Piezoresponse Force Microscopy

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Introduction

Coupling between electrical and mechanical phenomena is an important feature of functional inorganic materials and biological systems alike. The applications of electromechanically active materials include sonar, ultrasonic and medical imaging, sensors, actuators, and energy-harvesting technologies, as well as non-volatile computer memories. Electromechanical coupling in electromotor proteins and cellular membranes is the universal basis for biological functionalities from hearing to cardiac activity. The future will undoubtedly see the emergence of broad arrays of piezoelectric, biological, and molecular-based electromechanical systems to allow mankind the capability not only to "think" but also "act" on the nanoscale. The need for probing electromechanical functionalities has led to the development of Piezoresponse Force Microscopy (PFM) as a tool for local nanoscale imaging (Figures 1 and 2), spectroscopy, and manipulation of piezoelectric and ferroelectric materials.

Piezoresponse Force Microscopy is one of several microscopy techniques that can be implemented on an atomic force microscope (AFM) platform. Developed as a separate technique about 1996, PFM is now a well-established microscopy method [1-5] providing a pathway for revealing information about the electrical-mechanical coupling of a material that is not available from other techniques (see Figure 3). The AFM produces a topographic image of the specimen by moving a sharp tip over the surface in a raster pattern while recording changes in tip height with its laser-detector system (normal AFM contact mode). In PFM mode, the tip is conductive so an electrical potential can be applied between the tip and a piezoelectric material. The electric field thus produced induces a mechanical strain response and associated surface deformation (up or down) that is in addition to any roughness or topography on the specimen surface. A lock-in amplifier detection method allows minute periodic surface deformations to be separated from the static topography. This

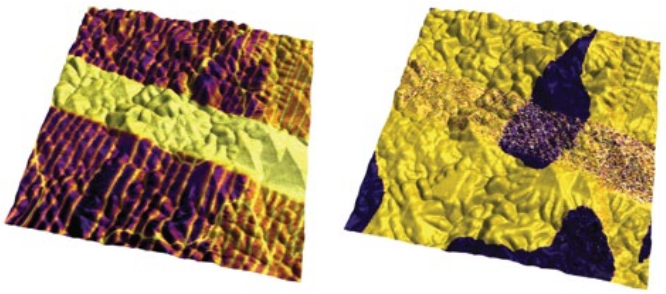

Figure 1: Vertical PFM amplitude overlaid on an AFM topography (left) and PFM phase overlaid on AFM topography (right) images of lead titanate film. Image width = 5 μm. Images courtesy of A. Gruverman and D. Wu, University of Nebraska-Lincoln. Sample courtesy H. Funakubo.

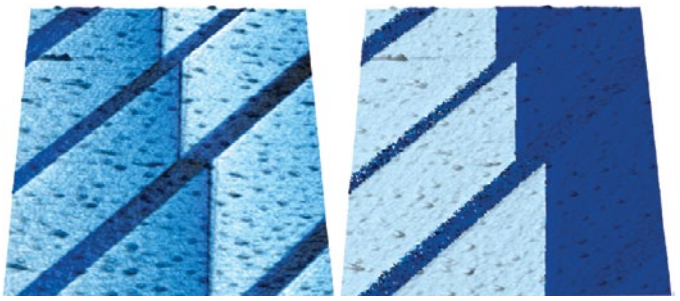

Figure 2: PFM amplitude overlaid on AFM topography (left) and PFM phase overlaid on topography (right) on (100) oriented BaTiO3 single crystal (from Castech Crystals). The amplitude and phase image show 90° and 180° domain walls in $BaTiO_3$. 10 μm scan. Courtesy of V. R. Aravind, K. Seal, S. Kalinin, ORNL, and V. Gopalan, Pennsylvania State University.

piezoresponse is the principle behind the "vertical" PFM mode and can be seen as the PFM amplitude in Figures 1 and 2. A major advantage of PFM is that it can produce images showing the location of polarized regions or domains where the material has responded to an electric field supplied by the tip.

