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**Depolarization as Driving Force in**   
**Antiferroelectric Hafnia and Ferroelectric Wake-up**

Patrick Dominic Lomenzo, Claudia Richter, Thomas Mikolajick, and Uwe Schroeder

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| Page 1 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54  55  56  57  58  59  60 | ACS Applied Electronic Materials  Depolarization as Driving Force in Antiferroelectric  Hafnia and Ferroelectric Wake-up  *Patrick D. Lomenzo,1\* Claudia Richter,1 Thomas Mikolajick,1,2 and Uwe Schroeder1*  1Nanoelectronic Materials Laboratory (NaMLab) gGmbH, 01187 Dresden, Germany  2Chair of Nanoelectronic Materials, TU Dresden, 01187 Dresden, Germany  \* patrick.lomenzo@namlab.com  KEYWORDS: Antiferroelectricity, Wake-up, Depolarization, Size Effect, Ferroelectric HfO2, Dead Layer  ABSTRACT: Antiferroelectricity and wake-up observed in thin hafnium oxide-based ferroelectrics are examined from the viewpoint of a macroscopic, quantitative model incorporating depolarization effects. Depolarization fields arising from finite screening, a nonferroelectric interface, and a ferroelectric/paraelectric phase mixture are shown to directly impact the switching properties and shape of ferroelectric hysteresis. Charge injection and trapping are used to demonstrate how the progressive stressing of a ferroelectric results in improved switching with electric field cycling. The description of ferroelectric hysteresis is applied to HfO2–based ferroelectrics where the longstanding debate concerning wake-up cycling and antiferroelectric properties can be shown to be driven by depolarization mechanisms. The calculated hystereses combine quantitative accuracy, simplicity, and compatibility to multiple microscopic  ACS Paragon Plus Environment |

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| 1 | ACS Applied Electronic Materials | Page 2 of 52 |
| interpretations which show depolarization fields can be the driving force of a field-induced first- |
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| order phase transition underlying antiferroelectric behavior. |
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| **1. Introduction** |
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| Ferroelectric hysteresis has long been the benchmark technique to characterize the macroscopic |
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| 16 | properties of ferroelectric materials. Plotting dynamic polarization vs. electric field can be traced |
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| back to 1930 with the original Sawyer-Tower circuit.1 The measurement circuit itself has gone |
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| 20 |
| through many iterations, but the unique features and extracted parameters of the hysteresis loop |
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| 23 | are hallmarks of ferroelectric material properties.2 Hysteresis loops are frequently the only direct |
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| measurement of macroscopic ferroelectric properties, but the phenomena of pinched hysteresis |
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| loops and wake-up can neither be predicted nor fully understood by the measurement despite |
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| 31 | widespread observation in many materials.3–8 Understanding such effects have far-reaching |
| 32 | implications for piezoelectric sensors and actuators,4,9–11 infrared detectors and energy |
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| harvesters,12–14 and particularly for emerging ferroelectric memory technologies,15–17 where the |
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| fluorite structure HfO2-based ferroelectrics have demonstrated CMOS compatibility and |
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| 39 | scalability down to several nanometers in thickness.18 |
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| The ambiguity over the interpretation of pinched hysteresis characteristics and wake-up has |
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| reached its crescendo in the recently discovered ferroelectric hafnium oxide material system.6,19,20 |
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| 47 | The simultaneous coexistence of the monoclinic (paraelectric), tetragonal (paraelectric), and |
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| orthorhombic (ferroelectric) phases and their respective phase transitions (i.e. monoclinic (m)  |
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| tetragonal (t), tetragonal (t) orthorhombic (o)) have generated several competing microscopic |
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| 54 | theories. Pinching of the hysteresis loop has been found to depend on the composition and dopant |
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| Page 3 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54  55  56  57  58  59  60 | ACS Applied Electronic Materials  type where antiferroelectric-like behaviour is hypothesized to originate from a reversible field-induced to phase-transition or defect-induced internal bias fields.19,21   Pristine ferroelectric HfO2 is commonly observed to be pinched initially, but gains more homogeneous switching properties with electric field cycling. This transformation of the ferroelectric loop with cycling has been proposed to be due to a cycling-induced phase transition or domain depinning arising from field-driven redistribution of defects.6,20,22 This so-called wake-up effect, where the remanent polarization increases with electric field excitation, is not unique to ferroelectric hafnium oxide but occurs in other ferroelectric materials such as lead zirconate titanate perovskites where paraelectric to ferroelectric phase transitions cannot explain the enhancement in Pr.4,7 With enough cycling, ferroelectrics usually begin to fatigue and the remanent polarization decays. In the perovskite ferroelectrics, two competing but not mutually exclusive theories of wake-up and fatigue were proposed: (1) The field-driven migration of oxygen vacancies and (2) interfacial charge trapping were both attributed to domain pinning and the loss of switchable polarization.23–25 Despite decades of controversy and indirect evidence supporting both hypotheses of electric field cycling, neither quantitative modelling nor experimental evidence has unambiguously crowned a victor. Due to widespread use and physically insightful macroscopic parameters, hysteresis curves are the optimal platform from which physical models can be reconciled with experiment.  The characteristic shape of hysteresis loops are influenced by the crystallinity of a ferroelectric (single or polycrystalline, orientation),26,27 defects,3,5,28,29 voltage shifts,30,31 electrical history,20,22 leakage and dielectric displacement currents,32 proximity of the ferroelectric to the Curie temperature,33 as well as nonferroelectric interfacial layers.34–36 Interested readers are referred to a thorough review on the various shapes manifest in hysteresis loops.2 While there are many  ACS Paragon Plus Environment |

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| 1 | ACS Applied Electronic Materials | Page 4 of 52 |
| proposals trying to account for constricted or pinched hysteresis loops including |
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| antiferroelectricity, field-induced phase transitions, and defect domain pinning,19–22 the lack of |
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| 8 | quantitative models to explain the pinched hysteresis loops often make the hypotheses untestable, |
| 9 | even if plausible, and the difficulty of direct experimental observation with simultaneous structural |
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| and electrical data have caused the field-induced and wake-up cycling phase transition theory to |
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| remain ambiguous despite indirect supporting evidence.37 |
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| 16 | The effects of depolarization have been known for many decades to be strongest in thin film |
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| ferroelectrics as a result of either the finite screening length in the electrodes or an interfacial dead |
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| layer.38,39 Tagantsev explained ferroelectric imprint in perovskite ferroelectrics as a result of the |
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| 24 | depolarization-induced interface field and the consequent injection of charge through a passive |
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| interfacial layer.40 Such a model has recently been called upon to explain imprint in ferroelectric |
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| HfO2.41 Even as many in the ferroelectric community are now turning their attention to this new |
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| 31 | fluorite structure-based ferroelectric material system, the unresolved debate from perovskite |
| 32 | ferroelectrics concerning oxygen vacancies and interfacial charge trapping has re-emerged at the |
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| center of these hotly debated phenomena in HfO2.6,20,42 |
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| Such longstanding controversies are fertile ground to revisit fundamental theories and |
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| 39 | techniques. In this work, we propose an alternative description of the macroscopic ferroelectric |
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| hysteresis which is general enough to allow for multiple microscopic interpretations, but specific |
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| enough to permit quantitative scrutiny which can support or reject the hypotheses in question. We |
| 44 |
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| 47 | perform simulations of ferroelectric hysteresis which incorporate the effects of depolarization to |
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| accurately predict dynamic switching. At a time when the behaviour of nanoscale ferroelectric |
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| phenomena has become more perplexing with the discovery of ferroelectric HfO2, we propose a |
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| Page 5 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54  55  56  57  58  59  60 | ACS Applied Electronic Materials  straightforward, alternative way in which the puzzling phenomena of antiferroelectricity and wake-up can be predicted.  The paper is organized in the following way:   (1) In section 2.1, we detail the simple mechanics used to simulate square-shaped ferroelectric and antiferroelectric hysteresis loops using macroscopic field parameters.  (2) In section 2.3, we propose a paraelectric-ferroelectric phase mixture case which is pertinent when several structural phases can coexist within one film. The depolarization models provide a concrete method to determine the macroscopic electric field in the ferroelectric, establishing the foundation for calculating hysteresis from section (1).  (3) In section 3 we combine the simulation mechanics of section (1) with the theoretical depolarization models presented in section (2). The calculated hysteresis models show the influence of depolarization on the shape of the hysteresis curves.  (4) The remainder of the paper applies the hysteresis calculations with realistic polarization switching distributions and leakage currents to compare with experimental measurements on Si-doped HfO2. Wake-up effects such as depinning, charge injection, and charge trapping are introduced into the model. Several microscopic models are propositioned as testable hypotheses with quantitatively extractable macroscopic parameters through the model.  **2 Modelling Ferroelectric Hysteresis**  **2.1 2nd Order Phase Transition Ferroelectric Hysteresis**   Ferroelectric hysteresis can be understood from the well-known displacement field in ferroelectrics given by   𝐷𝐹𝐸 = 𝑃 = 𝑃𝑑 + 𝑃𝐹𝐸 = 𝜀0𝜀𝑟𝐸𝑎𝑝𝑝 + 𝑃𝐹𝐸, (1)  ACS Paragon Plus Environment |

