

## Origin of Ferroelectricity in Thin Film HfO<sub>2</sub> Probed by Revolving STEM and PACBED

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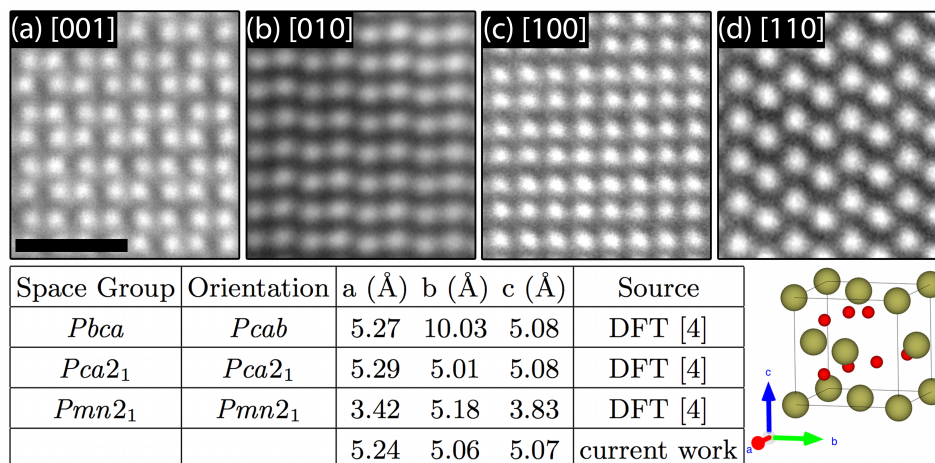
Ferroelectric HfO<sub>2</sub> thin films have recently become compelling candidate materials to replace lead-containing ferroelectrics [1-3]. Though many efforts have sought to control HfO<sub>2</sub> ferroelectricity through doping and capping layer confinement, the multiphase nature of the films has limited our understanding of the governing mechanisms. Current hypotheses suggest that ferroelectricity arises in these films through a stabilized non-centrosymmetric *Pca2*<sub>1</sub> [2,4] or *Pmn2*<sub>1</sub> [4] orthorhombic phase, yet x-ray diffraction studies have been unable to unambiguously refine the space groups of the phases present due to the complex nature of the thin film structures [2].

In this talk, we will present direct experimental evidence of the presence of the ferroelectric orthorhombic *Pca2*<sub>1</sub> phase in Gd-doped HfO<sub>2</sub> thin films. We utilize a combination of revolving scanning transmission electron microscopy (RevSTEM) [5] and position averaged convergent beam electron diffraction (PACBED) to characterize the structure of the films directly at the nanoscale. In particular, we will demonstrate that the high spatial resolution of STEM is required to uniquely identify the phases present within the film. With the combined accuracy and precision of RevSTEM, we will show that lattice parameters measured directly from real space confirm the presence of both monoclinic and orthorhombic phases. For example, different projections of the orthorhombic phase are shown in Fig. 1 (a) – (d). Moreover, the measured lattice constants (Fig 1. table) were inconsistent with the ferroelectric *Pmn2*<sub>1</sub> phase [4], but did not sufficiently delineate between the other candidate phases.

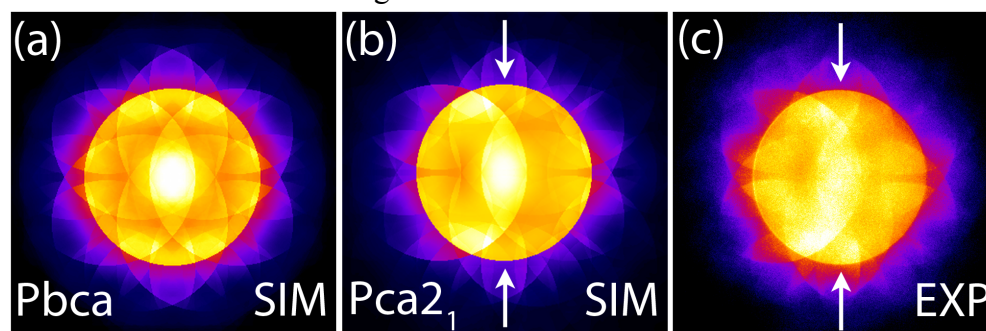
To verify the observed orthorhombic phase is non-centrosymmetric, we will discuss results from PACBED, which as has been demonstrated to readily reveal spontaneous polarization [6]. For example, Figs. 2 (a – c) compare [110] oriented HfO<sub>2</sub> PACBED patterns for (a) simulated centrosymmetric (here *Pbca*), (b) non-centrosymmetric *Pca2*<sub>1</sub>, and experiment (c). The experimental pattern in Fig. 2 (c) shows breaking of mirror symmetry along the vertical plane in good agreement with the simulated pattern for *Pca2*<sub>1</sub> (Fig. 2 (b)). Broken symmetry in PACBED is indicative of non-centrosymmetry suggesting that *Pca2*<sub>1</sub> is the most likely candidate structure for the orthorhombic phase in HfO<sub>2</sub>. Finally, we will discuss the possible sources of stabilization for the orthorhombic structure and possible routes to further control behavior [7].

## References:

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**Figure 1.** Experimental RevSTEM images for Gd:HfO<sub>2</sub> (scale bar: 1 nm) with zone axes labels assuming a *Pca2<sub>1</sub>* structure. The graphic depicts *Pca2<sub>1</sub>* unit cell with gold and red circles representing Hf and O atoms respectively. The table shows comparison of DFT simulated lattice parameters with parameters measured from RevSTEM images.



**Figure 2.** Simulated (SIM) *Pbca* (a), *Pca2<sub>1</sub>* (b), and experimental (EXP) (c) PACBED patterns for HfO<sub>2</sub> oriented along the [110] zone axis. Patterns in both (b) and (c) have broken mirror symmetry along the vertical plane indicated by the arrows. Black levels in (c) adjusted to account for noise.