Inverse Piezo Effect. The piezoresponse is caused by an electric dipole within the material, usually oriented along a specific crystallographic axis. Materials that exhibit this response are called piezoelectric materials, a group that includes all ferroelectrics. The classic example is lead zirconate titanate, PZT, a material that is often used in sensors, actuators, and ultrasonic transducers. Normally tetragonal (for small Zr contents) at room temperature, the titanium atom in the center of the unit cell forms an electric dipole along the [001] crystal direction. When a voltage V is applied along the [001] direction, a strain s appears in the material, either an expansion or contraction depending on the direction of polarization in the crystal. The induced strain is proportional to the applied voltage, V, through the piezoelectric strain constant, d. This

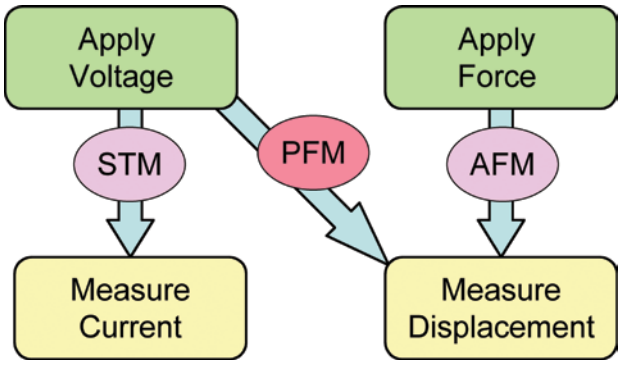

Figure 3: Diagram showing the relationship between PFM and the major scanning probe microscopies.

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phenomenon is known as the "inverse piezo effect" where the larger the piezoelectric constant, the larger the mechanical change in shape on the surface of the specimen. For an arbitrary field orientation, the relationship between induced strain and the applied electric field in piezoelectric materials is properly described by a third-rank tensor. However, for many materials the most important component for vertical PFM is d_{33}. For strongly piezoelectric materials the magnitude of d_{33} ranges from 100-300 pm/V; whereas, for biological materials such as collagen d_{33} is ~2 orders of magnitude weaker, as shown in Table 1.

Table 1: Selected materials with piezoelectric response characteristics useful in PFM imaging and spectroscopy

Material	Application	Strain constant d_{33} (pm/V)
PZT ceramics (bulk)	Actuators and transducers	100-500
PZT ceramic (thin film)	Capacitors	10-30
$LiNbO_3$ single crystals	Electro-optical devices	10-20
$BiFeO_3$ (thin film)	Ferroelectric non-volatile memories	3-10
Quartz	Balances, frequency standards	3
Polar semiconductors	RF devices, switches	0.1-2
Calcified tissue		0.5-3
Collagen		0.5-3

In the 15 years since its inception, PFM has grown into an entire sub-discipline with ever more intricate apparatus employed to understand the piezoresponse. In the present article, we will discuss the principal PFM imaging modes, lithography, spectroscopy, and some recent instrumental advances.

Operation of the PFM

By applying a bias voltage from the tip to the specimen, the piezoresponse force microscope tip causes some domains of PZT to expand and those of opposite polarization to contract. The cantilever measures the vertical motion of the sample surface producing a "vertical" PFM image as the tip scans over the specimen [6]. The left images in Figures 1 and 2 show vertical PFM amplitude images. In response to a sinusoidal "driving" voltage, the sample locally expands or contracts sinusoidally as shown in Figure 4. For typical low-frequency PFM (3-100 kHz), the voltage range is 0.5 to 10 V_{pp}, depending on the material. The piezoelectric response of the surface is detected as $A_{1\omega}$, the first harmonic component of the tip deflection, $A = A_o + A_{1\omega}\cos(\omega t + \varphi)$, which is induced by the periodic driving voltage. The tip deflection amplitude, $A_{1\omega}$, is determined by the motion of the tip and is given in units of length. The phase of the electromechanical response of the material, φ, provides direct information about the polarization direction in the material beneath the tip. For c^- domains (polarization vector oriented normal to the surface and pointing downward), the application of a positive tip bias voltage results in the expansion of the sample and will be recorded as a height increase in the vertical PFM amplitude image (Figure 4b). These surface oscillations are in phase with the tip voltage, so there is no phase shift, $\varphi = 0$. For c^+ domains, the response is opposite (Figure 4d) and the phase is $\varphi = 180°$. Thus, by displaying the PFM phase image, the location and polarity of ferroelecric domains can be determined (see Figures 1b and 2b). The PFM phase image also allows depiction of specific collagen fibers better than a topographic image obtained in AFM mode (see Figure 5).