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| where *P* is the measured polarization, *Pd* is the dielectric polarization (non-switching contribution), | | | | | | | |
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| *PFE* is the ferroelectric switching polarization, *ε0* is the free space permittivity, *εr* is the relative | | | | | | | |
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| 8 | permittivity of the ferroelectric, and *Eapp* is the applied electric field. We first consider | | | | | | | |
| 9 | ferroelectrics with a second-order phase transition which exhibit two polarization states or | | | | | | | |
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| transition into a paraelectric phase above the transition temperature. In the idealized case with | | | | | | | |
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| perfectly uniform polarization switching, the polarization during hysteresis of a ferroelectric with | | | | | | | |
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| 16 | a second-order phase transition can be defined as | | | | | | | |
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| 𝑃𝐹𝐸(𝐸𝐹𝐸) ={ 𝑃𝑆𝑆, if 𝐸𝐹𝐸 < |𝐸±  𝑃―𝑟, if 𝐸𝐹𝐸≤ 𝐸 ―  𝑐| , (2)  𝑃+ 𝑟, if 𝐸𝐹𝐸≥ 𝐸 + | | | | | | | |
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| where | 𝑃+ 𝑟 | and | 𝑃―𝑟 | are the positive and negative remanent polarization respectively, | 𝐸+ 𝑐 | and | 𝐸―𝑐 |
| 24 |
| 25 |
| 26 |
| are the positive and negative coercive field respectively, *EFE* is the electric field in the ferroelectric, | | | | | | | |
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| and *PSS* is the same state polarization. When a second-order ferroelectric is beyond its transition | | | | | | | |
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| 32 | temperature, *PFE* = 0 and *P* = *Pd*. Below the coercive fields, an ideal ferroelectric inherits its | | | | | | | |
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| previous polarization state (*PSS*). More realistic cases of the polarization field dependence will be | | | | | | | |
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| discussed further on. Regardless of the particular measurement circuit, a triangular voltage | | | | | | | |
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| 39 | (electric field) with a frequency (*f*) is applied across the ferroelectric and the polarization is then | | | | | | | |
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| measured as shown in Figure 1(a). | | | | | | | |
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| where *Emax* is the maximum applied electric field. An idealized 2nd-order ferroelectric hysteresis | |
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| can be produced by applying Eq. (1) – (3), as shown in Figure 1(b). The square shape of the | |
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| 8 | hysteresis loop and strong saturation above the coercive field is due to the absence of leakage | |
| 9 | current and the step-like switching process used to calculate the polarization. More realistic | |
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| hysteresis cases will be taken into account further on. . | |
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| **2.2 1st Order Phase Transition Ferroelectric and Antiferroelectric Hysteresis** | |
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| 16 | While antiferroelectricity has been hypothesized to arise from different microscopic | |
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| mechanisms, including sub-lattices with antiparallel dipole arrangements (inspired by classical | |
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| antiferromagnetism)43 or a reversible field-induced first-order phase transition,44 the observed | |
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| 24 | macroscopic antiferroelectric hysteresis remains the same. The macroscopic properties are derived | |
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| from the consideration of the Landau free energy of a ferroelectric material with a first-order phase | |
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| transition. The unique characteristics of the antiferroelectric hysteresis come about as switched | |
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| 31 | ferroelectric charge during electric field biasing vanishes when the field is removed, leading to a | |
| 32 | ‘double loop’. From Landau theory, this is understood to arise from a polar energy minimum | |
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| emerging with the application of an electric field, and once the field is removed, the polar state | |
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| becomes energetically unfavorable again compared to the nonpolar state.45 To reproduce the | |
| 37 |
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| 39 | macroscopic antiferroelectric hysteresis loop, we can modify Eq. (2) to account for when the | |
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| polarization diminishes to zero, | |
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| 𝑃𝑆𝑆 if 𝐸𝐹𝐸 < |𝐸±𝑐|,|𝐸 ±𝐵𝑆|  𝑃𝐹𝐸(𝐸𝐹𝐸) ={ 𝑃―  0, if 𝐸𝐹𝐸 ≤ 𝐸+  0, if 𝐸𝐹𝐸 ≥ 𝐸― 𝑟, if 𝐸𝐹𝐸≤ 𝐸 ―  𝐵𝑆 & 𝑃𝐹𝐸= 𝑃 +  𝐵𝑆 & 𝑃𝐹𝐸= 𝑃 ―  𝑐 & 𝑃𝐹𝐸= 0  𝑟,  𝑃+ 𝑟, if 𝐸𝐹𝐸≥ 𝐸 + 𝑐 & 𝑃𝐹𝐸= 0 | (4) |
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| where | 𝐸+ 𝐵𝑆 and | 𝐸―𝐵𝑆 are the positive and negative back-switching fields causing the loss of | | | | | |
| ferroelectric polarization. Throughout this paper, we will assume that | | | 𝐸+ 𝐵𝑆 = | 𝐸―𝑐 | and 𝐸―𝐵𝑆 = | 𝐸+ 𝑐 | . |
| Like the square-shaped ferroelectric loop, the idealized antiferroelectric inherits the pre-existing polarization state via the same state polarization *PSS* if the field across the material is weaker than the coercive or back-switching fields. While the nonpolar state distinguishes ferroelectric hysteresis loops with a first-order phase transition from second-order phase transition ferroelectrics, boundary conditions on the pre-existing polarization state are imposed to appropriately recreate the features of the antiferroelectric loop through Eq. (3) – (4) as shown in Figure 2.    **Figure 2.** Calculated antiferroelectric hysteresis loop with no remanent polarization when the applied electric field is removed. The antiferroelectric hysteresis loop is consistent with a first-order phase transition ferroelectric above its transition temperature.  It is important to note that the nonpolar state here is only defined macroscopically and several microscopic configurations could be macroscopically indistinguishable. The basic criterion which  ACS Paragon Plus Environment | | | | | | | |

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| defines an antiferroelectric, as proposed by Rabe,45 is that an applied electric field must cause a |
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| nonpolar to polar, first-order phase transition. Thus, the macroscopic model here satisfies the |
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| 8 | definition of antiferroelectricity since a nonpolar state (phase) is driven into a polar state (phase) |
| 9 | with an applied electric field. We note that, due to the close relationship between ferroelectrics |
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| with a first-order phase transition and antiferroelectric behavior, at times we use the term |
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| (anti)ferroelectric to avoid ambiguity. |
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| 16 | **2.3 Depolarization Models** |
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| Depolarization fields are produced when the switched ferroelectric charge is not fully |
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| compensated by screening charge. Three distinct cases which give rise to depolarization fields are: |
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| 24 | (1) Finite screening lengths in metal electrodes, (2) a non-switching interfacial dead layer, and (3) |
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| mixed ferroelectric and paraelectric phases. In this section we present the mixed |
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| paraelectric/ferroelectric phase model, while the well-known cases of finite screening and dead |
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| 31 | layer derivations are given in the supplementary. |
| 32 | **2.3.1 Ferroelectric-Paraelectric Phase Mixture** |
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| While the phase boundaries and structural differences in conventional perovskite ferroelectrics |
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| often enable the unambiguous determination of single-phase materials, the case of the HfO2-ZrO2 |
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| 39 | based material system proves to be more challenging due to the close structural similarities of the |
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| ferroelectric orthorhombic phase and the paraelectric tetragonal and cubic phases. In most studies, |
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| ferroelectric hafnia-based thin films are shown to exhibit a mixed phase composition comprising |
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| 46 |
| 47 | of the monoclinic, tetragonal, and/or orthorhombic phases.13,46 Furthermore, transmission electron |
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| microscopy investigations have shown evidence of both tetragonal interfacial layers and interphase |
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| grains.37,47 The paraelectric phase will necessarily impact the electric field distribution across the |
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| Under the assumption (2) above, some fraction of the paraelectric phase (*p*), the upper limit of | | | | | | | | | |
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| which can be experimentally estimated from grazing incidence x-ray diffraction (GIXRD), can be | | | | | | | | | |
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| 8 | used to estimate the thickness of the paraelectric layer in series with the ferroelectric as | | | | | | | | | |
| 9 | 𝑑𝑃, ⊥ = 𝑝𝑑𝐹𝐸. (5) | | | | | | | | | |
| 10 |
| 11 |
| Since a portion of the total film of thickness *dFE* that has been assumed to be only ferroelectric | | | | | | | | | |
| 12 |
| 13 |
| is now a paraelectric phase in this model, the resulting equivalent thickness of the ferroelectric | | | | | | | | | |
| 14 |
| 15 |
| 16 | becomes | | | | | | | | | |
| 17 |
| 18 |
| 𝑑∗𝐹𝐸 = (1 ― 𝑝)𝑑𝐹𝐸. (6) | | | | | | | | | |
| 19 |
| 20 |
| The electric displacement field of the paraelectric can be described by | | | | | | | | | |
| 21 |
| 22 |
| 23 | 𝐷𝑃, ⊥ = 𝜀0𝜀𝑃, ⊥ 𝐸𝑃, ⊥ , (7) | | | | | | | | | |
| 24 |
| 25 |
| where | 𝜀𝑃, ⊥ | | is the relative permittivity of the paraelectric and | | | 𝐸𝑃, ⊥ | | | is the applied electric field |
| 26 |
| 27 |
| 28 |
| 29 | across the paraelectric. The voltage across the capacitor stack with the paraelectric layer included | | | | | | | | | |
| 30 | thus becomes | | | | | | | | | |
| 31 |
| 32 |
| 𝑉𝑎𝑝𝑝 = 𝑑𝐹𝐸𝐸𝐹𝐸 + 𝑑𝑃, ⊥ 𝐸𝑃, ⊥ , (8) | | | | | | | | | |
| 33 |
| 34 |
| 35 |
| 36 | where 𝑑𝑃, ⊥ | | is the thickness of the paraelectric layer. Setting 𝐷𝑃, ⊥ | | | | | = *DFE* and applying Eq. (8), the | | |
| 37 |
| electric fields across the ferroelectric and dielectric layer respectively are | | | | | | | | | |
| 38 |
| 39 |
| 𝐸𝐹𝐸 =(𝑉𝑎𝑝𝑝 𝑑𝑃, ⊥―  𝜀𝑃, ⊥ | | | | | 𝜀0) 𝑑∗𝐹𝐸𝜀𝑃, ⊥ + 𝑑𝑃, ⊥ 𝜀𝐹𝐸 𝑑𝑃, ⊥ | | | (9) | |
| 40 |
| 41 |
| 42 |
| 43 |
| 𝐸𝑃, ⊥ =(𝑉𝑎𝑝𝑝 𝑑𝐹𝐸+   𝜀𝐹𝐸 | | | | 𝑑∗𝐹𝐸  𝜀0) 𝑑∗𝐹𝐸𝜀𝑃, ⊥ + 𝑑𝑃, ⊥ 𝜀𝐹𝐸 . (10) | | | | | |
| 44 |
| 45 |
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| 48 |
| 49 | Since the film can now contain areas which are completely paraelectric (see assumption (3) above), | | | | | | | | | |
| 50 |
| the parallel dielectric displacement field and switched polarization charge must now be considered | | | | | | | | | |
| 51 |
| 52 |
| together such that | | | | | | | | | |
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| 𝐷 = 𝑓𝑃,||𝐷𝑃,|| + (1 ― 𝑓𝑃,||)𝐷𝐹𝐸, (11) | | | | | | | | | |
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| Page 13 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39 | ACS Applied Electronic Materials  where *DP,||* is the linear dielectric displacement field in the paraelectric regions and *f*P,|| is the area fraction of the film which is completely paraelectric (the upper limit of this area fraction can also be constrained to the experimentally estimated phase fractions from GIXRD). Similar to the interfacial dead layer model described in the supplementary, both the thickness and the relative permittivity of the paraelectric layer impact the strength of the depolarization field. The observed macroscopic switched charge, however, is further reduced if the fraction of the non-switching paraelectric areas grows.  **2.3.2 Interfacial Dead Layer with Paraelectric-Ferroelectric Phases**   Since the interfacial dead layer and finite screening effects can influence the ferroelectric independently of any paraelectric phases coexisting with the ferroelectric phase throughout the film, we propose to combine the interfacial dead layer model with the mixed paraelectric/ferroelectric phase model. The interfacial dead layer can be treated solely as a result of finite screening (see supplementary).Treating the ferroelectric, dead layer, and paraelectric phase as being in-series layers, the respective electric fields can be described by | | | | | | | | | | | |
| (𝑉𝑎𝑝𝑝 ― | | | 𝜀0( 𝜀𝑖𝑛𝑡+ 𝑑𝑖𝑛𝑡 | | | | | 𝜀𝑃, ⊥)) | | | |
| 𝐸𝐹𝐸 = | 𝜀𝐹𝐸  𝑑∗𝐹𝐸 + 𝑑𝑖𝑛𝑡 𝜀𝑖𝑛𝑡+ 𝑑𝑃, ⊥ | | | | | | | | 𝜀𝐹𝐸 | (12) | |
| 40  41  42  43  44  45  46  47 | 𝜀𝑃, ⊥ |
| (𝑉𝑎𝑝𝑝 + | | | | 𝜀0( | | 𝜀𝐹𝐸)) | | | | | |
| 𝐸𝑖𝑛𝑡 = | 𝜀𝑖𝑛𝑡  𝑑𝑖𝑛𝑡 + 𝑑∗𝐹𝐸 𝜀𝐹𝐸+ 𝑑𝑃, ⊥ | | | | | | | | 𝜀𝑖𝑛𝑡 | (13) | |
| 48  49  50  51  52  53  54  55  56  57  58  59  60 | 𝜀𝑃, ⊥ |
| (𝑉𝑎𝑝𝑝 + | | | | | 𝜀0( | | 𝜀𝐹𝐸)) | | | | |
| 𝐸𝑃, ⊥ = | | 𝜀𝑃, ⊥ 𝜀𝑃, ⊥  𝑑𝑃, ⊥ + 𝑑∗𝐹𝐸 𝜀𝐹𝐸+ 𝑑𝑖𝑛𝑡 𝜀𝑖𝑛𝑡 | | | | | | | | | . (14) |
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| 1 | ACS Applied Electronic Materials | Page 14 of 52 |
| The non-switching paraelectric areas can be applied to this model via Eq. (11). |
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| **2.3.3 Depolarization Induced Nucleation Inhibition** |
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| 8 | In ferroelectric devices where the depolarization field is much smaller than the coercive field, |
| 9 | one can expect ferroelectric switching to proceed at the coercive field. However, once the |
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| 12 | depolarization field can equal or exceed the coercive field, nucleation and switching of domains |  |
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|  | become affected by the depolarization energy. If domains were to nucleate and create a |  |
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| 16 | depolarization field that exceeded the back-switching field in a ferroelectric with a first-order |
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| phase transition, the newly-formed domains would be unstable and back-switch immediately. |
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| Domain formation should only occur when nucleating lowers the free energy in the film, and thus, |
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| 24 | the depolarization energy must be overcome for nucleation to take place. In a second-order phase |
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| transition ferroelectric, since the free energy cannot be lowered by back-switching into a nonpolar |
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| state, the magnitude of switched charge decreases as the depolarization energy drives the |
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| 31 | ferroelectric closer to its phase transition.39 The decline in the measured remanent polarization |
| 32 | with stronger depolarization fields has been verified in ferroelectrics with a second-order |
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| ferroelectric phase transition and it is hypothesized that the domain wall activation field in |
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| ferroelectrics can be determined by the depolarization field.48 Our theory of depolarization- |
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| 39 | induced nucleation inhibition is thus an excellent corollary to thin films which do not exhibit |
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| 41 |
| Kolmogorov–Avrami–Ishibashi switching, but on nucleation limited switching or inhomogeneous |
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| field switching.49,50 We therefore allow the condition that the observed coercive field in a first- |
| 44 |
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| 47 | order ferroelectric can increase until the total field in the ferroelectric, when summed with the |
| 48 |
| switching-induced depolarization field, is smaller than the back-switching field. Such |
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| depolarization induced nucleation inhibition can further explain the shift of the observed coercive |
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| 54 | field in ZrO2 antiferroelectrics.21,51 |
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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Page 15 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54  55  56  57  58  59  60 | ACS Applied Electronic Materials  **2.4 Ferroelectric Hysteresis with Depolarization**   For convenient comparison of the different depolarization models, we can express the total field in the ferroelectric as   𝐸𝐹𝐸 = 𝐸𝑎𝑝𝑝 + 𝐸𝑑 + 𝐸𝑖, (15)  where *Ei* is an internal bias field.  **Table 1.** Applied electric field and depolarization field for different depolarization models.   |  |  |  |  |  | | --- | --- | --- | --- | --- | |  | Finite Screening | Dead Layer | Mixed Phase | DL + Mixed Phase | | Eapp | Vapp  dFE | (Vapp dint) dFEεint + dintεFE dint | (Vapp dP, ⊥) d\*FEεP, ⊥ + dP, ⊥ εFE dP, ⊥ | Vapp   |  |  | | --- | --- | | \* εFE | εFE | | dFE + dint εint+ dP, ⊥ | εP, ⊥ | | | Ed | |  |  | | --- | --- | |  | P + q0 | | - | ε0εFE | | -( ε0) dFEεint + dintεFE dint | -( ε0) d\*FEεP, ⊥ + dP, ⊥ εFE dP, ⊥ | |  |  |  |  | | --- | --- | --- | --- | |  | ε0( εint+ dint | εP, ⊥) | | | - | εFE  d\*FE + dint εint+ dP, ⊥ | | εFE | |  | εP, ⊥ | |   By virtue of the electric field in the film, polarization switching and back-switching are set into motion. It now becomes transparent, through Eq. (15) and (4), that the depolarization field inevitably impacts ferroelectric polarization switching during the applied electric field excitation. If the depolarization field is considerably smaller than the coercivefield, then ferroelectric polarization switching commences unperturbed when *Eapp* ≈ *Ec*. The depolarization fields in HfO2-based ferroelectrics, however, can approach the same order of magnitude as the coercive field and thus cannot be neglected.41,52 The depolarization field caused exclusively by finite screening and an interfacial dead layer can be strong enough to force ferroelectric-based HfO2 to undergo a ferroelectric-to-antiferroelectric hysteresis transformation with scaling down of the ferroelectric thickness (see supplementary).  Antiferroelectric-like hysteresis loops in HfO2-based ferroelectrics frequently show a strong dependence on the doping concentration and the relative fraction of the polar orthorhombic phase vs. the paraelectric tetragonal phase.21 The theory of a reversible field-induced  ACS Paragon Plus Environment |

