the first contact resonance frequency of the probe, providing for quantitative data. In high-frequency and resonance-enhanced PFM, the operation is performed at or above the first or higher resonance frequency. This provides a better signal to noise ratio but requires complex calibration for quantitative data interpretation. This is primarily because the tip-sample contact stiffness can cause strong coupling between the topography and the apparent PFM signal. The typical driving voltages range from about 1 V_{pp} for strongly piezoelectric (about 500 pm/V for relaxor ferroelectrics) to 10-100 V_{pp} for weakly piezoelectric materials (e.g. 1-5 pm/V for biopolymers). The typical oscillation amplitudes are about 10-100 pm, which necessitates careful compensation of capacitive cross-talk between the driving signal and the photodiode response signal.

The operation of PFM is complementary to that in conventional SPMs. For techniques such as scanning tunneling microscopy (STM), a bias is applied to a metal tip, and the current is measured. In the case of force-based atomic force microscopy (AFM), a loading force is applied, and the resulting tip-deflection is measured. In PFM, a bias is applied to a tip, and the tip deflection resulting from the deformation of the sample due to the applied bias is measured. This determines the image formation mechanism, including such aspects as sensitivity to surface topography and the applicability of resonance enhancement. The contact stiffness of the tip-surface junction scales proportionally with the contact radius, resulting in the topographic cross-talk inherent to many force-based SPM imaging modes. In comparison, the electromechanical response in PFM does not depend on the tip-contact area, thus minimizing cross-talk for low frequency imaging.

Imaging electromechanical systems

In the decade since its development, PFM has been primarily used as a tool for studying ferroelectric materials with relatively high (about 10-500 pm/V) coupling coefficients. In ferroelectrics, PFM allows direct imaging of ferroelectric domain structures with about 10 nm resolution as well as their evo-



PFM combines high sensitivities with the high spatial resolution typical of SPMs. Image: S. V. Kalinin, B. J. Rodriguez, S. Jesse, and R. Proksch

lution during phase transitions, ferroelectric fatigue, domain wall motion, and relaxation. Advances in PFM have allowed its applications to extend beyond ferroelectrics to other polar materials.

The rapidly growing body of PFM applications has expanded to include piezoelectric biopolymers. The strong variation of electromechanical activity between piezoelectric biopolymers and non-piezoelectric hydroxyapatite (HAp), combined with high spatial resolution and the relative insensitivity of PFM to topographic cross-talk, renders it a natural tool for high-resolution imaging of the microstructure of calcified and connective tissues.

PFM in a liquid environment

SPM studies of biological systems necessitate the use of a liquid environment to maintain native conditions for biomolecules and cells to minimize sample damage. The typical operating conditions in PFM (e.g. driving voltages of about $10 V_{pp}$) may seem counterintuitive for liquid imaging, however, in 2006, we demonstrated that high-frequency (about 0.1 - 2 MHz) PFM imaging can be implemented in conductive liquid environments, including solvents such as deionized water, alcohols, and even 10^{-4} to 10^{-3} M NaCl solutions. This is possible because the use of high excitation frequencies precludes electrochemical reactions, even for high voltage amplitudes.

However, control of the DC probe potential presents a much more complicated problem. This is important for applications that require maintaining a predefined electrochemical or membrane potential, as is the case for electrochemical or electrophysiological measurements, respectively. The conductivity of the solution results in stray tip-surface currents and associated potential drops, heating, and electrochemical reactions in the tip-surface junction. Experimental studies using ferroelectrics as an indicator of field propagation in solution indicated that DC potentials can be controlled only in poorly conductive solvent such as isopropanol, while in more conductive solvents the solution is biased uniformly and electrochemical reactions proliferate. In the future, PFM-based probing of electrophysiology of biological systems will benefit from the development of shielded probes. In these, only the end of the probe is in contact with solution, preventing stray currents to the solution. Currently, shielded and insulated probes have been demonstrated by several groups; however, their wide adoption by the SPM community will only be possible after they become commercially available.