The spatial resolution of PFM is highly material-dependent, ranging from 3-5 nm ($BiFeO_3$ and tooth protein) to 20-50 nm (most ferroelectrics including PZT) to 100-300 nm ($LiNbO_3$). Resolution is limited by the tip radius and humidity, as well as by the dielectric properties of the material.

PFM Imaging Modes

Both amplitude and phase PFM images can be detected in three orthogonal directions. Detection of the lateral components of tip vibrations provides information on the in-plane surface displacement, known as lateral PFM. Vertical PFM and lateral PFM images provide complementary views of the three-dimensional domain structure at the surface of piezoelectric materials (see Figures 6a, 6b, 7b, and 7c). A third component of the displacement vector can be determined by

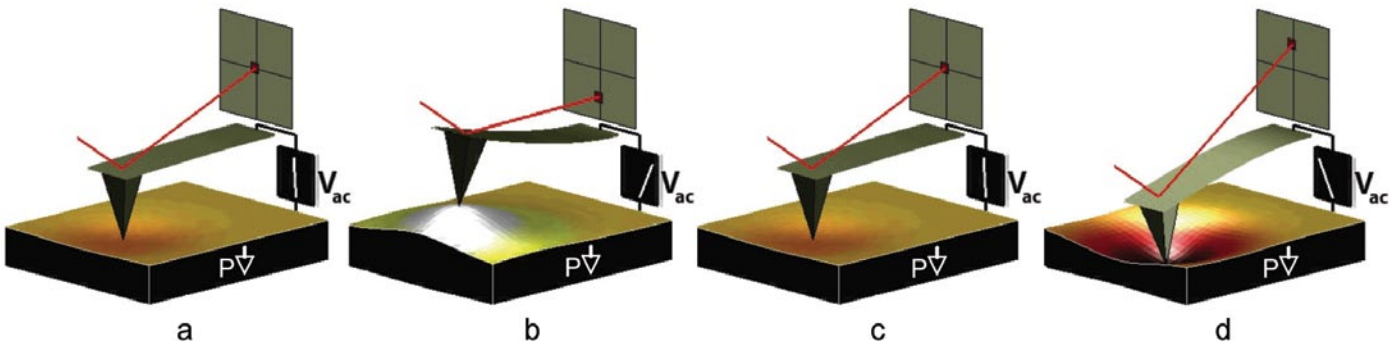

Figure 4: Schematic of PFM operation. (a) through (d) show how a piezoelectric specimen, with a polarization pointing downward, deforms as the instantaneous amplitude of the ac voltage changes. As the voltage becomes positive (a) to (b), the local surface of the material expands. The upward motion of the cantilever causes the reflected laser beam to move downward on the position-sensitive photodetector. Diagrams courtesy of S. Jesse, ORNL.