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| 1 | ACS Applied Electronic Materials | Page 16 of 52 |
| tetragonalorthorhombic first-order phase transition, as proposed by first principles and DFT |
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| calculations,53,54 has been adopted by researchers in the field to explain the experimental results.8 |
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| 8 | Nevertheless, the driving force behind the reversible field-induced first-order phase transition is |
| 9 | unknown. We adopt the first-order phase transition switching model given by Equation (4) to better |
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| understand ferroelectric-based HfO2 and ZrO2 thin films. |
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| Applying a simple-step like switching model using Equations (4), (9), and (15), the ferroelectric- |
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| 16 | paraelectric phase hysteresis model is implemented by adjusting the percentage of the paraelectric |
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| tetragonal phase in series with the polar orthorhombic phase as shown in Figure 4. It is clear that |
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| with just 50 % of the paraelectric tetragonal phase introduced into the ferroelectric HfO2 thin film, |
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| 23 | the ferroelectric hysteresis transforms into an antiferroelectric hysteresis loop. When the film is |
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| overwhelmingly tetragonal, the observed coercive field shifts to higher applied electric fields. |
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| These trends are in excellent agreement with the increases in the coercive field as ferroelectric |
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| 30 |
| 31 | HfO2 thin films are progressively doped to exhibit greater antiferroelectric properties.21,55,56 From |
| 32 | these results, it can be understood that the increasing presence of the nonpolar tetragonal phase is |
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| 34 |
| leading to a large depolarization field and that the polar phase becomes unstable as the applied |
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| field is removed. Irrespective of whether or not a structural, field-driven to phase transition is |
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| 39 | occurring in some portion of the film or if the total polarization vector is neutralized by some other |
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| microscopic arrangement (i.e. random domain arrangement, antiparallel dipoles, in-plane domains, |
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| etc), a macroscopic first-order phase transition is generated when the depolarization field |
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| 47 | destabilizes the out-of-plane polar state. |
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| Page 17 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54  55  56  57  58  59  60 | ACS Applied Electronic Materials    **Figure 4.** Calculated hysteresis loops produced by the ferroelectric/paraelectric phase mixture model with varying amounts of the paraelectric tetragonal phase (*εP,⊥* = 45). Both the non-switchable tetragonal areas of the film and the tetragonal phase layer in-series with the switching orthorhombic phase are scaled. Commonly observed ferroelectric properties for FE HfO2-based films are used to simulate the square hysteresis loops (*Pr* = 15 µC/cm2, *εFE* = 30, *Ec* = 1 MV/cm).  Now that the depolarization mechanisms and their respective influences on the hysteresis characteristics have been evaluated for idealized, abrupt-switching ferroelectric loops, it is instructive to use more realistic switching distributions, as detailed in section 4, and verify the model’s validity to previous work which observed tilting of the hysteresis loop with the introduction of linear capacitors placed in-series with the ferroelectric.48   Ferroelectrics which undergo a first-order phase transition show both tilting and pinching of the ferroelectric hysteresis curves as a low-permittivity linear dielectric layer grows in thickness when  ACS Paragon Plus Environment |

