Research Highlight for DOE BES

Probing Kinetics and Thermodynamics of Phase Transitions on a Single Defect Level

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The kinetics and thermodynamics of first-order phase transitions and the microstructure and properties of materials are universally controlled by defects. Examples are as diversified as dislocation nucleation, motion, and pinning that control mechanical properties, heterogeneous nucleation processes involved in the crystallization of metals, oxides, and polymers, rain and snow formation, and nucleation centers in solid-state and electrochemical reactions. The majority of these processes involve a complex interplay between structural changes, order parameter dynamics, and heat and mass exchange, thus obviating the development of a universal theoretical framework for understanding these phenomena. Ferroelectric materials provide a convenient model system for investigating the role of defects in phase transitions: a system in which bias-induced phase transition between two equivalent polarization states is reversible and is not associated with diffusion, mass, or significant heat exchange and strain effects.

Seminal work by Landauer [J. Appl. Phys. **28**, 227 (1957)] has demonstrated that the experimentally observed switching fields correspond to impossibly large (~10^3 - 10^5 kT) values for the nucleation activation energy in polarization switching. To resolve this discrepancy, the presence of discrete switching centers initiating low-field nucleation and controlling macroscopic switching is required. We have developed a spectroscopic approach based on atomic force microscopy (AFM) to visualize and probe individual nucleation centers. The approach is based on acquisition of multiple local hysteresis loops on a closely spaced grid [1], providing 3 order magnitude increase in data acquisition speed compared to state of the art. Figure 1 illustrates the internal structure of ferroelectric nanodot delineating switching and non-switching regions, obtained with ~5 nm resolution [2]. The probe concentrates an electric field to a nanoscale volume of material (~10 nm), as shown in Fig. 2(a), and induces local domain formation. Simultaneously, the probe detects the onset of nucleation and the size of a forming domain via detection of the electromechanical response [3]. As in the macroscopic case, the presence of defects is expected to lower the nucleation energy or, equivalently, the bias required for switching. Hence, a map of local nucleation voltages represents the spatial and energy distribution of local switching centers.

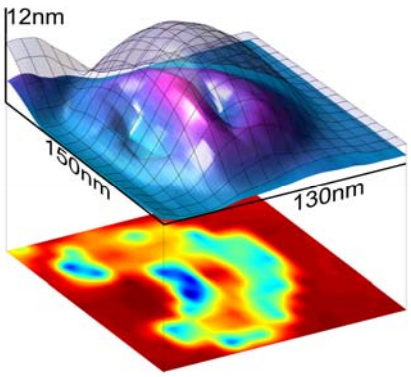

Fig. 1. The surface topography (wire frame) and frozen polarization layer (solid) in PZT nanoparticle. The bottom image represents built-in electric field distribution [2]

Shown in Fig. 2(b) is the nucleation voltage map of an epitaxial lead zirconate-titanate thin film. The dark spots on the image correspond to local nucleation centers, and corresponding bias provides the information on local activation barrier on switching. The analysis of both positive and negative nucleation bias maps allows extracting the components of random bond (variation in

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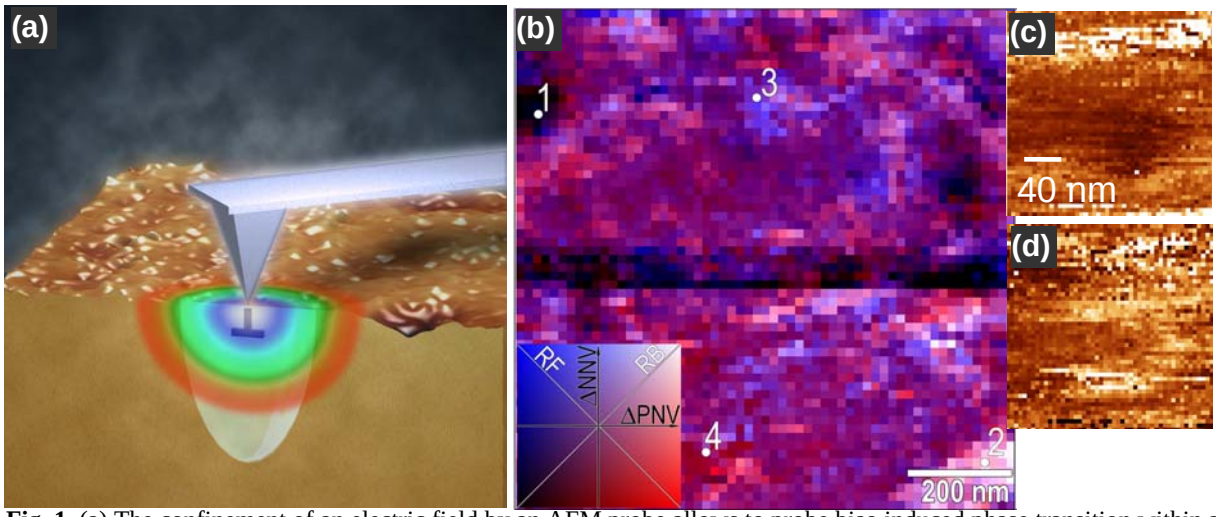

Fig. 1. (a) The confinement of an electric field by an AFM probe allows to probe bias-induced phase transition within a defect free volume [3] or at a given separation from defects [4]. The color map illustrates the RF and PB disorder potential in an epitaxial PZT film [4]. (c,d) A single defect imaged in multiferroic $BiFeO_3$ [5]

depolarization energy of domain wall energy) and random field (built-in polarization) disorder components independently. This provides real space imaging of parameters that previously been accessible only in theoretical models, and are universal for all ferroic systems.

Understanding of the switching behavior in ferroelectrics on the nanometer scale is directly relevant to the development and optimization of applications such as non-volatile random access memories, and high-density data storage. Beyond ferroelectrics, this approach can be extended to studies of the role of defects on the thermodynamics and kinetics of other local reversible voltage-induced transitions, including phase-change materials and electrochemical reactions. This will provide a universal framework for studying the role of defects in nucleation and growth of new phases and in electrochemical reaction kinetics one defect at a time, opening a pathway to understand the structure-property relationships of defect sites, and hence the optimization and control of these processes .

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