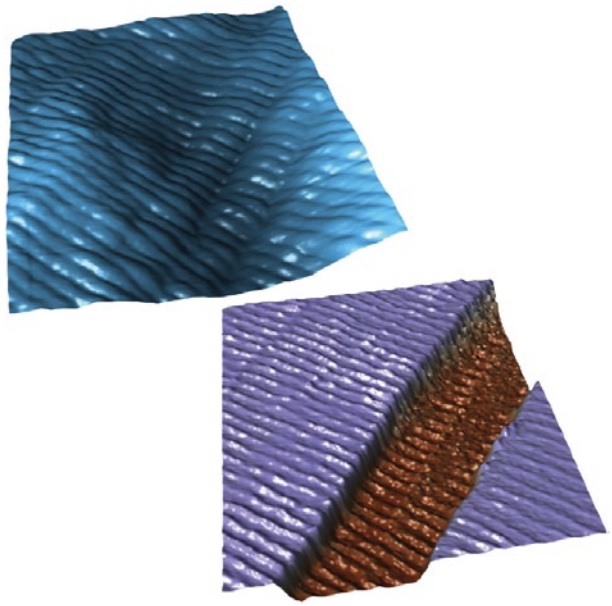

Figure 5: Topographic (top) and PFM phase (bottom) images of collagen fibers, 1.4 μm scan. Image courtesy of D. Wu and A. Gruverman, University of Nebraska-Lincoln. Sample courtesy G. Fantner.

imaging the same region of the sample after rotation by 90° (Figure 6c). Provided that the vertical and lateral PFM signals are properly calibrated, the complete electromechanical response vector can be determined, an approach referred to as vector PFM (Figure 6d). Thus, the three PFM imaging modes are:

- Vertical PFM—out-of-plane polarization measured by recording the vertical tip-deflection signal at the frequency of modulation.
- Lateral PFM—in-plane component of polarization detected as lateral motion of the cantilever due to bias-induced surface shearing.
- Vector PFM—real-space reconstruction of polarization orientation from the three components of piezoresponse: vertical PFM plus at least two orthogonal lateral PFM signals [7].

PFM can also be used in the top-electrode arrangement, in which the field is created by macroscopic top electrode, and the localized tip is used as a strain sensor. This arrangement has been proven particularly useful in the exploration of ferroelectric non-volatile memory capacitors [8-9].

Lithography

For ferroelectric applications, PFM can be used to modify the ferroelectric polarization of the sample through the application of a bias voltage. When the applied field is large enough (for example, greater than the local coercive field), it can induce ferroelectric polarization reversal. This technique can be used to "write" single domains [10], domain arrays, and complex patterns without changing the surface topography.

Spectroscopy

PFM spectroscopy refers to the local generation of hysteresis loops in ferroelectric materials. From these hysteresis loops, information on local ferroelectric behavior such as imprint, local work of switching, and nucleation biases can be obtained. Understanding the switching behavior in ferroelectrics on the nanometer scale is directly relevant to the development and optimization of applications such as ferro-electric non-volatile random access memory (FRAM) and high-density data storage. Multiple studies have addressed the role of defects and grain boundaries on domain nucleation and growth, domain wall pinning, and domain behavior during fatigue. A new spectroscopy technique, Switching Spectroscopy PFM (SS-PFM), provides relationships between micro- and nano-structures and local switching behavior of ferroelectric materials. Figure 8 shows an example image of a $LiNbO_3$ sample with the PFM signal overlaid on top. The image was taken after switching spectroscopy. The graph shows the hysteresis loops measured at one point on the surface.

Recent PFM Developments

Application of PFM for many materials is limited by the small piezoelectric constant. For example, a 1-V_{pp} oscillation applied to material with piezoelectric constant of 10 pm/V (common for some ferroelectrics, III-V nitrides, and biological systems), the response will be only 10 pm, a distance that is only a small percentage of an atomic radius. This small response is comparable with the Brownian motion of conventional room-temperature AFM cantilevers. Thus, instrmental improvements are needed to detect small responses.

High-Voltage PFM. Perhaps the most obvious option for improving the response of PFM is to simply increase the drive amplitude. The signal is usually proportional to the