Polarization dynamics in ferroelectrics

Switchable polarization and narrow (1-2 unit cell) domain walls in ferroelectric materials have attracted significant attention in information technology applications such as FeRAM, data storage, and tunneling barriers, necessitating studies of localized ferroelectric properties. The use of a sharp SPM tip allows the electric field to be concentrated on about 10-nm scale, inducing local polarization switching within the material. For data storage applications, domains as small as 5 nm, corresponding to greater than 10 TBit/in² storage density, have been demonstrated.

Understanding polarization dynamics on the nanometer scale has spurred the development of PFM spectroscopy, wherein the DC bias offset on the probe follows a triangular (~1 Hz) waveform envelope. In ferroelectric materials, the DC bias induces polarization switching, and the size of the ferroelectric domain formed below the tip is related to a change in the electromechanical response detected at a probing frequency of about 10 kHz - 2 MHz. In a general sense, hysteresis loops in PFM are analogous to force-distance spectroscopy in AFM. These measurements can be performed in the switching spectroscopy PFM (SS-PFM) mode, where hysteresis loops are acquired at each point on the surface

yielding a 3-D data array. The data can be further processed to yield 2-D maps of the local work of switching (the area within a loop), coercive and nucleation biases, remanent response, and other parameters that define the operation of ferroelectric devices. The typical acquisition time for a 64 x 64 point image is about two to four hours.

New dynamic modes

Some of the recent developments in PFM are related to the introduction of new excitation and detection modes beyond the paradigm of sinusoidal excitation in conventional SPMs. Specifically, PFM measurements of weakly piezoelectric materials and quantitative PFM spectroscopy require resonant enhancement of the electromechanical response. The resonant frequency of a cantilever in contact with a surface is determined by the contact stiffness, a function of both the material properties of the tip and sample and the contact area. One way to benefit from the enhanced signal to noise ratio of contact resonance while avoiding unwanted topographical crosstalk is to operate a feedback loop that keeps the oscillation frequency at resonance as it changes due to changes in contact stiffness. However, the phase response in PFM depends on domain polarity, thus precluding the use of standard phase-locked loop based techniques for tracking the resonance frequency. Furthermore, both local losses (i.e. Q-factor) and the electromechanical response of the surface determine the amplitude at the resonance, complicating deconvolution of the two. This limitation is also common in other techniques based on direct electrical driving of the probe.

Excitation modes based on simultaneous driving of the cantilever oscillations by two or more driving frequencies (referred to as DualAC) or, alternately, a signal spanning a band of frequencies—referred to as band excitation (BE)—offer alternatives. These modes allow independent measurement of amplitude, resonant frequency, and Q-factor of the cantilever, circumventing the limitations of traditional sinusoidal excitation that allow only two parameters (e.g. amplitude and phase for constant frequency, or amplitude and resonant frequency for frequency-tracking) to be determined. Both the BE and DualAC methods require slower scanning than conventional PFM but provide fundamentally new information on the local response and energy dissipation that cannot be obtained by conventional single-frequency excitation methods.

The growing field of PFM

Electromechanical coupling is a ubiquitous, but relatively unexplored aspect of nanoscale systems. Piezoresponse force microscopy, originally developed for the characterization of domain structures and polarization dynamics in inorganic ferroelectrics, has matured as the technique for probing electromechanical coupling in polar semiconductors, calcified and connective tissues, and macromolecular systems. It yields both an approach for high (about 10 nm) resolution imaging of materials structure and molecular orientation, and the probing of electromechanical functionality, including polarization dynamics in perovskites and electrophysiology in biological systems. The difference in the image formation mechanism between PFM and classical force- and current-based SPMs, as well as PFM imaging in liquid environments, has stimulated the development of novel probes, as well as control and driving schemes, resulting in rapidly growing interest in this technique.

—Sergei V. Kalinin and Brian J. Rodriguez,

Materials Science and Technology Div. and Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

—Stephen Jesse,

Materials Science and Technology Div. Oak Ridge National Laboratory

—Roger Proksch, Asylum Research