Mapping the Space Charge Region in BaTiO3 and SrTiO3 using 4-Dimensional Scanning Transmission Electron Microscopy

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Ceramic capacitors are passive electronic components designed to store and release electrical energy through an electric field [1]. Polycrystalline barium titanate (BaTiO3) and strontium titanate (SrTiO3) have been widely employed in ceramic capacitors due to their reliable dielectric properties, compact size, and cost-effectiveness [2]. However, this material experiences degradation, such as increased leakage current, as a result of diminishing resistance under elevated temperatures and voltage stress. According to the ionic de-mixing model, the primary cause of this degradation is the migration of oxygen vacancies, which move toward grain boundaries and eventually reach the cathode [3].

The migration of oxygen vacancies can be effectively altered by doping with elements such as Fe and Mn. This doping modifies the Fermi level and the space charge region (SCR) at grain boundaries. The SCR is the result of an accumulation or depletion of oxygen vacancies and cations around grain boundaries, limiting their migration and preventing degradation. However, this general description lacks validation of the details such as the influence of grain boundary character on the SCR due to limited microscopic observations of grain boundaries and SCR in ceramic capacitors, making it challenging to further develop the theory.

In this study, we employ 4-dimensional scanning transmission electron microscopy (4D-STEM) [4] in combination with electron precession to map electric fields at grain boundaries in Fe-doped BaTiO3 and SrTiO3. Unlike conventional differential phase contrast (DPC) analysis, electric field mapping by 4D-STEM reduces diffraction and channeling artifacts thus enabling accurate measurement of electric field and charge density at the grain boundary. Combining it with an in-situ biasing TEM setup, we can visualize SCRs under different biasing conditions at various temperatures. Through our presentation, we aim to showcase our methodological developments and observations of SCRs in BaTiO3 and SrTiO3. These findings promise to significantly advance the fundamental scientific understanding of ceramic capacitor performance and illuminate the degradation mechanisms under high voltage stress.

Keywords:

Space Charge Layer, 4D-STEM

Reference:

[1] K. Hong, T. H. Lee, J. M. Suh, S.-H. Yoon, and H. W. Jang, “Perspectives and challenges in multilayer ceramic capacitors for next generation electronics,” Journal of Materials Chemistry C, vol. 7, no. 32, pp. 9782–9802, 2019.
[2] Vijatović, M. M., J. D. Bobić, and Biljana D. Stojanović. "History and challenges of barium titanate: Part II." Science of Sintering 40.3 (2008): 235-244.
[3] R. Giesecke, R. Hertwig, T. J. M. Bayer, C. A. Randall, and A. Klein, “Modification of the Schottky barrier height at the RuO2 cathode during resistance degradation of Fe-doped SrTiO3,” Journal of the American Ceramic Society, vol. 100, no. 10, pp. 4590–4601, 2017.
[4] Kang, Sangjun, et al. "Direct observation of quadrupolar strain fields forming a shear band in metallic glasses." Advanced Materials 35.25 (2023): 2212086.