

Ferroionic states: coupling between surface electrochemical and bulk ferroelectric functionalities on the nanoscale

Stephen Jesse,* Anton Ievlev, Nina Balke, and Sergei V. Kalinin

¹Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, 37831

*Corresponding author: (sjz.ievlevav.n2b.sv9@ornl.gov)

Abstract

We explore the coupling between ferroelectric and ionic phenomena. At surfaces, coupling between surface (electro)chemistry and bulk ferroelectric instability in nanoscale ferroelectrics gives rise to a ferroionic states characterized by a continuum of polarization values and highly susceptible to environment and pressure. We further show that polarization switching can be associated with significant changes of cationic composition in the near-surface layers, presumably as an effect of depolarization field screening under kinetic limitations. Overall, these studies show important and often poorly recognized role of surface and near-surface chemistry and electrochemistry on ferroelectrics, and suggest pathways for tuning of these materials beyond classical substrate strain and octahedral tilt.

1. Introduction

Ferroelectricity on the nanoscale has remained a subject of much fascination in condensed matter physics for the last several decades. It is well-recognized that stability of the ferroelectric state necessitates effective polarization screening, and hence screening mechanism and screening charge dynamics become strongly coupled to ferroelectric phase stability and domain behavior. Previously, the role of the screening charge in macroscopic ferroelectrics was observed in phenomena such as potential retention above the Curie temperature, back switching of ferroelectric domains, and chaos and intermittency during domain switching. In the last several years, multiple reports claiming ferroelectricity in ultrathin ferroelectrics based on formation of remanent polarization states, local hysteresis loops, and pressure induced switching were made. However, similar phenomena were reported for traditionally non-ferroelectric materials, creating a significant level of uncertainty in the field. We pose that in the nanoscale systems, the ferroelectric state is fundamentally inseparable from the electrochemical state of the surface, leading to the emergence of coupled electrochemical-ferroelectric states.

2. Experimental

The scanning probe microscopy measurements were performed using contact Kelvin Probe Force Microscopy (cKPFM), the technique extending the classical piezoresponse force spectroscopy to 2D via probing the bias dependence of electromechanical interactions in the remanent read-out state, and implemented on Asylum Research Cypher microscope using custom-designed electronics [1]. The phase field theory was realized using classical Fortran codes and also COMSOL environment.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was used to study chemical phenomena associated with ferroelectric switching induced by biased tip of atomic force microscope (AFM) in the $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ (PZT) thin film. Topography and domain structure within freshly switched regions were characterized using contact mode AFM and piezoresponse force microscopy (PFM) respectively (Fig. 1). ToF-SIMS were further utilized to reveal surface and bulk chemical phenomena associated with ferroelectric switching (Fig. 2).

3. Results and Discussion

Analytical theory predicts that interaction between surface electrochemistry and bulk ferroelectric instability leads to the emergence of continuous (rather than binary as in bulk materials) polarization states, very sensitive to the chemical potential of volatile components (e.g. atmospheric pressure), and mechanical pressure. The basic mechanisms of emergence of these coupled states is further explored using phase-field formulation for domain evolution. In the presentation, we will discuss the thermodynamics and thickness evolution of this state, and demonstrate the experimental pathway to establish its presence based on a spectroscopic enhancement of piezoresponse force microscopy[2-5].

We further extend the studies of chemical effects in ferroelectrics to probe chemistry changes in the near-surface regions associated with polarization switching. Here, we use ToF-SIMS on in-situ switched samples to trace the evolution of chemical composition. ToF-SIMS investigations clearly demonstrated concentration inhomogeneity of the Pb^+ and Ti^+ PZT base elements, which was correlated with the direction of spontaneous polarization. In particular, Pb^+ showed the formation of a concentration wave with ~6% concentration increase

near the surface and ~2% decrease at the depth of about 2.2 nm. Observed chemical inhomogeneity was found to be reversible with the application of voltage of opposite polarity (+4V). These results were attributed to screening of the depolarization fields induced on the polar surfaces of freshly switched ferroelectrics with absence of the top electrode.

