Supplementary information for "Small Signal Capacitance in Ferroelectric Hafnium Zirconium Oxide: Mechanisms and Physical Insights"

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Small signal capacitance simulation of metal-ferroelectric-metal (MFM) stacks

For comparison with MFIM results presented in the main manuscript, we simulated the small signal capacitance MFM stacks with the phase-field framework. The MFM structure with a total of 10nm thick HZO layer consists of 8 nm ferroelectric HZO with 1 nm dead layer HZO on either side (Fig. S1a). Dead layers typically form at the interface of HZO and metal electrodes due to the absorption of oxygen ions by the electrodes [1, 2]. The dead layers have degraded ferroelectric properties and result in improper screening of polarization. In this work, we treat dead layers as dielectric, with the same material permittivity as ferroelectric HZO. The parameters of TDGL equation (Fig. S1b) are calculated based on experimental data [3] showing a good match between simulated and experimental charge characteristics (Fig. S1c).

The average simulated capacitance voltage characteristics of 50 MFM samples replicate the butterfly characteristics observed in experiments [3, 4, 5] (Fig. S1d). On dividing the total capacitance into dielectric (C_{de}) and polarization (C_P) components, we observe the inverted butterfly characteristics for dielectric capacitance and the characteristic butterfly shape for C_P (Fig. S1e). We have further quantified the contributions of domain bulk and domain wall regions to the polarization capacitance following the procedure discussed in Section-6. Similar to the MFIM stacks with 10 nm HZO, domain bulk contributes higher than domain wall regions (Fig. S1f). Interestingly, we do not observe the formation of conical domain walls with wide or "softer" domain wall regions near the interface at high negative or positive voltages (Fig. S2a, d) in MFIM stacks. The absence of conical domains is mainly due to the increased permittivity of the HZO dead layers compared to Al_2O_3 dielectric, leading to improved charge compensation and lower depolarization field. As a result, the contribution of wide-domain wall response at the interface is absent in MFM stacks.

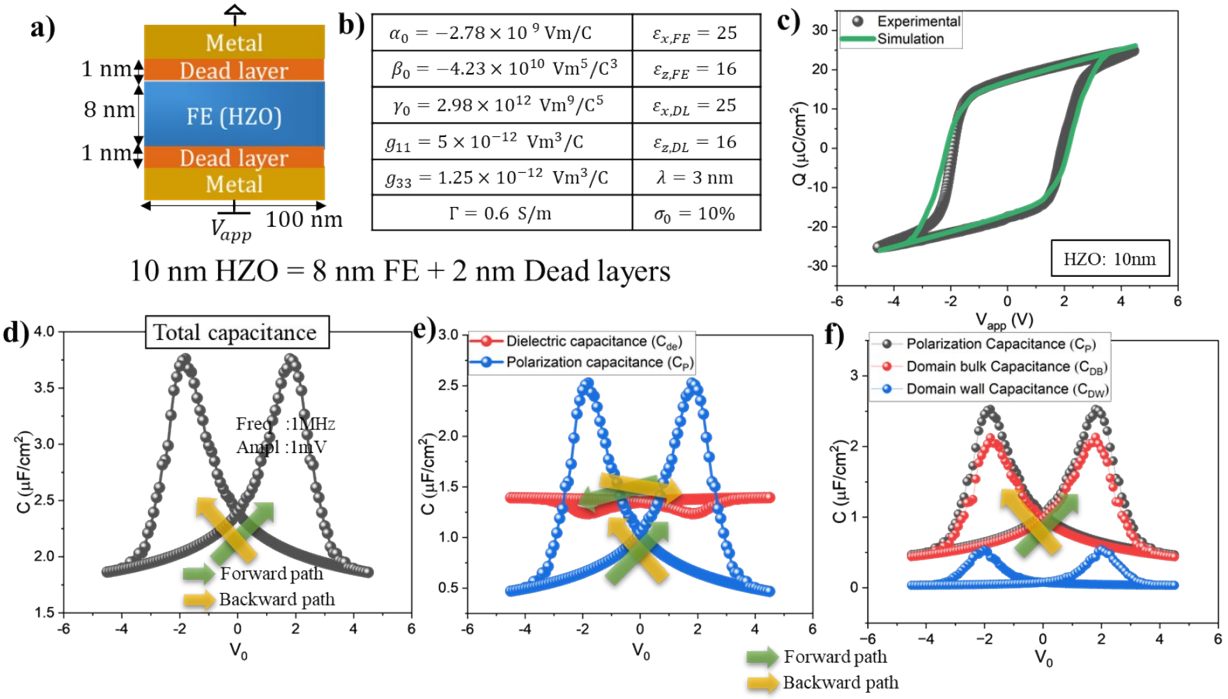

Fig. S1. a) 2D reference MFM structure with 8nm FE HZO, 2nm dead layers and a width of 100nm. b) The calibrated phase-field parameters for MFM. c) Comparison of experimental [1] and simulated (average of 20 samples) charge (Q) vs. voltage (V_{app}) characteristics for MFM with 10nm HZO. d) Simulated total capacitance versus bias voltage (V_0) for MFM, displaying butterfly shaped behavior. e) Dielectric (C_{de}) and polarization (C_P) capacitance components exhibiting inverted butterfly and butterfly characteristics respectively. f) Polarization capacitance (C_P) divided into domain bulk and domain wall contributions signifying the dominance of domain bulk contribution and the absence of wide domain wall response.

