Operando observation of reversible oxygen migration and phase transitions in ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ thin films

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Abstract:

Unconventional ferroelectricity, robust at reduced nanoscale sizes, exhibited by hafnia-based thin-films presents tremendous opportunities in nanoelectronics. However, the exact nature of polarization switching remains controversial. We investigate epitaxial $Hf_{0.5}Zr_{0.5}O_2$ (HZO) capacitors, interfaced with oxygen conducting metals ($La_{0.67}Sr_{0.33}MnO_3$, LSMO) as electrodes, using atomic resolution electron microscopy while *in situ* electrical biasing (*1*).

We utilize differential phase contrast (DPC) STEM imaging in conjunction with *in situ* biasing, and follow directly interpretable oxygen dynamics at an atomic scale. These are complimented with operando nanobeam x-ray diffraction experiments.

We concretely show that:

a) Oxygen voltammetry is very much intertwined with ferroelectric switching in these devices.

b) HZO acts as a fast conduit for oxygen migration between reactive electrodes (such as LSMO/TiN), rendering ferroelectric switching possible. However, under longer time scales (DC stressing), HZO acts as sink and source of oxygen vacancies resulting in structural phase transitions.

c) Oxygen voltammetry still exists even when one of the electrodes is not reactive (Au, for e.g.). But in this case even in the short-term (milliseconds) HZO acts as a sink or source of oxygen vacancies.

In addition to these, I will also discuss the insights obtained on the mechanical response of HZO during ferroelectric switching, and corresponding "strange" electromechanical coefficients.

Our results unmistakably demonstrate that oxygen voltammetry is very much intertwined with polarization switching in HZO. Time permitting, I will also discuss some results on in-situ heating of these materials again using DPC STEM to identify the ferro-para phase transitions in these unconventional ferroelectrics (*2*).

Reference

1. P. Nukala et al., Reversible oxygen migration and phase transitions in hafnia-based ferroelectric devices, *Science*, 372, pp:630 (2021).
2. P. Nukala et al., In situ heating studies on temperature-induced phase-transitions in epitaxial $Hf_{0.5}Zr_{0.5}O_2$/ $La_{0.67}Sr_{0.33}MnO_3$ heterostructure, *Appl. Phys. Lett.*, 118, 062901 (2021).