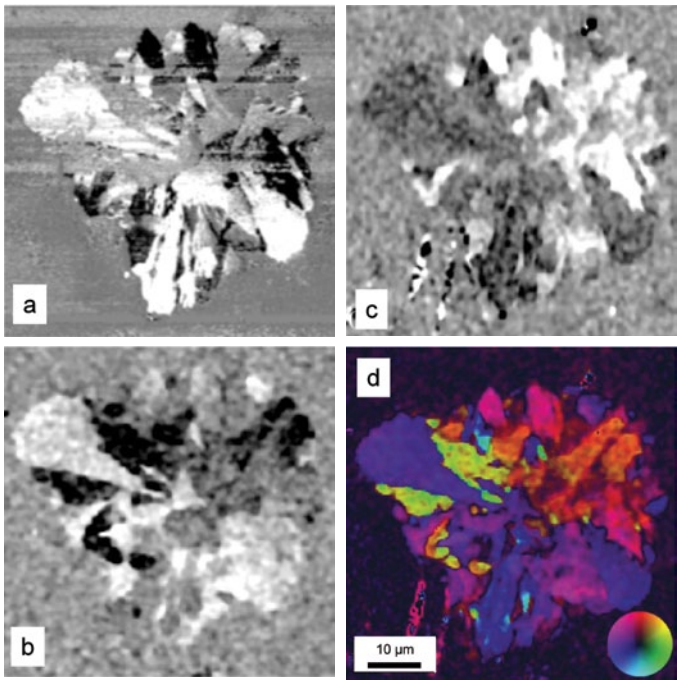

Figure 6: Three-dimensional PFM imaging of a ferroelectric $LaBGeO_5$ cystallite in a paraelectric glass matrix. (a) vertical PFM image, (b) x-lateral PFM, (c) y-lateral PFM, and (d) 2-D vector PFM image. The latter image contains information of the in-plane orientation of the electromechanical response vector. The orientation angle is coded by the color as reflected in the "color wheel," and the magnitude of the response is given by the intensity (dark for zero response, bright for strong response) [7]. Courtesy of Microscopy Society of America.

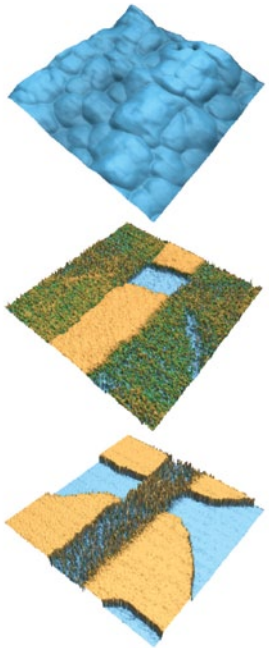

Figure 7: Three PFM images of a lead titanate film. Topography (top), lateral PFM phase (center), and vertical PFM phase (bottom). 3 μm scan. Courtesy of A. Gruverman and D. Wu, University of Nebraska-Lincoln. Sample courtesy of H. Funakubo.

drive voltage, so increasing the drive voltage by 10× will result in a 10× improvement in the signal-to-noise ratio (SNR). A more powerful drive amplifier also enables operation at higher frequencies. Recent programmable modules allow bias voltages of up to +220V and frequencies on the order of MHz. High probing voltages can both characterize weaker piezoelectric samples (such as biological materials) and ensure the capability of switching the polarization of high-coercivity ferroelectric materials. The downsides of this approach are rather obvious; higher voltages can inadvertently switch the polarization in some materials. In extreme cases, the sample might actually break down, leading to large current and thereby tip and sample damage or even destruction.

Contact Resonance as a PFM Amplifier. Another method to increase the SNR for small PFM signals is to make use of contact resonance. The contact resonant frequency of the cantilever is the natural frequency at which the cantilever is oscillated to achieve maximum amplitude when the tip is in contact with the surface. Resonance enhances the signal by the natural gain of the cantilever, a factor of ~100 for a typical PFM cantilever. However, simply driving near the contact resonance at a fixed frequency will lead to topographic cross-coupling, where topographic features that modify the resonance frequency bleed over into the PFM amplitude and phase data. To avoid this, and to maintain the advantages of resonance, the drive frequency must be varied to keep the cantilever oscillating at resonance, even though the topography is changing it. Methods for automatically tracking frequency are now commercially