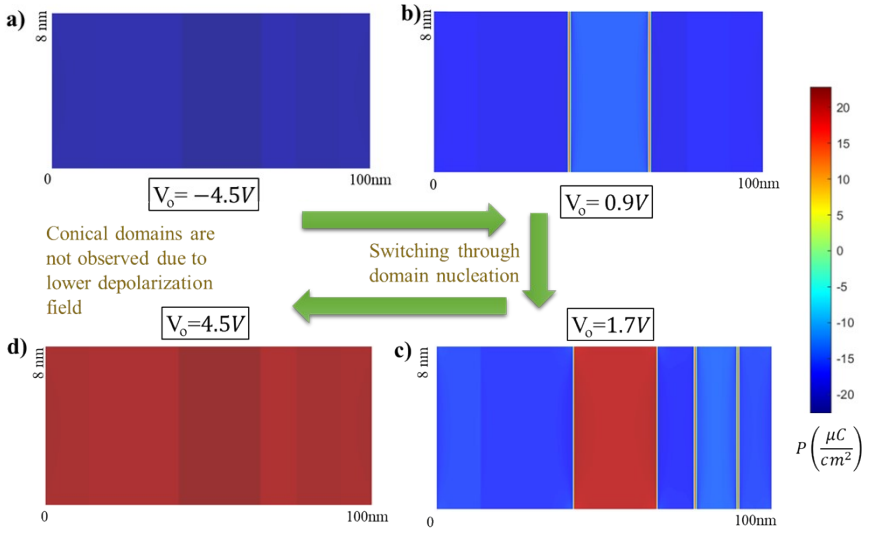

Fig. S2. Polarization profiles of the MFM stack at different bias voltages (V_0) of a) -4.5V, showing the absence of conical domains with softer-domain walls. b) 0.9V illustrating polarization switching initiated by domain nucleation. c) 1.7V, showing the polarization switching via domain growth and domain nucleation, and d) 4.5V after the sample has completely switched, showing the absence of conical domains at even high positive bias voltages.

Anisotropic structure of HZO and impact of polycrystallinity

HZO exhibits anisotropic structure [6, 7] consisting of fully polar (FP) layer (red stripes in Fig. S3) along on cross section and alternate polar-spacer (APS) (Green strips in Fig. S3) layers along the other. Lower gradient energy of APS direction leads to elastically independent polarization switching along FP layers and stripe-like domains. Due to this, we believe that 2D simulations comprising the FP layer and the thickness direction can reasonably capture the polarization switching properties of HZO.

However, the polycrystalline grains and their different orientations can disrupt the alignment of FP layer across the grains (Fig. S3a). The 2D simulations can be considered as a special case where the FP layers across the grains are aligned as in Fig. S3b.

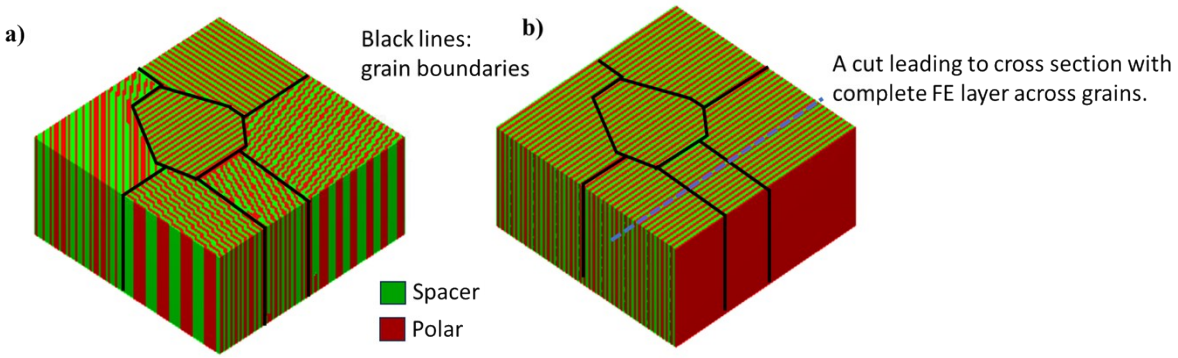

Fig. S3. a) Polycrystalline HZO with disrupted alignment between alternate polar spacer (APS) and fully polar (FP) layers across grains due to the varying orientations in polycrystalline structure. b) Special case structure with APS and FP layers aligned across grains with the cross section (in blue dash line) showing the FP and thickness direction simulated in 2D simulations.

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