## **Conductance and Electrochemistry of Charged Domain Walls in Lead Zirconate Titanate**

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The discovery of conducting domain walls in BiFeO<sub>3</sub> in early 2008 ignited the effort to understand conduction phenomena in ferroelectric films and their coupling to the ferroic order parameters. Despite numerous cases where conducting domain walls has subsequently been observed, the basic phenomena underlying these mechanisms are still elusive. Most interpretations lean toward modification of the Schottky barrier at the film's interfaces by electric field and/or vacancy accumulation due to domain walls. Our effort in this direction has brought out the importance of charged domain walls, wherein the conductivity is mediated by the compensating mechanism of polarization charges at the domain wall. In this way, the domain wall can genuinely modify electronic conduction through the bulk of the ferroelectric film, rather than merely its interfaces. And only in such geometries one expects to achieve substantial electronic conductivity, far in excess of limited picoSiemens range that is frequently observed. Conceptually dynamic polarization distortions are very different from electroresistance effects in complex oxides, calling for new advances in both theory and experiments.

The involvement of charge domain walls or domain wall junctions in conduction phenomena has been motivated by three observations: (1) dynamic and hysteretic conductivity of domain walls in bismuth ferrite [1]; (2) anisotropic conductance of domain walls in BiFeO<sub>3</sub>, as a function of their orientation to the in-plane polarization vector [2]; (3) an insulator-metal transition in lead zirconate [3], which is observed any time a ferroelectric nanodomain (with the radius of < 10 nm) is created by localized electric fields. Here electronic conductance locally increases by 4-6 orders of magnitude – one of the largest effects reported so far.

In the case of lead zirconate titanate, we recently compared a variety of compositions of epitaxial PZT films, intentionally chosen with different growth conditions. The variability primarily manifested in the overall magnitude of local current, which ranged by orders of magnitude between different films. However, even for the most insulating lead zirconate films, ferroelectric nanodomains exhibited small thermal activation barriers of only ~ 50 meV. In contrast, leakage through the bulk would occur with barriers as high as 0.9 eV. Based on the I-V characteristics, the mechanism most compatible with these results involves tunneling into a highly conducting state in the bulk of the film, therefore implying a heavily doped or metallic state associated with tilted and charged domain boundaries of the nanodomains.

The experiments with scanning probe microscopy provide only indirect evidence that the conductance is controlled by charged walls. We turned to modeling of the morphology of ferroelectric nanodomains and the respective charge compensating mechanisms via solutions of Landau-Ginzburg-Devonshire (LGD) theory for ferroelectric semiconductors with analytical and phase-field methods. Analytical calculations in a reduced 1D geometry predicted up to 3 orders higher local density of compensating charges at tilted domain walls compared to background density

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due to ionized dopants and intrinsic carriers, depending on the domain wall tilt [3]. At the same time, both holes and electrons can be accumulated, depending on the tilting direction relative to the polar axis. These calculation imply that a charged domain wall in a ferroelectric semiconductor acts as a heavily doped n- or p-channel, and a metal-insulator transition can occur *within* a domain wall itself. Phase-field modeling extended these calculations onto more realistic 3D geometry. The simulations clearly indicate that the [00-1] domain is nucleated under the tip, continues to grow in cone-shape (Fig. 1a), and forms positively charged head-to-head tilted domain walls (Fig. 1b) with wall segregated compensating electrons. Under certain bias condition, the nucleus and tilted domain walls are stabilized with electronic screening. Experiments to test some of the detailed results are currently on-going [4].

Finally, we will discuss the possibility of electrochemical effects caused by local ferroelectric switching. Specifically, we have explored the regime of few hundred thousand switching cycles, finding significant changes in local topography and conductivity (Fig. 1c,d). LGD simulations reveal that even with efficient compensation, charged domain walls still develop large local electric fields due to finite Debye screening length. Presumably these fields are responsible for creation/and or motion of charged vacancies inside the material. Altogether these studies pave way to better understanding of coupled transport phenomena in ferroelectric films and novel approaches to control ferroelectric switching toward desired properties.



Figure 1. Phase-field simulation of 180° domain switching in PZT (a) domain switching; (b) polarization charge evolution showing tilted domain walls under certain conditions; (c) Surface topography change following 150 thousand consecutive local switching cycles; (d) Local conductance progressively increases with repeated switching.

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[1] Maksymovych et al., Nano Lett. (2011), 11, 1906; [2] Vasudevan et al., Nano Lett. (2012), 12, 5524; [3] Maksymovych et al., Nano Lett. (2012) 12, 209. [4] Ye et al., to be published.