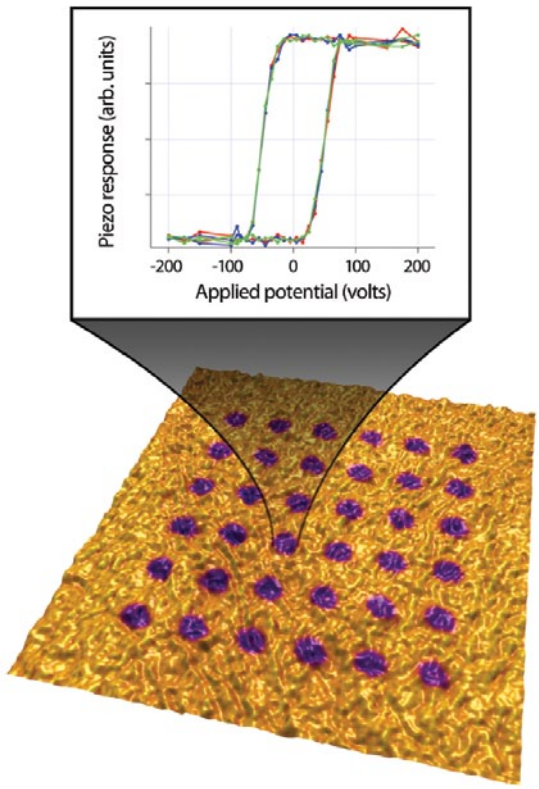

Figure 8: Rendered topography of a $LiNbO_3$ crystal with the PFM hysteresis curve overlaid on top. 4 μm scan.

available. Using one such method, called Dual AC Resonance Tracking (DART), additional information can be obtained about the domains and microstructure of $BiFeO_3$ nanofibers (Figure 9). The alternatives are the band excitation method [11] and compound cantilevers with built-in mechanical amplification [12].

High Frequency PFM. High-frequency imaging allows for an improved SNR by avoiding 1/f noise. Furthermore, inertial stiffening of the cantilever improves contact conditions. By probing the PFM signal with higher-frequency resonances (up to 1 MHz and above), topographic imaging can be performed with a soft cantilever that is almost always better for reducing tip-sample damage and artifacts, while PFM is performed with a higher mode where the dynamic stiffness is much greater.

Applications of Piezoresponse Force Microscopy

Fundamental Materials Science
- Domains
- Phase Transitions and Critical Phenomena
- Size Effects
- Nucleation Dynamics
- Multiferroics
- Ferroelectric Polymers
- Liquid Crystals
- Composites
- Relaxor Ferroelectrics

Piezoelectric Materials
- Micro ElectroMechanical Systems (MEMS)
- Sensors and Actuators
- Energy Storage and Harvesting
- RF Filters and Switches
- Sonar
- Balance and Frequency Standards
- Giant k Dielectrics
- Capacitors

Ferroelectric Materials
- Domain Engineering
- Non-volatile Memory
- Data Storage Devices
- Domain Energetics and Dynamics

Bio-electromechanics
- Cardiac
- Auditory
- Cell Signaling
- Structural Electromechanics
- Biosensors

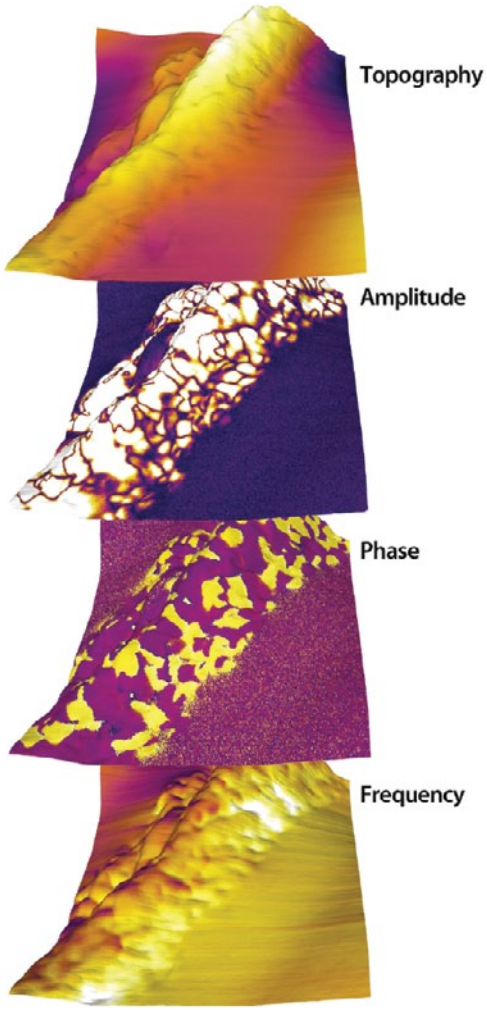

Figure 9: Piezresponse force microscopy imaging of multiferroic $BiFEO_3$ nanofibers. 1 μm scan. Collaboration with S. Xie, Xiangtan University, China, and J.Y. Li, University of Washington.