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| 1 | ACS Applied Electronic Materials | Page 18 of 52 |
| placed in-series with the ferroelectric as shown in Figure 5(a). If the switching polarization were |
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| 4 |
| to remain constant, as assumed in Figure 5(a),(b), depolarization-induced nucleation inhibition |
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| 8 | would cause an increase in the coercive field. It may also be possible that the switching polarization |
| 9 | could decline with greater depolarization when the linear series capacitance decreases, in which |
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| 11 |
| case the coercive field increase could be prevented. Nonetheless, unlike the second-order |
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| ferroelectric which must decrease its polarization or become completely paraelectric to minimize |
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| 15 |
| 16 | its free energy around the transition, the first-order ferroelectric has the ability to use back- |
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| switching as an energy-lowering mechanism such that higher polarization energy minima are |
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| capable of being established with an applied electric field despite the material being pushed beyond |
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| 23 |
| 24 | its transition point. Thus, when depolarization-induced nucleation inhibition is considered |
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| alongside of the Landau free energy description of first-order ferroelectrics, the increase in the |
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| coercive field seen in Figure 5(b) can be expected. |
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| **Figure 5.** Calculated hysteresis loops produced by introducing a low permittivity paraelectric |
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| material of varying thickness in-series with a ferroelectric of first-order (a),(b) and second-order |
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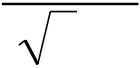
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| Page 19 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54  55  56  57  58  59  60 | ACS Applied Electronic Materials  (c),(d) phase transitions. Tilting of the hysteresis loop with a smaller in-series capacitance (i.e. larger paraelectric thickness) is readily apparent in the commonly plotted polarization vs. applied voltage curves.  We observe tilting of the hysteresis loop as the linear capacitance is decreased in Figure 5 (c) and our model also predicts the coercive field would be unchanged in second-order ferroelectrics when the linear series capacitance decreases as shown in Figure 5 (d), similar to a previous study on second-order ferroelectric materials.48 It should be noted that the remanent polarization was held constant in our calculations for simplicity, but in fact the observed remanent polarization with applied voltage has been observed to decrease.  **3 Experiment**   12 nm thick TiN electrodes were reactively sputtered at room temperature on (100) Si substrates. Si-doped HfO2 thin films were then deposited at 280 °C with a film thickness of 5.4 nm and 10 nm thick Si-doped HfO2 films with 2 % and 2.2 % Si doping respectively. Tetrakis[ethylethylamino]hafnium and N,N,N′,N′-tetraethylsilanediamine were used as the hafnia andsilica ALD precursors respectively. H2O was used as the oxidizer to grow HfO2 while O2 plasma was used for the SiO2 growth, in accordance with previous studies.56 10 nm thick TiN top electrodes were sputtered at room temperature using a Bestec PVD tool. After metallization, the 5.4 nm thick Si-doped films were annealed at 800 °C for 20 s in N2 while the 10 nm thick Si-doped HfO2 thin films were annealed at 650 °C for 600 s in N2. The lower temperature anneal was chosen to stabilize antiferroelectric-like behavior in 10 nm thick films. Lower annealing temperatures have been shown in previous reports of Si-doped HfO2 thin films to stabilize antiferroelectric-like hysteresis loops.57 A 10 nm Ti adhesion layer followed by 50 nm of Pt was evaporated through a shadow mask to form the top contacts. The capacitor geometry was formed by using the Pt dots as  ACS Paragon Plus Environment |

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| 1 | ACS Applied Electronic Materials | | | | | Page 20 of 52 |
| a hard mask during an SC1 wet etch of the blanket top TiN layer. The area of the devices were | | | | |
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| measured directly with an optical microscope and ranged from 29,000 – 31,000 µm2. | | | | |
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| 8 | X-ray reflectometry (XRR) and GIXRD were performed with a Bruker D8 Discover for | | | | |
| 9 | film thickness and crystal structure determination. Deconvolution of the tetragonal and | | | | |
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| orthorhombic peaks was performed by Gaussian fitting where the respective 2θ peak positions | | | | |
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| were set at 30.8 ° and 30.4 °. The relative phase fractions were quantified by integrating the area | | | | |
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| 16 | under the fitted Gaussians, as reported elsewhere.46 Polarization vs. electric field (P-E) hysteresis | | | | |
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| measurements were carried out on an aixACCT Systems TF Analyzer 3000 with a measurement | | | | |
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| frequency of 1 kHz and 10 kHz on the 10 nm and 5.4 nm thick Si-doped HfO2 thin films | | | | |
| 21 |
| 22 |
| 23 | respectively to illustrate the frequency independence of the hysteresis calculations. The bottom | | | | |
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| electrode was grounded during hysteresis measurements. Electric field cycling (wake-up) was | | | | |
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| performed at 10 kHz with bipolar square waves. All of the modelling parameters are given in the | | | | |
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| 31 | supplementary. | | | | |
| 32 | **4 Results and Discussion** | | | | |
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| **4.1 Modelling Experimental Polarization Switching** | | | | |
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| To allow direct comparison of the depolarization models with the experimental results, it is | | | | |
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| 39 | necessary to provide an accurate mathematical description of the macroscopically observed | | | | |
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| polarization switching process, irrespective of the atomistic and domain-level mechanics. During | | | | |
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| dynamic hysteresis measurements, the switching currents exhibit a nonlinear shape which can be | | | | |
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| 47 | accurately reproduced using a Gaussian function. Proceeding on this observation, we describe the | | | | |
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| total ferroelectric switching current as the sum of individual Gaussian-shaped switching currents, | | | | |
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| 𝐽𝑠𝑤(𝑡) = | 𝑛 |  | (𝑡 ― 𝑡𝑠𝑤,𝑖)2 | |
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|  | ∑𝐽0,𝑖𝑒 | ― | 2𝑡2𝑤,𝑖 | , (16) |  |
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| Page 21 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51 | ACS Applied Electronic Materials  where *J0* is the switching current density peak magnitude, *t* is time, *tSW* is the switching time, *tw* is the switching width, *i* is the switching current index, and *n* is the total number of switching peaks. The Gaussian form of the switching current profile is not merely a convenient mathematical construct to replicate the switching profile, however, but can be related to ferroelectric switching based on the inhomogeneous field mechanism of disordered ferroelectrics.49,50 Integrating an individual switching current yields the saturated polarization charge,   ∞ | | | | |
| 𝑃𝑠 = | ∫ | 𝐽𝑠𝑤(𝑡)𝑑𝑡 = 𝐽0𝑡𝑤2𝜋. (17) | | |
| ―∞  Furthermore, we can describe the analytical time-dependency of the polarization charge by using the error function to solve the bounded indefinite integral of the Gaussian function such that 1 + 𝑒𝑟𝑓( 2𝑡𝑤)   𝑡 ― 𝑡𝑠𝑤   𝑃𝑠𝑤(𝑡) = 𝑃𝑠( 2 ) . (18)  Although ferroelectric P-E loops are not explicitly expressed in the time domain, Eq. (3) can be used to readily translate between the electric field and time domains. To properly model dynamic hysteresis measurements, one must take into account the dielectric displacement current and the conduction current. The dielectric displacement current can be expressed as   𝑑𝐸𝐹𝐸(𝑡)   𝐽𝑑(𝑡) = 𝜀0𝜀𝐹𝐸 𝑑𝑡 . (19)  The conduction current is assumed to be Ohmic (i.e. representable by a parallel resistor) and defined as | | | | |
| 𝐽𝜎(𝑡) = | | | 𝐸𝐹𝐸(𝑡)𝑑𝐹𝐸 | (20) |
| 52  53  54  55  56  57  58  59  60 | 𝑅𝜎 |
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| 1 | ACS Applied Electronic Materials | Page 22 of 52 |
| where Rσ is the parallel resistance. Thus, the total current in the ferroelectric during dynamic |
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| hysteresis measurements can be expressed as |
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| 8 | 𝐽𝐹𝐸(𝑡) = 𝐽𝑠𝑤(𝑡) + 𝐽𝑑(𝑡) + 𝐽𝜎(𝑡). (21) |
| 9 | **4.2 Antiferroelectric by Depolarization** |
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| The relative fraction of the 10 nm thick antiferroelectric Si-doped HfO2 thin film phases were |
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| estimated to be roughly 83 % tetragonal and 17 % polar orthorhombic (see supplementary). Due |
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| 16 | to the large amount of the tetragonal phase present throughout the film and prior observations of a |
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| distinct tetragonal interfacial layer in FE HfO2,37 a non-switching mixed t/o phase dead layer was |
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| introduced at the top and bottom ferroelectric/electrode interfaces in the depolarization model |
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| 23 | which could also account for the finite screening effects of the TiN electrodes. Thus, the interfacial |
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| dead layer and mixed ferroelectric/paraelectric phase depolarization model was adopted to |
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| characterize the experimental hysteresis loop. |
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| 31 | The depolarization model used to reproduce the antiferroelectric hysteresis characteristics in this |
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| section assumes that the entire film area can be switched (as long as |*EFE*| > |*EC*|). Thus, completely |
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| paraelectric regions in parallel with the ferroelectric portions of the film are neglected. Using the |
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| same procedure as was done in section 2 but with the more realistic switching distributions as just |
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| 39 | described, the ferroelectric hysteresis simulated with depolarization effects can reproduce the |
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| experimentally measured antiferroelectric hysteresis properties in excellent detail as shown in |
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| Figure 6. Field cycling the antiferroelectric film resulted in only very small shifts in the switching |
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| 47 | current peaks which could be explained by an increase in the effective trap density, as will be |
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| discussed in the following section. |
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| Page 23 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54  55  56  57  58  59  60 | ACS Applied Electronic Materials    **Figure 6.** (a) Polarization vs. applied electric field and (b) current density vs. applied electric field showing the experimental hysteresis of the 10 nm Si-doped HfO2 thin film compared to the hysteresis loop obtained from the depolarization model.  The antiferroelectric switching process can be understood to be caused by depolarization through careful consideration of the hysteresis properties. When the applied electric field is zero at the beginning of the measurement, the ferroelectric polarization is also roughly zero (*Ed* ≈ 0). When the applied electric field exceeds the coercive field, polarization switching commences and a depolarization field is created which is opposite in direction to the applied field. As the applied  ACS Paragon Plus Environment |

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| 1 | ACS Applied Electronic Materials | Page 24 of 52 |
| electric field is then ramped back to smaller applied field strengths, the depolarization field exceeds |
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| the opposite coercive field causing back-switching. The field in the (anti)ferroelectric during the |
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| 8 | hysteresis measurement is illustrated in Figure 7, where the coercive field is exceeded in every |
| 9 | quadrant – resulting in polarization switching and subsequent back-switching. Hence, a field- |
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| 11 |
| induced first-order phase transition can be driven by depolarization fields in ferroelectric hafnium |
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| 13 |
| and zirconium oxide thin films. The electric field in Figure 7 is a macroscopic parameter |
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| 16 | representing the electric field over the entire ferroelectric crystal and can be interpreted as the |
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| averaged, collective response of all actively switching ferroelectric domains. Local electric fields |
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| of individual ferroelectric domains and grains would require extending the calculations down to |
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| 24 | the microscopic level and would be complementary to the methods proposed here. |
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| 48 | **Figure 7.** The electric field in the (anti)ferroelectric vs. the applied electric field during dynamic |
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| hysteresis switching. The field in the (anti)ferroelectric in quadrant IV exceeds the negative |
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| Page 25 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54  55  56  57  58  59  60 | ACS Applied Electronic Materials  coercive field, while in quadrant II the field exceeds the positive coercive field – thus back-switching occurs during hysteresis as a consequence.  **4.2 Wake-up and Depolarization**   To thoroughly evaluate the wake-up process through depolarization phenomena, it is constructive incorporate processes in the model which have been postulated to cause wake-up. Pinned domains have traditionally been associated with both wake-up and imprint in perovskite ferroelectrics. Pinned domains do not switch due to charged defects, an in-plane polarization orientation, and/or an unfavourable local electric field.4,23,29 Since pinned domains do not switch but still contribute to the overall dielectric displacement current, we can incorporate the influence of pinning by modifying Eq. (1) to   𝑃 = 𝑃𝑑 + (1 ― 𝛽)𝑃𝐹𝐸 = 𝜀0𝜀𝐹𝐸𝐸𝑎𝑝𝑝 + (1 ― 𝛽)𝑃𝐹𝐸, (22)  where *β* is the fraction of pinned ferroelectric domains. Thus, the increase in polarization with electric field cycling can be quantified by domain depinning. A conventional ferroelectric domain depinning process is shown in Figure 8.    **Figure 8**. A depiction of domain depinning through charged defect redistribution in a ferroelectric.  When modelling ferroelectric hysteresis curves with depolarization fields which can exceed the coercive field, adjusting the switchable polarization magnitude results in a significant change in the coercive field because of depolarization induced nucleation inhibition (see section 2.3.3). The observed coercive fields thus become dependent on both the phase mixture, interfacial dead layer,  ACS Paragon Plus Environment |

