

Materials on the edge between Ferroelectricity and Electrochemistry

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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. These behaviors become even more complicated in the hybrid perovskites, in which ionic dynamics and consequently redox equilibria on surfaces and interfaces become an integral part of the materials functionality. In this presentation, I will illustrate several recent results on ferroelectric and ferroic – chemical coupling in these materials. In classical inorganic ferroelectrics, we show that at the nanoscale the ferroelectric state is fundamentally inseparable from electrochemical state of the surface, leading to emergence of coupled electrochemical-ferroelectric states. I will present the results of experimental and theoretical work exploring the basic mechanisms of emergence of these coupled states including the basic theory and phase-field formulation for domain evolution. I further discuss the thermodynamics and thickness evolution of this state using analytical theory and phase-field modelling. These considerations further stimulate the development of the novel SPM modalities addressing time-dependent dynamics and chemical changes during SPM imaging. I will further delineate the applications of *in-situ* SPM – time of flight secondary ion mass spectrometry (ToF SIMS) to map the changes in surface chemistry during tribological and local electrochemical experiments, including ferroelectric polarization switching and pressure-induced resistance changes in oxides. In the hybrid perovskite, we further extend SPM techniques to explore the coupling between ferroelectricity and ionic motion and light-induced phenomena, whereas ToF-SIMS of active device structures provides insight into associated ionic dynamics.

I will further present recent results on pushing this understanding to the atomic level as enabled by physics-informed big data and machine learning technologies applied to static and dynamic Scanning Transmission Electron Microscopy. The deep learning models trained on theoretically simulated images or labeled library data demonstrate extremely high efficiency in extracting atomic coordinates and trajectories, converting massive volumes of statistical and dynamic data into structural descriptors. I further present a method to take advantage of atomic-scale observations of chemical and structural fluctuations and use them to build a generative model (including near-neighbor interactions) that can be used to predict the phase diagram of the system in a finite temperature and composition space. Similar approach is applied to probe the kinetics of solid-state reactions on a single defect level and defect formation in solids via atomic-scale observations. These advances position STEM towards transition from purely imaging tool for atomic-scale laboratory of electronic, polarization, and chemical phenomena.

References

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