Electrostatic interactions between the cantilever and the surface can result in a signal at the drive frequency, the same as the PFM signal. This background can sometimes swamp the small PFM signal. The use of higher modes can greatly reduce this electrostatic background. Finally, resonance enhancement can be used on the higher modes to amplify weak PFM signals. It should be noted that in this regime, the response is strongly dependent on the local mechanical contact conditions, and hence, an appropriate frequency tracking method is required to avoid PFM/topography cross-talk.

Biological Applications. Piezoresponse force microscopy allows the organic and mineral components of biological systems to be differentiated and provides information on the material's microstructure and local properties. The use of vector PFM may enable protein orientation to be determined in real space. For example, the internal structure of protein microfibrils in human tooth enamel might be determined with a spatial resolution of several nanometers. PFM may help in understanding electromechanical coupling at the nanometer level, establishing the role of surface defects on polarization switching. This microscopy technique could potentially facilitate studies of electrophysiology at the cellular and molecular levels,

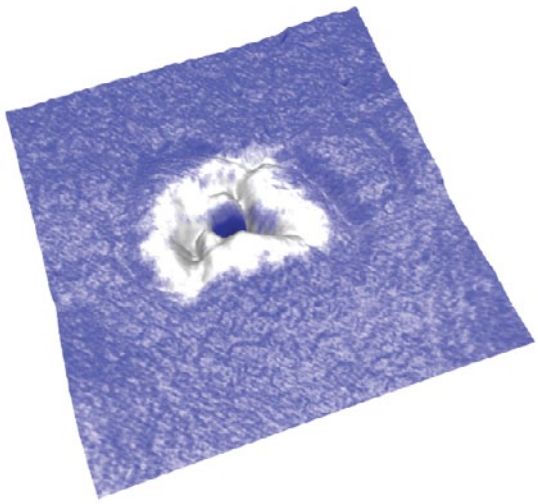

Figure 10: Top surface of a red blood cell. The surface shape was rendered to show the topography while the PFM phase channel was overlaid to show the piezo response. A small sub-micron region on top (white) of the cell exhibited a much different piezo response from the surrounding cell surface. 2 μm scan. Courtesy of B. Rodriguez and S. Kalinin, ORNL.

for example with signal propagation in neurons. Ultimately, on the molecular level, PFM may allow reactions and energy transformation pathways to be understood. Recent PFM studies of biomolecules have demonstrated electromechanical behavior in lysozyme polymers, bacteriorhodopsin, and connective tissue [13-14]. As an example, Figure 10 shows a composite image of a red blood cell with the piezoresponse shown as the overlaid PFM phase signal in white.

Conclusion

The coupling of electrical and mechanical phenomena in biological systems and electronic devices is an important research area. Piezoresponse force microscopy can reveal critical details about the mechanical response to electrical stimuli. It is likely that PFM will play a critical role in these areas because of its unique combination of high resolution and high sensitivity to nanoscale electromechanical phenomena. MT