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| and the magnitude of the switched polarization. Once the coercive fields and the polarization | | | | | | | |
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| switching currents are fitted accurately to the experimental data from the dynamic hysteresis | | | | | | | |
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| 8 | measurements, it may occur that the back-switching fields appear later than predicted by the | | | | | | | |
| 9 | depolarization models developed thus far. | | | | | | | |
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| The offset in the back-switching fields can be explained by charge injection and trapping of | | | | | | | |
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| charge carriers at the ferroelectric/dielectric layer interfaces which screen the switched | | | | | | | |
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| 16 | polarization. The injected charge can be quantified by calculating the amount of screening charge | | | | | | | |
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| needed to shift the observed back-switching field away from the predicted depolarization back- | | | | | | | |
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| switching field (i.e. when |*EBS*|=-|*Ec*|), | | | | | | | |
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| 23 | 𝜀0(𝐸𝐵𝑆(*d\*FE + dint εint+ dP,* ⊥  *εFE* | | | | | | *εP,* ⊥) ― 𝑉𝑎𝑝𝑝) | |
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| 𝜎 = ―𝑃 ― | 𝑑𝑖𝑛𝑡  𝜀𝑖𝑛𝑡+ | | 𝑑𝑃, ⊥ | | , (23) | | |
| 27 |
| 28 |
|  | 𝜀𝑃, ⊥ | |  |
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| 30 | where *σ* is the injected screening charge. Figure 9 illustrates how the injected screening charge can | | | | | | | |
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| offset the back-switching fields. | | | | | | | |
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| 36 | Since the amount of screening charge has been determined by the shift in the back-switching | | | | | | | |
| 37 | field, an additional charge injection current should be introduced to account for the trapping and/or | | | | | | | |
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| 39 |
| detrapping current during hysteresis. The form of the charge injection current is somewhat | | | | | | | |
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| arbitrary for the hysteresis simulations because it is known in advance the quantity of injected | | | | | | | |
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| 43 |
| 44 | charge needed to satisfy the back-switching field. Nonetheless, we follow the example set by | | | | | | | |
| 45 |
| 46 | Tagantsev and use a Poole-Frenkel/thermionic conduction model of the form40 | | | | | | | |
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| 48 |
| 𝐽𝐶𝐼(𝐸𝑖𝑛𝑡) = 𝐴( | | 𝐸𝑡ℎ) 𝑒(  𝛼 | | 𝛽 𝐸𝑡ℎ) | | | (24) |
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| Page 27 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54  55  56  57  58  59  60 | ACS Applied Electronic Materials  where *Eth* is the thermionic or threshold activation field and *α*, *β*, and *A* are parameters that depend on the conduction mechanism and electric field interval.  Wake-up cycling in ferroelectric HfO2-based thin films has also been postulated to be either produced from domain de-pinning or a phase transition with some indirect supporting experimental evidence.37 If a paraelectric to ferroelectric phase transition occurs with electric field cycling, this can be incorporated into the model by adjusting the fraction of paraelectric phase and non-switching paraelectric regions in Eq. (5) – (6). Conjectured wake-up related phenomena of pinning/depinning, charge-injection, interface trapped charge, and phase transitions in hafnium oxide ferroelectrics can be tested and quantified directly from ferroelectric hysteresis using the depolarization models described in this work as we will now show.    ACS Paragon Plus Environment |

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| **Figure 9.** (a) Current density vs. applied electric field showing how charge injection and |
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| subsequent screening can shift the back-switching field. (b) Charge injection and interface |
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| 8 | screening charge during hysteresis. |
| 9 | 5.4 nm thick films Si-doped HfO2 films were cycled until breakdown which occurred after 104 |
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| 12 |
| cycles with 3.5V (6.5 MV/cm). GIXRD was used to estimate the film phase composition which |
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| yielded 27 % tetragonal, 37 % monoclinic, and 36 % polar orthorhombic (see supplementary). A |
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| 18 | thin dead layer with a low permittivity was introduced to account for finite screening and/or the |
| 19 | formation of a TiOxN1-x interface.6,20,58 The dead layer and mixed phase depolarization model is |
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| 21 |
| again used to compute the hysteresis loop. We assumed that all of the monoclinic phase existed as |
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| parallel paraelectric regions in the film and were not in series with the ferroelectric layer since |
| 24 |
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| 26 | increases in the tetragonal phase are associated with progressive pinching leading to |
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| antiferroelectric characteristics.21 The tetragonal phase was considered to coexist both in series |
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| with the polar orthorhombic phase and as separate paraelectric regions in parallel with the |
| 31 |
| 32 |
| 33 |
| 34 | switching regions. |
| 35 |
| Given the suppressed and asymmetric polarization switching in the 5.4 nm thick Si-doped HfO2 |
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| thin films (Figure 10), up to 75 % of the negative switching domains and 49 % of positive |
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| 41 | switching domains were pinned (non-switchable) initially. The asymmetry of the loop was |
| 42 | produced by an internal bias field of 0.7 MV/cm. There are several notable features in the |
| 43 |
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| hysteresis which change with wake-up cycling. |
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| Firstly, the positive (peak I) and negative (peak III) coercive field shift to lower electric field |
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| 49 | values with cycling. The reduction in the observed coercive field can be described by the decrease |
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| in the depolarization field via depolarization-induced nucleation inhibition. |
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| Page 29 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54  55  56  57  58  59  60 | ACS Applied Electronic Materials    **Figure 10.** Calculated and measured (a) polarization vs. applied electric field and (b) current density vs. applied electric field for 5.4 nm thick Si-doped HfO2 with wake-up cycling up to 104 cycles. Polarization switching peaks are labelled I and III, whereas back-switching peaks are labelled II and IV in (b).  Several possibilities can be put forth to explain the reduction in the depolarization:  ACS Paragon Plus Environment |

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| 1 | ACS Applied Electronic Materials | Page 30 of 52 |
| (1) An increase in the interface screening trapped charge density with cycling reduces the |
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| effective thickness of the interfacial dead layer. |
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| 8 | (2) The series tetragonal phase is transforming into the ferroelectric orthorhombic phase with |
| 9 | cycling. |
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| (3) Charge injection leads to charge trapping and screening at the t-phase/o-phase interfaces. |
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| (4) The magnitude of the switched polarization is decreasing with cycling. |
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| 16 | (5) Ferroelastic domain wall motion aligns the polar axis of ferroelectric dipoles toward the |
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| out-of-plane direction. |
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| It is clear that the magnitude of the switching polarization is not decreasing with wake-up |
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| 24 | cycling, so case (4) can be ruled out. In case (2), the transformation of the in-series paraelectric |
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| tetragonal phase to the orthorhombic phase can lower the depolarization field. Nonetheless, the |
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| magnitude of the field across the paraelectric t-phase could also facilitate injected charges to be |
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| 31 | carried to the ferroelectric/paraelectric interfaces which would mean that case (2) and (3) could |
| 32 | look very similarly since screening is improved in both scenarios. Ferroelastic domain wall motion |
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| (5) is another possibility,4,59,60 but requires further clarification from atomic scale imaging to model |
| 35 |
| 36 |
| since it is unknown to what extent charged domain walls and/or local polarization vector disorder61 |
| 37 |
| 38 |
| 39 | is present in (anti)ferroelectric HfO2 and ZrO2 thin films. Due to the fact that the interfacial dead |
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| 41 |
| layer is exposed to the highest fields in the device stack (> 10 MV/cm), and because charge |
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| injection is necessary to account for the shift in back-switching fields, it was reasonable to adopt |
| 44 |
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| 47 | case (1) to model the reduction in the depolarization field. |
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| The second significant change with wake-up cycling which can be seen prominently is the |
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| 50 |
| migration of the back-switching peaks (II & IV) toward the coercive fields. This shift is primarily |
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| 54 | attributed to the enhancement of injected screening charge at the ferroelectric/dead layer interface |
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| Page 31 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54  55  56  57  58  59  60 | ACS Applied Electronic Materials  as shown in Figure 11(a). The interface trap density is much larger at one electrode/ferroelectric interface than the other and is in good agreement with trap densities calculated from leakage currents on ferroelectric Hf0.5Zr0.5O2.62 Asymmetry in the ferroelectric/metal electrode interfaces has been observed in previous reports on wake-up cycling.20 If one assumes electron injection, then the top electrode interface must have a significantly higher density of electron traps than the bottom electrode interface. This could be due to the creation of oxygen vacancies and/or defect states at the top ferroelectric interface during sputtering or via oxygen scavenging from the top TiN electrode during the crystallization anneal. Since the bottom electrode is oxidized during the deposition of the hafnia ferroelectric film, the oxygen vacancy density could be significantly smaller than at the top interface.6,20    **Figure 11.** (a) Interface trap density with electric field cycles. A much larger trap concentration results when a negative bias is applied to the top electrode. (b) Switchable ferroelectric area with electric field cycles. The extent of depinning for negative and positive switching domains can be seen. All values have been extracted from the calculated hysteresis models.  The last significant change which can be clearly observed is that the magnitude of the switched polarization is increasing with electric field cycling. Depinning of ferroelectric domains accounts  ACS Paragon Plus Environment |

