Deciphering the Mechanisms of Bias-Induced Phase Transitions on a Single Defect Level

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Thrust area: Origins of Functionality in Nanoscale Systems

Research Achievement

The mechanisms of the phase transitions and electrochemical reactions in solids are determined by the atomistic and mesoscopic defects that act as nucleation centers for new phases and pinning sites for moving transformation fronts. In materials with several thermodynamically equivalent states (e.g. domains in ferroics or orientation variants in martensite) the defects can also select the transformation pathways and determine the final state of the system. The atomic and electronic structures of defects have become accessible with the advances in electron microscopy; however, the dynamic mechanisms of phase transitions on a single defect level until recently remained an enigma.

We aim to establish a set of scanning probe microscopy techniques for probing bias-induced phase transition locally on a level of a single defect and correlate the mechanisms with atomic and mesoscopic structure. Ferroelectric materials are used as prototypical systems in which bias-induced phase transition is (a) fully reversible and (b) can be studied *quantitatively* through the local electromechanical response. The classical Piezoresponse Force Microscopy does not allow efficient use of resonance enhancement methods, hence limiting energy resolution of spectroscopic methods. To address this limitation we have developed

- A family of novel SPM methods based on the excitation signal having finite density in a selected band in frequency domain, as compared to a single frequency in classical SPMs (R&D 100 award in 2008, licensed by Asylum Research)
- A spectroscopic imaging method based on PFM spectroscopy

Following demonstration of imaging capability [1], imaging within a single nanoparticle [2], and single defect resolution [3], these techniques were used to study polarization switching behavior on a number of well-defined systems, including

- 24° grain boundary in (100) rhombohedral ferroelectric (in-house research) [4]
- 180° domain wall in uniaxial ferroelectric (user proposal with V. Gopalan, Penn State)
- Ferroelastic 71° wall in (100) rhombohedral ferroelectric (user proposal by R. Ramesh, UC Berkeley) [5]
- Ferroelectric capacitors (user proposal by S. McKinstry, Penn State) [6]

Recently, the electromechanical detection was integrated with the current and resonance frequency measurements in the ultra-high vacuum environments, enabling

- Probing domain wall conductance in ferroelectrics (user proposal by R. Ramesh) [7]
- Controlling local metal-insulator transitions (user proposal by R. Ramesh) [8]

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- Implementation of polarization-controlled tunneling (in-house research) [9]
- Determination of intrinsic switching mechanisms (in-house research) [10,11]

We have shown that the SPM can be used to control the in-plane switching in ferroelectric materials, opening the pathway for controlling ferroelastic structures, magnetic ordering, and creation of long-thought vortex states [5]. The overarching achievement of this program is the demonstration that synergy between advance imaging capabilities and mesoscopic theory (L.Q. Chen, Penn State, A. Morozovska, Ukranian NAS) allows ***deterministic*** polarization reversal mechanisms to be determined on a single-defect level.

Future work:

In the future, we aim to extend the studies of local phase transitions to that in electrochemical systems and also thermal phase transition. To achieve this goal, we aim to:

- Develop dynamic thermal imaging and spectroscopy methods (Nikiforov)
- Develop microwave imaging capabilites (Tselev)
- Integrate the SPM and *in-situ* sample synthesis/controlled atmosphere

In collaboration with ORNL colleagues in electron microscopy, we expect to develop capacity for simultaneous SPM-STEM probing of local bias-induced dynamics on atomic level.

Publications: In total, ~50 peer-reviewed papers (3 Nature Mat., 1 PNAS, 3 Adv. Mat., 5 Phys. Rev. Lett., + 1 Science, 1 PNAS, and 1 Nature Nanotechnology under review), R&D 100 Award 2008 (SJ and SVK), AVS Peter Mark Award for Young Scientists (SVK), ACerS Robert L. Coble award (SVK), MicroBeam Society Cosslett award (SJ, APB, and SVK), BE technology licensed by Asylum Research.

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