Final Report

DOE award # and name of the recipient: DE-FG02-07ER46416; University of Michigan

Project Title and name of the PI: "Structure and Dynamics of Domains in Ferroelectric Nanostructures – In-situ TEM Studies", Xiaoqing Pan

The goal of this project was to explore the structure and dynamic behaviors of ferroelectric domains in ferroelectric thin films and nanostructures by advanced transmission electron microscopy (TEM) techniques in close collaboration with phase field modeling. The experimental techniques used include aberration-corrected sub-Å resolution TEM and *in-situ* TEM using a novel scanning tunneling microscopy (STM) - TEM holder that allows the direct observation of nucleation and dynamic evolution of ferroelectric domains under applied electric field. Specifically, this project was aimed to (1) to study the roles of static electrical boundary conditions and electrical charge in controlling the equilibrium domain structures of $BiFeO_3$ thin films with controlled substrate constraints, (2) to explore the fundamental mechanisms of ferroelectric domain nucleation, growth, and switching under an applied electric field in both uniform thin films and nanostructures, and to understand the roles of crystal defects such as dislocations and interfaces in these processes, (3) to understand the physics of ferroelectric domain walls and the influence of defects on the electrical switching of ferroelectric domains.

Our research activities for the current project involve the atomic scale characterization of ferroelectric domain structures under different boundary conditions and dynamic behaviors of ferroelectric domains under applied electric field in ferroelectric thin films using sub-angstrom resolution aberration-corrected TEM in combination with custom-designed, *in-situ* scanning probe techniques. Our effort has led to advances in the basic understanding of the effect of electromechanical boundary conditions and defects on domain structures and dynamic behaviors in ferroelectric thin films and heterostructures. This DOE grant resulted in 14 papers published[1-20] in archival journals. In this project, we have made a significant effort in developing *in-situ* TEM techniques for the observation of ferroelectric domain switching. Using these methods, we have extensively studied dynamic phenomena of nanoscale ferroelectric switching.

Atomic scale polarization mapping and spontaneous vortex domains

In this project, we have developed an image processing suite to determine the spatial distribution of polarization in displacive ferroelectric materials in which the polarization originates from a physical offset of ions.[21] Using this mapping method, spontaneous vortex nano-domain arrays intrinsically formed at ferroelectric hetero-interfaces have been observed for the first time. The electric polarization in $BiFeO_3$ films near the interface with $TbScO_3$ changes gradually across the ferroelectric domain walls and rotates continuously around the vortices providing electric flux closure analogous to the magnetic field closure domains seen in magnets. It is found that the polarization is drastically enhanced in the nanodomains near the vortices. This finding demonstrates the powerful capability of quantitative atomic resolution transmission electron microscopy in combination with image processing techniques. Such vortices are attractive as low cross-talk memory elements and are likely to play a dominant role in the dynamic behavior of polarization switching as possible seed domains. Thus, the existence of the spontaneous polarization vortices can fundamentally change the switching mechanism of ferroelectric domains in memory devices.

Changes in crystal structure and symmetry induced by charged domain walls

Charged domain walls (CDWs) are of significant scientific and technological importance as they have been shown to play a critical role in controlling the switching mechanism and electric, photoelectric, and piezoelectric properties of ferroelectric materials. The atomic scale structure and properties of CDWs, which are critical for understanding the emergent properties, have, however, been rarely explored. In this project, using a spherical-aberration-corrected transmission electron microscope with subangstrom resolution, we have found that the polarization bound charge of the CDW in rhombohedral-like BiFeO3 thin films not only induces the formation of a tetragonal-like crystal structure at the CDW but also stabilizes unexpected nanosized domains with new polarization states and unconventional domain walls.[17] These findings provide new insights on the effects of bound charge on ferroelectric domain structures and are critical for understanding the electrical switching in ferroelectric thin films as well as in memory devices.

Dynamics of ferroelectric switching studied by in-situ TEM

Using our unique TEM holder, we can follow the dynamic behavior of polarization switching in real time. We locally switch a region of ferroelectric thin film by applying a voltage between the probe and an epitaxial bottom electrode. Using aberration-corrected transmission electron microscopy (TEM) in combination with the *in situ* scanning probing holder, the kinetics and dynamics of ferroelectric switching is followed at millisecond temporal and sub-angstrom spatial resolution in epitaxial ferroelectric (PZT) and multiferroic ($BiFeO_3$) thin films.[22,23] We observed localized nucleation events at the electrode interface, domain wall pinning on point defects, and the formation of metastable ferroelectric states localized to the ferroelectric and ferromagnetic interface. These studies show how defects and interfaces impede full ferroelectric switching of a thin film. It was also found that 180° polarization switching in PZT initially forms domain walls along unstable planes due to the inhomogeneous electric field from the small switching electrode. After removal of the external field, they tend to relax to low energy orientations.[24] In sufficiently small domains, this results in complete backswitching. These findings suggest that even thermo-dynamically favored domain orientations are still subject to retention loss, which must be mitigated by overcoming a critical domain size.

Ferroelastic domain-wall-mediated ferroelectric switching

Polarization switching in ferroelectric thin films occurs via nucleation and growth of 180° domains through a highly inhomogeneous process in which the kinetics are largely controlled by defects, interfaces and pre-existing domain walls. Here we present the first real-time, atomic-scale observations and phase-field simulations of domain switching dominated by pre-existing, but immobile, ferroelastic domains in $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films. Our observations reveal a novel hindering effect, which occurs via the formation of a transient layer with a thickness of several unit cells at an otherwise charged interface between a ferroelastic domain and a switched domain.[16] This transient layer possesses a low-magnitude polarization, with a dipole glass structure, resembling the dead layer. The present study provides an atomic level explanation of the hindering of ferroelectric domain motion by ferroelastic domains. Hindering can be overcome either by applying a higher bias or by removing the as-grown ferroelastic domains in fabricated nanostructures. In similar experiments, we also find that ferroelastic domains can be effectively and permanently stabilized by dislocations at the substrate interface while similar domains at free surfaces without pinning dislocations can be removed by either electric or stress fields.[15] For both electrical and mechanical switching, ferroelastic switching is found to occur most readily at the highly active needle points in ferroelastic domains. Our results provide new insights into the understanding of polarization switching dynamics as well as the engineering of ferroelectric devices.

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