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| 1 | ACS Applied Electronic Materials | Page 32 of 52 |
| for the change in the switched polarization magnitude and does not lead to changes in the |
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| depolarization field. The depolarization field is unchanged since the model we employed assumed |
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| 8 | pinned areas were non-switching parallel regions that did not increase the out-of-plane |
| 9 | spontaneous polarization of switchable domains once depinned. Depinning of negative and |
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| positive switching domains as a function of electric field cycles as evaluated from the calculated |
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| model is shown in Figure 11(b). |
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| 15 |
| 16 | The microscopic nature of the depinning process is not yet fully understood, but there are several |
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| reasonable candidates. First, the overall reduction in the depolarization field with charge screening |
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| enhancement is a good candidate. Reductions in the depolarization field through a to phase |
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| 24 | transition or effective interface thickness reduction (due to enhanced occupation of screening |
| 25 |
| charges) are other possible candidates for depinning.In addition, electric field driven drift of |
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| oxygen vacancies represents another possibility, whereby ferroelectric domains are locally |
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| 31 | depinned as the vacancies become redistributed throughout the film with cycling. Since the |
| 32 | hysteresis simulations can quantify the depinning process, we predict it can serve as an excellent |
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| framework toward understanding the microscopic nature of the depinning phenomena. The |
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| discussed impact of depolarization fields on the polarization hysteresis during wake-up cycling is |
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| 39 | in good correlation to former discussions on the internal bias field as extracted by FORC |
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| 41 |
| measurements.19 |
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| **5 Conclusion** |
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| 47 | Ferroelectric hysteresis has been re-examined and reformulated to account for the depolarization |
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| fields produced in ferroelectric materials with first-order and second-order phase transitions. The |
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| depolarization effects produced from finite screening length, interfacial dead layer, and mixed |
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| 54 | ferroelectric/paraelectric film composition models were described in detail. Through the analysis |
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| Page 33 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54  55  56  57  58  59  60 | ACS Applied Electronic Materials  of square-shaped, idealized hysteresis loops with HfO2-based ferroelectric film properties, the depolarization models caused a clear evolution in the hysteresis of ferroelectrics with a first-order phase transition from a pinched to antiferroelectric shape as the depolarization field increased. Thus, the coexistence of a large enough proportion of the paraelectric tetragonal phase with the polar orthorhombic phase was demonstrated to be able to generate antiferroelectric behavior in HfO2 and ZrO2 based thin films based upon the assumption that both materials obey a first-order phase transition.  Depolarization induced nucleation inhibition was postulated to account for the delayed initiation of polarization switching when the depolarization field exceeds the coercive field of the first-order ferroelectric. Ferroelectric domains are thus unable to nucleate until the total field in the ferroelectric is able to overcome the back-switching field. Experimental hysteresis measurements were accurately described by the depolarization models in 5 nm and 10 nm thick Si-doped HfO2 films which exhibited ferroelectric wake-up and antiferroelectricity respectively. The simplicity and modest number of parameters of the depolarization model which can reproduce antiferroelectric hysteresis characteristics provides a quantitative and phenomenologically grounded theory which can be tested against experiments. The macroscopic model proposed here is compatible to the field-driven first-order phase transition theory of antiferroelectricity and could support various hypotheses on the microscopic nature of antiferroelectricity.  Incorporating wake-up processes such as charge injection, depinning, field-independent and cycling induced phase transitions, and interface traps in the calculation of the hysteresis loop made it possible to recreate wake-up cycling behaviour. Charge injection and subsequent screening was shown to be able to lower the depolarization field after polarization switching, thereby delaying the onset of back-switching. With the increase of charge injection with cycle number, the back-  ACS Paragon Plus Environment |

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| 1 | ACS Applied Electronic Materials | Page 34 of 52 |
| switching fields migrated toward the coercive fields. The interface trap density was calculated |
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| based upon the screening charge needed to shift the back-switching field to the experimental |
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| 8 | observation, and it was found that there was a much higher concentration of traps at one |
| 9 | electrode/ferroelectric interface than the other. |
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| 11 |
| Meanwhile, during wake-up cycling the coercive fields migrated to lower applied fields because |
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| of a reduction in the depolarization field through additional mechanisms. This depolarization field |
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| 16 | can be related to the internal bias fields extracted from FORC measurements. The reduction in |
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| depolarization was modelled as an effective thickness reduction of the interfacial dead layer due |
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| to an increase in the interfacial trap density with cumulative voltage stressing, though other |
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| 24 | microscopic mechanisms such as a phase transition brought about by defect redistribution and/or |
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| charge accumulation between polar and nonpolar interfaces remain as testable hypotheses for the |
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| depolarization models presented in this work. Domain depinning was shown to increase the |
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| 31 | switching polarization as the ferroelectric film underwent electric field cycling and could be |
| 32 | attributed to the overall reduction in depolarization. |
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| The striking similarities of pre-cycled ferroelectric HfO2 and ZrO2 based capacitors which show |
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| strong wake-up effects and their antiferroelectric counterparts are no coincidence, both effects can |
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| 39 | be driven by a single phenomenon – depolarization. Modelling the internal electric fields across |
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| the layers in the device stack can be used to better understand and control both the stability and |
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| field-cycling induced changes associated with antiferroelectricity and wake-up. Since |
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| 47 | antiferroelectricity and wake-up can be well-described by depolarization fields in ferroelectric |
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| HfO2, the methods introduced here can be extended to other first-order ferroelectric and |
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| antiferroelectric material systems. This new perspective on antiferroelectric behaviour can thus |
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| 54 | open up a paradigm shift in the design of a variety of ferroelectric and antiferroelectric devices. |
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| (1) | Sawyer, C. B.; Tower, C. H. Rochelle Salt as a Dielectric. *Physical Review***1930**, *35* (3), |
| 269–273. https://doi.org/10.1103/PhysRev.35.269. | |
| (2) | Schenk, T.; Yurchuk, E.; Mueller, S.; Schroeder, U.; Starschich, S.; Böttger, U.; Mikolajick, |
| T. About the Deformation of Ferroelectric Hystereses. *Applied Physics Reviews***2014**, *1* (4), 041103. https://doi.org/10.1063/1.4902396.  ACS Paragon Plus Environment | |

