

Chemical State Evolution in Ferroelectric Films During Polarization and Electroresistive Switching: Secondary Ion Mass Spectrometry Study

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In the vast majority of experimental and theoretical work, ferroelectric switching is analyzed with the implicit assumption of unchanged stoichiometry of chemical elements and the driving force given by the volume integral of polarization-electric field product. However, it is well recognized that even bulk polarization is unstable unless it is screened at the surfaces, by either metallic electrodes, band bending, or surface ionic charges. By the date all screening investigations are done through the interpretation of secondary phenomena (e.g. electric potential change or domain structure evolution) or analyzing data of concomitant spectroscopic techniques (e.g. Raman scattering, X-ray scattering). At same time, Secondary Ion Mass Spectrometry (SIMS) provides capabilities for direct spatially resolved mapping of chemical composition as a function of depth, offering a natural pathway to explore chemical changes on ferroelectric surface and bulk induced by locally applied SPM tip bias.

Here we used SIMS to study surface and bulk modifications in chemical composition of ferroelectric thin films induced by the local electric field of the Scanning Probe Microscope (SPM) tip. Reversible ferroelectric and irreversible electro-resistive switching have been considered and demonstrated changes in the surface and bulk chemistry. This confirmed significant role of the surface chemistry on the process of ferroelectric polarization reversal. Furthermore, presence of the ions (e.g. Cl⁻) that are not anticipated based on chemistry of the system has been revealed. These ions were concentrated on the surface in the pristine sample and could be locally introduced deeply into the film electric field.

Explored phenomena are important from both practical and fundamental points of view. It potentially enables new applications of tip-mediated electrochemical reactions and local material modification and allows systematic study of the chemical processes following ferroelectric switching.

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