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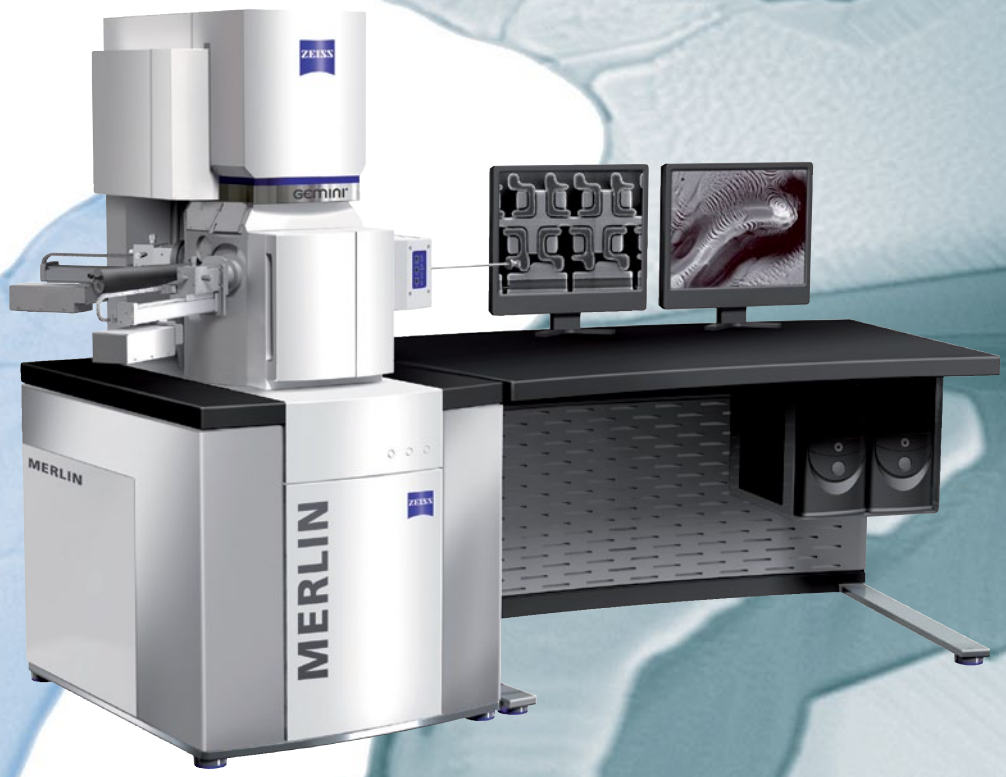

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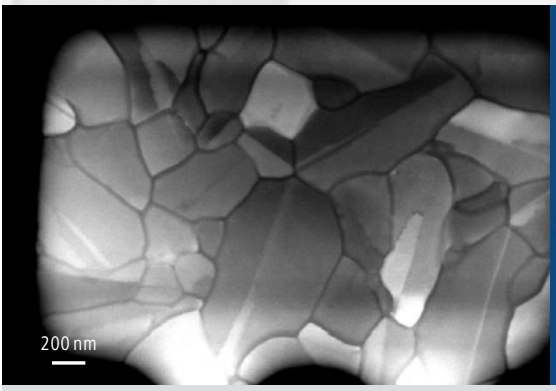

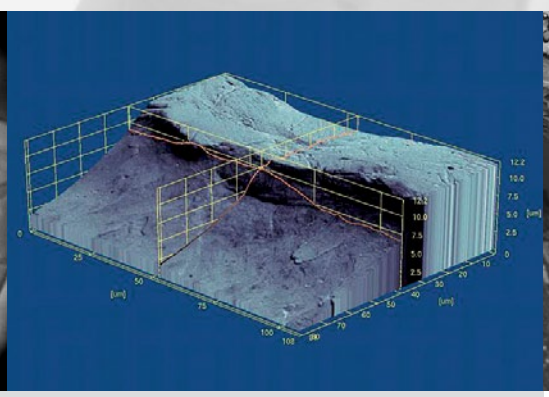

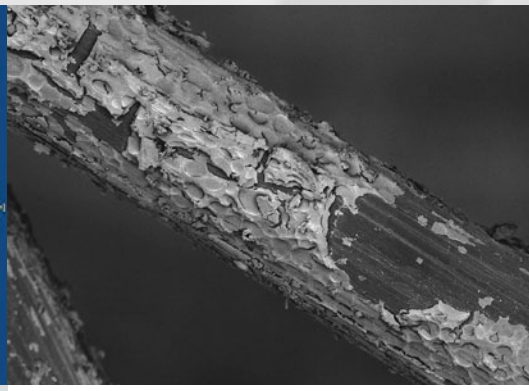

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