35

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| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 1 | ACS Applied Electronic Materials | | | | | | | | | | | | | Page 36 of 52 |
| (3) | Carl, K.; Hardtl, K. H. Electrical After-Effects in Pb(Ti,Zr)O3 Ceramics. *Ferroelectrics* | | | | | | | | | | | |
| 2 |
| 3 |
| 4 |
| **1977**, *17* (1), 473–486. https://doi.org/10.1080/00150197808236770. | | | | | | | | | | | | |
| 5 |
| (4) | Kohli, M.; Muralt, P.; Setter, N. Removal of 90° Domain Pinning in (100) | | | | | | | | | | | |
| 6 |
| Pb(Zr0.15Ti0.85)O3 Thin Films by Pulsed Operation. *Appl. Phys. Lett.***1998**, *72* (24), | | | | | | | | | | | | |
| 7 |
| 8 | 3217–3219. https://doi.org/10.1063/1.121554. | | | | | | | | | | | | |
| 9 | (5) | Yuan, G. L.; Yang, Y.; Or, S. W. Aging-Induced Double Ferroelectric Hysteresis Loops in | | | | | | | | | | | |
| 10 | BiFeO3 Multiferroic Ceramic. *Applied Physics Letters***2007**, *91* (12), 122907. | | | | | | | | | | | | |
| 11 |
| https://doi.org/10.1063/1.2786013. | | | | | | | | | | | | |
| 12 |
| (6) | Lomenzo, P. D.; Takmeel, Q.; Zhou, C.; Fancher, C. M.; Lambers, E.; Rudawski, N. G.; | | | | | | | | | | | |
| 13 |
| Jones, J. L.; Moghaddam, S.; Nishida, T. TaN Interface Properties and Electric Field | | | | | | | | | | | | |
| 14 |
| Cycling Effects on Ferroelectric Si-Doped HfO 2 Thin Films. *Journal of Applied Physics* | | | | | | | | | | | | |
| 15 |
| 16 | **2015**, *117* (13), 134105. https://doi.org/10.1063/1.4916715. | | | | | | | | | | | | |
| 17 | (7) | Walters, G.; Chojecki, P.; Garraud, A.; Nishida, T.; Summerfelt, S.; Rodriguez, J. A.; | | | | | | | | | | | |
| 18 | Acosta, A. G. High-Temperature and High-Field Cycling Reliability of PZT Films | | | | | | | | | | | | |
| 19 |
| Embedded within 130 Nm CMOS. In *2018 IEEE International Reliability Physics* | | | | | | | | | | | | |
| 20 |
| *Symposium* | | *(IRPS)*; | | IEEE: | Burlingame, | | CA, | 2018; | p | P-MY.3-1-P-MY.3-6. | | |
| 21 |
| https://doi.org/10.1109/IRPS.2018.8353676. | | | | | | | | | | | | |
| 22 |
| (8) | Park, M. H.; Hwang, C. S. Fluorite-Structure Antiferroelectrics. *Rep. Prog. Phys.***2019**, *82* | | | | | | | | | | | |
| 23 |
| 24 | (12), 124502. https://doi.org/10.1088/1361-6633/ab49d6. | | | | | | | | | | | | |
| 25 | (9) | Starschich, S.; Schenk, T.; Schroeder, U.; Boettger, U. Ferroelectric and Piezoelectric | | | | | | | | | | | |
| 26 |
| Properties of Hf1-xZrxO2 and Pure ZrO2 Films. *Appl. Phys. Lett.***2017**, *110* (18), 182905. | | | | | | | | | | | | |
| 27 |
| https://doi.org/10.1063/1.4983031. | | | | | | | | | | | | |
| 28 |
| (10) Kirbach, S.; Kuhnel, K.; Weinreich, W. Piezoelectric Hafnium Oxide Thin Films for | | | | | | | | | | | | |
| 29 |
| Energy-Harvesting Applications. In *2018 IEEE 18th International Conference on* | | | | | | | | | | | | |
| 30 |
| 31 | *Nanotechnology* | | | *(IEEE-NANO)*; | | | IEEE: | Cork, | Ireland, | | 2018; | pp | 1–4. |
| 32 | https://doi.org/10.1109/NANO.2018.8626275. | | | | | | | | | | | | |
| 33 | (11) Ghatge, M.; Walters, G.; Nishida, T.; Tabrizian, R. An Ultrathin Integrated | | | | | | | | | | | | |
| 34 |
| Nanoelectromechanical Transducer Based on Hafnium Zirconium Oxide. *Nat Electron* | | | | | | | | | | | | |
| 35 |
| **2019**, *2* (11), 506–512. https://doi.org/10.1038/s41928-019-0305-3. | | | | | | | | | | | | |
| 36 |
| (12) Park, M. H.; Kim, H. J.; Kim, Y. J.; Moon, T.; Kim, K. D.; Hwang, C. S. Toward a | | | | | | | | | | | | |
| 37 |
| Multifunctional Monolithic Device Based on Pyroelectricity and the Electrocaloric Effect | | | | | | | | | | | | |
| 38 |
| 39 | of Thin Antiferroelectric HfxZr1−xO2 Films. *Nano Energy***2015**, *12*, 131–140. | | | | | | | | | | | | |
| 40 | https://doi.org/10.1016/j.nanoen.2014.09.025. | | | | | | | | | | | | |
| 41 | (13) Jachalke, S.; Schenk, T.; Park, M. H.; Schroeder, U.; Mikolajick, T.; Stöcker, H.; Mehner, | | | | | | | | | | | | |
| 42 |
| E.; Meyer, D. C. Pyroelectricity of Silicon-Doped Hafnium Oxide Thin Films. *Applied* | | | | | | | | | | | | |
| 43 |
| *Physics Letters***2018**, *112* (14), 142901. https://doi.org/10.1063/1.5023390. | | | | | | | | | | | | |
| 44 |
| (14) Mart, C.; Kämpfe, T.; Zybell, S.; Weinreich, W. Layer Thickness Scaling and Wake-up | | | | | | | | | | | | |
| 45 |
| Effect of Pyroelectric Response in Si-Doped HfO2. *Applied Physics Letters***2018**, *112* (5), | | | | | | | | | | | | |
| 46 |
| 47 | 052905. https://doi.org/10.1063/1.5019308. | | | | | | | | | | | | |
| 48 | (15) Mueller, S.; Müller, J.; Hoffmann, R.; Yurchuk, E.; Schlösser, T.; Boschke, R.; Paul, J.; | | | | | | | | | | | | |
| 49 |
| Goldbach, M.; Herrmann, T.; Zaka, A.; Schröder, U.; Mikolajick, T. From MFM Capacitors | | | | | | | | | | | | |
| 50 |
| Toward Ferroelectric Transistors: Endurance and Disturb Characteristics of HfO2-Based | | | | | | | | | | | | |
| 51 |
| FeFET Devices. *IEEE Transactions on Electron Devices***2013**, *60* (12), 4199–4205. | | | | | | | | | | | | |
| 52 |
| https://doi.org/10.1109/TED.2013.2283465. | | | | | | | | | | | | |
| 53 |
| 54 | (16) Pesic, M.; Knebel, S.; Hoffmann, M.; Richter, C.; Mikolajick, T.; Schroeder, U. How to | | | | | | | | | | | | |
| 55 | Make DRAM Non-Volatile? Anti-Ferroelectrics: A New Paradigm for Universal Memories. | | | | | | | | | | | | |
| 56 | ACS Paragon Plus Environment | | | | | | | | | | | | |
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| Page 37 of 52  1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54  55  56  57  58  59  60 | ACS Applied Electronic Materials  In *2016 IEEE International Electron Devices Meeting (IEDM)*; 2016; pp 11.6.1-11.6.4. https://doi.org/10.1109/IEDM.2016.7838398.  (17) Mulaosmanovic, H.; Breyer, E. T.; Mikolajick, T.; Slesazeck, S. Ferroelectric FETs With 20-Nm-Thick HfO2 Layer for Large Memory Window and High Performance. *IEEE* | | | | | | | | | | | | | | | |
| *Transactions* | | *on* | | *Electron* | | *Devices* | | | **2019**, | *66* | | (9), | | 3828–3833. | |
| https://doi.org/10.1109/TED.2019.2930749.  (18) Tian, X.; Shibayama, S.; Nishimura, T.; Yajima, T.; Migita, S.; Toriumi, A. Evolution of Ferroelectric HfO2 in Ultrathin Region down to 3 nm. *Appl. Phys. Lett.***2018**, *112* (10), 102902. https://doi.org/10.1063/1.5017094.  (19) Schenk, T.; Hoffmann, M.; Ocker, J.; Pešić, M.; Mikolajick, T.; Schroeder, U. Complex Internal Bias Fields in Ferroelectric Hafnium Oxide. *ACS Appl. Mater. Interfaces***2015**, *7* (36), 20224–20233. https://doi.org/10.1021/acsami.5b05773.  (20) Zhou, D.; Xu, J.; Li, Q.; Guan, Y.; Cao, F.; Dong, X.; Müller, J.; Schenk, T.; Schröder, U.  Wake-up Effects in Si-Doped Hafnium Oxide Ferroelectric Thin Films. *Applied Physics Letters***2013**, *103* (19), 192904. https://doi.org/10.1063/1.4829064.  (21) Müller, J.; Böscke, T. S.; Schröder, U.; Mueller, S.; Bräuhaus, D.; Böttger, U.; Frey, L.; Mikolajick, T. Ferroelectricity in Simple Binary ZrO2 and HfO2. *Nano Letters***2012**, *12* (8), 4318–4323. https://doi.org/10.1021/nl302049k.  (22) Schenk, T.; Schroeder, U.; Pešić, M.; Popovici, M.; Pershin, Y. V.; Mikolajick, T. Electric Field Cycling Behavior of Ferroelectric Hafnium Oxide. *ACS Applied Materials & Interfaces***2014**, *6* (22), 19744–19751. https://doi.org/10.1021/am504837r.  (23) Scott, J. F.; Dawber, M. Oxygen-Vacancy Ordering as a Fatigue Mechanism in Perovskite | | | | | | | | | | | | | | | |
| Ferroelectrics. | | | *Appl.* | *Phys.* | | | *Lett.* | **2000**, | | *76* | | (25), | | 3801–3803. | |
| https://doi.org/10.1063/1.126786.  (24) Tagantsev, A. K.; Stolichnov, I.; Colla, E. L.; Setter, N. Polarization Fatigue in Ferroelectric Films: Basic Experimental Findings, Phenomenological Scenarios, and Microscopic | | | | | | | | | | | | | | | |
| Features. | *Journal* | | | *of* | *Applied* | | *Physics* | | **2001**, | *90* | | (3), | | 1387–1402. | |
| https://doi.org/10.1063/1.1381542.  (25) Duiker, H. M.; Beale, P. D.; Scott, J. F.; Paz de Araujo, C. A.; Melnick, B. M.; Cuchiaro, J.  D.; McMillan, L. D. Fatigue and Switching in Ferroelectric Memories: Theory and | | | | | | | | | | | | | | | |
| Experiment. | | *Journal* | | *of* | *Applied* | | *Physics* | | **1990**, | | *68* | (11), | | | 5783–5791. |
| https://doi.org/10.1063/1.346948.  (26) Foster, C. M.; Bai, G.-R.; Csencsits, R.; Vetrone, J.; Jammy, R.; Wills, L. A.; Carr, E.; Amano, J. Single-Crystal Pb(ZrxTi1−x)O3 Thin Films Prepared by Metal-Organic Chemical Vapor Deposition: Systematic Compositional Variation of Electronic and Optical | | | | | | | | | | | | | | | |
| Properties. | | *Journal* | | *of* | *Applied* | | *Physics* | | **1997**, | | *81* | | (5), | 2349–2357. | |
| https://doi.org/10.1063/1.364239.  (27) Yu, Z.; Guo, R.; Bhalla, A. S. Orientation Dependence of the Ferroelectric and Piezoelectric Behavior of BaTi1-xZrxO3 Single Crystals. *Applied Physics Letters* **2000**, *77* (10), 1535-1537 (28) Lambeck, P. V.; Jonker, G. H. The Nature of Domain Stabilization in Ferroelectric Perovskites. *Journal of Physics and Chemistry of Solids***1986**, *47* (5), 453–461. https://doi.org/10.1016/0022-3697(86)90042-9.  (29) Rojac, T.; Kosec, M.; Budic, B.; Setter, N.; Damjanovic, D. Strong Ferroelectric Domain-Wall Pinning in BiFeO3 Ceramics. *Journal of Applied Physics***2010**, *108* (7), 074107. https://doi.org/10.1063/1.3490249.  ACS Paragon Plus Environment | | | | | | | | | | | | | | | |