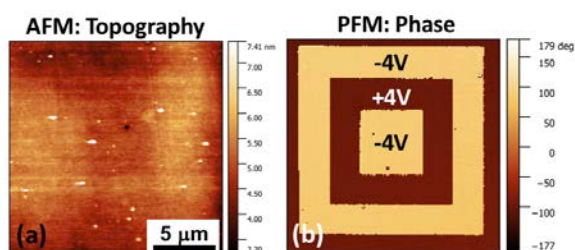


Fig.1: Local polarization switching in PZT thin film. (a) AFM topography and (b) PFM phase signals.

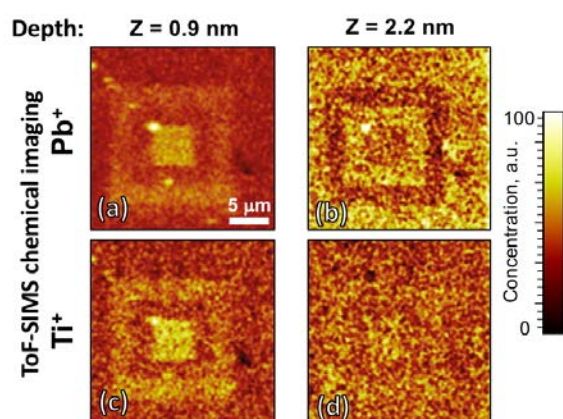


Fig.2: ToF-SIMS study of the chemical phenomena associated with local ferroelectric switching. Signals of Pb^+ (a,b), and Ti^+ (c,d), at 0.9 nm (a,c) and 2.2 nm (b,d) depth.

4. Conclusion

Chemical effects play a large, and often non-recognized, role in nanoscale ferroelectrics. In surface controlled systems, these can lead to continuous ferroionic states resembling relaxor or electret systems in terms of detectable responses. This analysis reconciles multiple prior studies, and set forward the predictive pathways for new generations of ferroelectric devices and applications.

In the bulk, ToF-SIMS investigations clearly demonstrated concentration inhomogeneity of the Pb^+ and Ti^+ PZT base elements, which was correlated with direction of spontaneous polarization. In particular, Pb^+ showed formation of the concentration wave with

~6% concentration increase near the surface and ~2% decrease. This suggests that near-surface electrochemistry can be a part of ferroelectric switching, and may affect phenomena such as ferroelectric fatigue or ferroelectric phase stability, and near-surface wall pinning.

References

- [1] N. Balke, P. Maksymovych, S. Jesse, A. Herklotz, A. Tselev, C.B. Eom, I.I. Kravchenko, P. Yu, and S.V. Kalinin, *Differentiating Ferroelectric and Nonferroelectric Electromechanical Effects with Scanning Probe Microscopy*, ACS Nano **9**, 6484 (2015).
- [2] S.M Yang, A.N. Morozovska, R. Kumar, E.A. Eliseev, Y. Cao, L. Mazet, N. Balke, S. Jesse, R.K. Vasudevan, C. Dubourdieu, and S.V. Kalinin, *Mixed electrochemical-ferroelectric states in nanoscale ferroelectrics*, Nature Physics **13**, 812 (2017).
- [3] A.N Morozovska, E.A. Eliseev, N.V. Morozovsky, and S.V. Kalinin, *Ferroionic states in ferroelectric thin films*, Phys. Rev. B **95**, 195413 (2017).
- [4] A.N Morozovska, E.A. Eliseev, N.V. Morozovsky, and S.V. Kalinin, *Piezoresponse of ferroelectric films in ferroionic states: Time and voltage dynamics*, Appl. Phys. Lett. **110**, 182907 (2017)
- [5] R.K. Vasudevan, N. Balke, P. Maksymovych, S. Jesse, and S.V. Kalinin, *Ferroelectric or non-ferroelectric: why so many materials exhibit ferroelectricity on the nanoscale*, Applied Physics Reviews **4**, 021302 (2017). arXiv:1701.01128