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Operando Observation of Reversible Oxygen Migration and Phase Transitions in Hafnia-based Ferroelectric Devices

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Unconventional ferroelectricity, exhibited by hafnia-based thin-films presents tremendous opportunities in nanoelectronics. This is a microelectronics friendly ferroelectricity owing to hafnia exhibiting simple chemistry, being compatible with Si, and most importantly ferroelectricity getting enhanced with device miniaturization. The lack of all these qualities in conventional ferroelectrics such as PZT ($Pb(Zr,Ti)O_3$) have plagued their utility as potential low-power electronic devices [1]. However, the exact nature of polarization switching remains controversial. While some groups argue that the origin of ferroelectricity comes from a peculiar polar orthorhombic phase, some other groups argue that this is an extrinsic effect [2,3].

In order to partly resolve this debate, 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 [3]. We utilize differential phase contrast (DPC) STEM imaging in conjunction with *in situ* biasing, and follow directly interpretable oxygen vacancy dynamics at an atomic scale. These are complimented with operando nanobeam x-ray diffraction experiments [3].

We concretely show that
a) The polarization switching observed in real devices cannot be explained by the presence of a weakly polar phase in HZO thin films
b) Oxygen voltammetry across the electrodes through the HZO layer is very much intertwined with ferroelectric switching in these devices
c) 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 also acts as sink and source of oxygen vacancies resulting in structural phase transitions.

d) The rhombohedral polar phase of HZO is an oxygen deficient phase and transforms to an oxygen rich monoclinic phase upon oxygenation through electric field. This is a reversible phase-transformation

e) 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.

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