Insights into Texture and Phase Coexistence in Polycrystalline and Polyphasic Ferroelectric HfO_2 Thin Films using 4D-STEM

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The realization of competitively scaled and reliable ferroelectric non-volatile memories has been hindered for several decades by absence of a ferroelectric that maintains sufficient polarization when integrated into a full CMOS flow scaled thicknesses of around 10 nm. In 2011, Böscke and coworkers [1] reported ferroelectricity in 10 nm thick HfO_2 thin films grown on Si (001) with atomic layer deposition (ALD), which has catalyzed research to realize next-generation memories with its ferroelectric properties. Epitaxial films have been grown, and the domain and grain sub-structuring of both epitaxial [2] and polycrystalline [3] HfO_2 have started to be revealed. Strain commonly imparts unique electrical and magnetic properties to many materials, and studies are revealing that HfO_2 is no exception. The growth of epitaxial non-centrosymmetric $Pca2_1$ orthorhombic HfO_2 shows an important dependence on the substrate [2], and first principles calculations have outlined the important stabilizing influence of grain size and surface energy for the various stable and metastable HfO_2 polymorphs [4]. ALD HfO_2 samples are crystallized between two polycrystalline TiN electrodes via rapid thermal annealing [1,3]. The small grain sizes with multiple HfO_2 polymorphs and small TiN grains at both electrodes have hindered a complete understanding of the degree of texture, strain, and orientation relationship in these materials.

In this talk, we utilize an electron microscope pixel array detector (EMPAD [5]) to provide insight into texture and phase distribution in ferroelectric HfO_2 thin films. The EMPAD can acquire 4D data sets comprised of full diffraction patterns acquired pixel-by-pixel across the sample [5]. The bottom TiN electrode in these materials, which is deposited directly on the Si (001) surface, exhibits strong texture with prominent (002) and (-111) Bragg peaks within ~20° to either side of the film normal (see Figure 1b,c). On the other hand, the orientation of the top TiN electrode is much more random (see Figure 1a,c), likely driven by its deposition onto the non-uniform amorphous HfO_2 surface before annealing. In Figure 2, diffraction patterns are displayed from two adjacent regions in the HfO_2 thin film that may be existing within a single grain across a coherent interphase boundary [3]. The pattern in Region 1 exhibits a much more orthogonal structure, suggesting it is the orthorhombic phase. On the other hand, the pattern in Region 2 shows strong monoclinic distortion. The combination of texture information provided by the EMPAD and new insights into phase distribution enhance the understanding of how the film structure and texture influences the film properties.. Moreover, this technique provides a new avenue for quantifying the effects of processing on the film response, potentially enabling the improvement of the ferroelectric response of ALD grown polycrystalline HfO_2 films [6].

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References:

[1] TS Böscke *et al*, Applied Physics Letters **99** (2011) p. 102903.
[2] K Katayama *et al*, Journal of Applied Physics **119** (2016) p. 134101.
[3] ED Grimley *et al*, Advanced Materials Interfaces (2018) p. 1701258.
[4] R Materlik, C Künneth, and A Kersch, Journal of Applied Physics **117** (2015) p. 134109.
[5] MW Tate *et al*, Microscopy and Microanalysis **22** (2016) p. 237.
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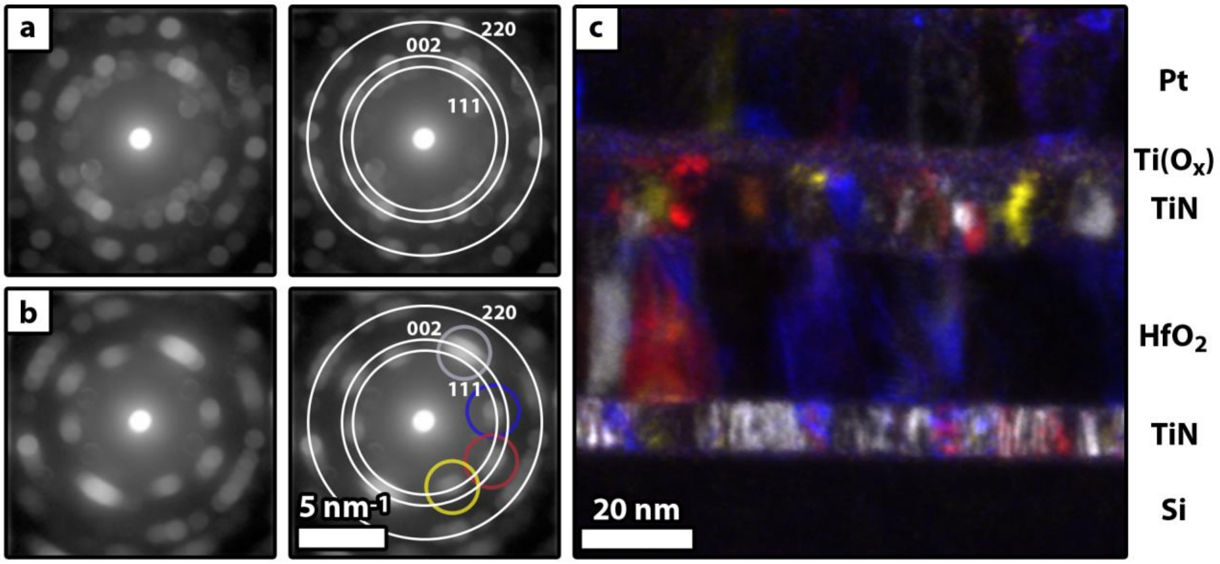

Figure 1. EMPAD detector mean log-scale diffraction patterns from the top TiN electrode (a) and bottom TiN electrode (b). (c) Composite image colored according to the Bragg peaks in (b). Diffraction patterns (128 x 128 pixels) and image (256 x 256 pixels) are digitally magnified.

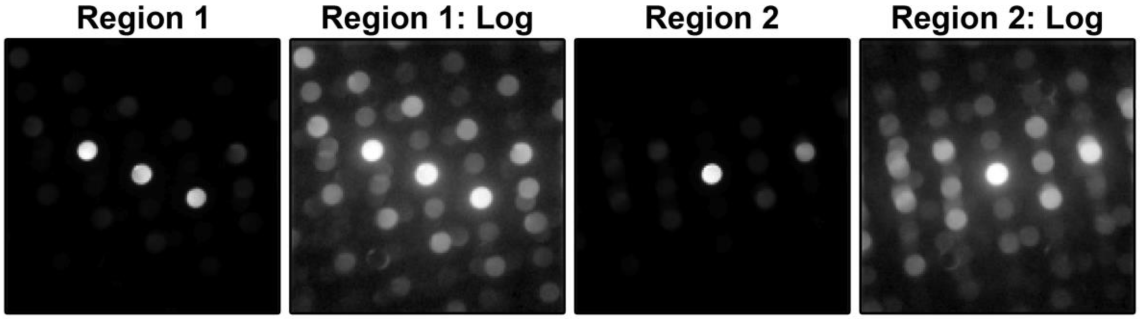

Figure 2. EMPAD detector diffraction patterns from two adjacent portions of the HfO_2 film where the Bragg peaks shift slightly between Region 1 and Region 2. Region 2 shows a strong monoclinic distortion that is largely absent in Region 1.