37

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 1 | ACS Applied Electronic Materials | | | | | | | | | | | | | | | | | Page 38 of 52 |
| (30) Pike, G. E.; Warren, W. L.; Dimos, D.; Tuttle, B. A.; Ramesh, R.; Lee, J.; Keramidas, V. | | | | | | | | | | | | | | | | |
| 2 |
| 3 |
| 4 |
| G.; Evans, J. T. Voltage Offsets in (Pb,La)(Zr,Ti)O3 Thin Films. *Applied Physics Letters* | | | | | | | | | | | | | | | | |
| 5 |
| **1995**, *66* (4), 484–486. https://doi.org/10.1063/1.114064. | | | | | | | | | | | | | | | | |
| 6 |
| (31) Warren, W. L.; Dimos, D.; Pike, G. E.; Tuttle, B. A.; Raymond, M. V.; Ramesh, R.; Evans, | | | | | | | | | | | | | | | | |
| 7 |
| 8 | J. T. Voltage Shifts and Imprint in Ferroelectric Capacitors. *Applied Physics Letters***1995**, | | | | | | | | | | | | | | | | |
| 9 | *67* (6), 866–868. https://doi.org/10.1063/1.115531. | | | | | | | | | | | | | | | | |
| 10 | (32) Dawber, M.; Rabe, K. M.; Scott, J. F. Physics of Thin-Film Ferroelectric Oxides. *Rev. Mod.* | | | | | | | | | | | | | | | | |
| 11 |
| *Phys.***2005**, *77* (4), 1083–1130. https://doi.org/10.1103/RevModPhys.77.1083. | | | | | | | | | | | | | | | | |
| 12 |
| (33) Merz, W. J. Double Hysteresis Loop of BaTiO3 at the Curie Point. *Phys. Rev.***1953**, *91* (3), | | | | | | | | | | | | | | | | |
| 13 |
| 513–517. https://doi.org/10.1103/PhysRev.91.513. | | | | | | | | | | | | | | | | |
| 14 |
| (34) Black, C. T.; Farrell, C.; Licata, T. J. Suppression of Ferroelectric Polarization by an | | | | | | | | | | | | | | | | |
| 15 |
| 16 | Adjustable Depolarization Field. *Appl. Phys. Lett.***1997**, *71* (14), 2041–2043. | | | | | | | | | | | | | | | | |
| 17 | https://doi.org/10.1063/1.119781. | | | | | | | | | | | | | | | | |
| 18 | (35) Chang, L.-W.; Alexe, M.; Scott, J. F.; Gregg, J. M. Settling the “Dead Layer” Debate in | | | | | | | | | | | | | | | | |
| 19 |
| Nanoscale | | Capacitors. | | | *Advanced* | | | | *Materials* | | | **2009**, | *21* | | (48), | 4911–4914. |
| 20 |
| https://doi.org/10.1002/adma.200901756. | | | | | | | | | | | | | | | | |
| 21 |
| (36) Stengel, M.; Spaldin, N. A. Origin of the Dielectric Dead Layer in Nanoscale Capacitors. | | | | | | | | | | | | | | | | |
| 22 |
| *Nature***2006**, *443* (7112), 679–682. https://doi.org/10.1038/nature05148. | | | | | | | | | | | | | | | | |
| 23 |
| 24 | (37) Grimley, E. D.; Schenk, T.; Sang, X.; Pešić, M.; Schroeder, U.; Mikolajick, T.; LeBeau, J. | | | | | | | | | | | | | | | | |
| 25 | M. Structural Changes Underlying Field-Cycling Phenomena in Ferroelectric HfO2 Thin | | | | | | | | | | | | | | | | |
| 26 |
| Films. | *Advanced* | | | | *Electronic* | | | | *Materials* | | | **2016**, | | *2* | (9), | 1600173. |
| 27 |
| https://doi.org/10.1002/aelm.201600173. | | | | | | | | | | | | | | | | |
| 28 |
| (38) Mehta, R. R.; Silverman, B. D.; Jacobs, J. T. Depolarization Fields in Thin Ferroelectric | | | | | | | | | | | | | | | | |
| 29 |
| Films. | *Journal* | | *of* | | *Applied* | | | | *Physics* | | | **1973**, | *44* | | (8), | 3379–3385. |
| 30 |
| 31 | https://doi.org/10.1063/1.1662770. | | | | | | | | | | | | | | | | |
| 32 | (39) Batra, I. P.; Silverman, B. D. Thermodynamic Stability of Thin Ferroelectric Films. *Solid* | | | | | | | | | | | | | | | | |
| 33 | *State* | *Communications* | | | | **1972**, | | | *11* | (1), | | 291–294. | | https://doi.org/10.1016/0038- | | | |
| 34 |
| 1098(72)91180-5. | | | | | | | | | | | | | | | | |
| 35 |
| (40) Tagantsev, A. K.; Stolichnov, I.; Setter, N.; Cross, J. S. Nature of Nonlinear Imprint in | | | | | | | | | | | | | | | | |
| 36 |
| Ferroelectric Films and Long-Term Prediction of Polarization Loss in Ferroelectric | | | | | | | | | | | | | | | | |
| 37 |
| Memories. | | *Journal* | | | *of* | *Applied* | | | *Physics* | | | **2004**, | *96* | | (11), | 6616–6623. |
| 38 |
| 39 | https://doi.org/10.1063/1.1805190. | | | | | | | | | | | | | | | | |
| 40 | (41) Buragohain, P.; Erickson, A.; Kariuki, P.; Mittmann, T.; Richter, C.; Lomenzo, P. D.; Lu, | | | | | | | | | | | | | | | | |
| 41 | H.; Schenk, T.; Mikolajick, T.; Schroeder, U.; Gruverman, A. Fluid Imprint and Inertial | | | | | | | | | | | | | | | | |
| 42 |
| Switching in Ferroelectric La:HfO 2 Capacitors. *ACS Appl. Mater. Interfaces***2019**, *11* (38), | | | | | | | | | | | | | | | | |
| 43 |
| 35115–35121. https://doi.org/10.1021/acsami.9b11146. | | | | | | | | | | | | | | | | |
| 44 |
| (42) Huang, F.; Chen, X.; Liang, X.; Qin, J.; Zhang, Y.; Huang, T.; Wang, Z.; Peng, B.; Zhou, | | | | | | | | | | | | | | | | |
| 45 |
| P.; Lu, H.; Zhang, L.; Deng, L.; Liu, M.; Liu, Q.; Tian, H.; Bi, L. Fatigue Mechanism of | | | | | | | | | | | | | | | | |
| 46 |
| 47 | Yttrium-Doped Hafnium Oxide Ferroelectric Thin Films Fabricated by Pulsed Laser | | | | | | | | | | | | | | | | |
| 48 | Deposition. | | *Phys.* | | *Chem.* | | | *Chem.* | | | *Phys.* | | **2017**, | *19* | | (5), | 3486–3497. |
| 49 |
| https://doi.org/10.1039/C6CP07501K. | | | | | | | | | | | | | | | | |
| 50 |
| (43) Sawaguchi, E.; Maniwa, H.; Hoshino, S. Antiferroelectric Structure of Lead Zirconate. | | | | | | | | | | | | | | | | |
| 51 |
| *Phys. Rev.***1951**, *83* (5), 1078–1078. https://doi.org/10.1103/PhysRev.83.1078. | | | | | | | | | | | | | | | | |
| 52 |
| (44) Hao, X.; Zhai, J.; Kong, L. B.; Xu, Z. A Comprehensive Review on the Progress of Lead | | | | | | | | | | | | | | | | |
| 53 |
| 54 | Zirconate-Based Antiferroelectric Materials. *Progress in Materials Science***2014**, *63*, 1–57. | | | | | | | | | | | | | | | | |
| 55 | https://doi.org/10.1016/j.pmatsci.2014.01.002. | | | | | | | | | | | | | | | | |
| 56 | ACS Paragon Plus Environment | | | | | | | | | | | | | | | | |
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| KGaA: | Weinheim, | | Germany, | | 2013; | pp | | 221–244. | |
| https://doi.org/10.1002/9783527654864.ch7.  (46) Hyuk Park, M.; Joon Kim, H.; Jin Kim, Y.; Lee, W.; Moon, T.; Seong Hwang, C. Evolution of Phases and Ferroelectric Properties of Thin Hf0.5Zr0.5O2 Films According to the Thickness and Annealing Temperature. *Appl. Phys. Lett.***2013**, *102* (24), 242905. https://doi.org/10.1063/1.4811483.  (47) Grimley, E. D.; Schenk, T.; Mikolajick, T.; Schroeder, U.; LeBeau, J. M. Atomic Structure of Domain and Interphase Boundaries in Ferroelectric HfO 2. *Adv. Mater. Interfaces***2018**, *5* (5), 1701258. https://doi.org/10.1002/admi.201701258.  (48) Zhao, D.; Lenz, T.; Gelinck, G. H.; Groen, P.; Damjanovic, D.; de Leeuw, D. M.; Katsouras, I. Depolarization of Multidomain Ferroelectric Materials. *Nat Commun***2019**, *10* (1), 2547. https://doi.org/10.1038/s41467-019-10530-4.  (49) Zhukov, S.; Genenko, Y. A.; Hirsch, O.; Glaum, J.; Granzow, T.; von Seggern, H. Dynamics of Polarization Reversal in Virgin and Fatigued Ferroelectric Ceramics by Inhomogeneous | | | | | | | | | |
| Field | Mechanism. | *Physical* | | *Review* | *B* | **2010**, | | *82* | (1). |
| https://doi.org/10.1103/PhysRevB.82.014109.  (50) Hyun, S. D.; Park, H. W.; Kim, Y. J.; Park, M. H.; Lee, Y. H.; Kim, H. J.; Kwon, Y. J.; Moon, T.; Kim, K. D.; Lee, Y. B.; Kim, B. S.; Hwang, C. S. Dispersion in Ferroelectric Switching Performance of Polycrystalline Hf0.5Zr0.5O2 Thin Films. *ACS Appl. Mater. Interfaces***2018**, *10* (41), 35374–35384. https://doi.org/10.1021/acsami.8b13173.  (51) Wang, Z.; Gaskell, A. A.; Dopita, M.; Kriegner, D.; Tasneem, N.; Mack, J.; Mukherjee, N.; Karim, Z.; Khan, A. I. Antiferroelectricity in Lanthanum Doped Zirconia without Metallic Capping Layers and Post-Deposition/-Metallization Anneals. *Appl. Phys. Lett.***2018**, *112* (22), 222902. https://doi.org/10.1063/1.5037185.  (52) Lomenzo, P. D.; Slesazeck, S.; Hoffmann, M.; Mikolajick, T.; Max, B.; Thomas Mikolajick.  Ferroelectric Hf1-XZrxO2 Memories: Device Reliability and Depolarization Fields. In *2019 Non-Volatile Memory Technology Symposium (NVMTS)*; IEEE: Durham, North Carolina, USA, 2019; pp 1–8.  (53) Huan, T. D.; Sharma, V.; Rossetti, G. A.; Ramprasad, R. Pathways towards Ferroelectricity in Hafnia. *Phys. Rev. B***2014**, *90* (6), 064111. https://doi.org/10.1103/PhysRevB.90.064111. (54) Reyes-Lillo, S. E.; Garrity, K. F.; Rabe, K. M. Antiferroelectricity in Thin-Film ZrO2 from | | | | | | | | | |
| First | Principles. | *Phys.* | *Rev.* | *B* | **2014**, | *90* | (14), | 140103. | |
| https://doi.org/10.1103/PhysRevB.90.140103.  (55) Lomenzo, P. D.; Chung, C.-C.; Zhou, C.; Jones, J. L.; Nishida, T. Doped Hf0.5Zr0.5O2 for High Efficiency Integrated Supercapacitors. *Appl. Phys. Lett.***2017**, *110* (23), 232904. https://doi.org/10.1063/1.4985297.  (56) Richter, C.; Schenk, T.; Park, M. H.; Tscharntke, F. A.; Grimley, E. D.; LeBeau, J. M.; Zhou, C.; Fancher, C. M.; Jones, J. L.; Mikolajick, T.; Schroeder, U. Si Doped Hafnium Oxide-A “Fragile” Ferroelectric System. *Advanced Electronic Materials***2017**, *3* (10), 1700131. https://doi.org/10.1002/aelm.201700131.  (57) Lomenzo, P. D.; Takmeel, Q.; Moghaddam, S.; Nishida, T. Annealing Behavior of Ferroelectric Si-Doped HfO2 Thin Films. *Thin Solid Films***2016**, *615*, 139–144. https://doi.org/10.1016/j.tsf.2016.07.009.  ACS Paragon Plus Environment | | | | | | | | | |

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| 1 | ACS Applied Electronic Materials | | | | | | | | | | Page 40 of 52 |
| (58) Hamouda, W.; Pancotti, A.; Lubin, C.; Tortech, L.; Richter, C.; Mikolajick, T.; Schroeder, | | | | | | | | | |
| 2 |
| 3 |
| 4 |
| U.; Barrett, N. Physical Chemistry of the TiN/Hf0.5Zr0.5O2 Interface. *Journal of Applied* | | | | | | | | | |
| 5 |
| *Physics***2020**, *127* (6), 064105. https://doi.org/10.1063/1.5128502. | | | | | | | | | |
| 6 |
| (59) Shimizu, T.; Mimura, T.; Kiguchi, T.; Shiraishi, T.; Konno, T.; Katsuya, Y.; Sakata, O.; | | | | | | | | | |
| 7 |
| 8 | Funakubo, H. Ferroelectricity Mediated by Ferroelastic Domain Switching in HfO 2 -Based | | | | | | | | | |
| 9 | Epitaxial | Thin | Films. | *Appl.* | *Phys.* | *Lett.* | **2018**, | *113* | (21), | 212901. |
| 10 | https://doi.org/10.1063/1.5055258. | | | | | | | | | |
| 11 |
| (60) Lederer, M.; Kämpfe, T.; Olivo, R.; Lehninger, D.; Mart, C.; Kirbach, S.; Ali, T.; | | | | | | | | | |
| 12 |
| Polakowski, P.; Roy, L.; Seidel, K. Local Crystallographic Phase Detection and Texture | | | | | | | | | |
| 13 |
| Mapping in Ferroelectric Zr Doped HfO2 Films by Transmission-EBSD. *Appl. Phys. Lett.* | | | | | | | | | |
| 14 |
| **2019**, *115* (22), 222902. https://doi.org/10.1063/1.5129318. | | | | | | | | | |
| 15 |
| 16 | (61) Tang, Y. L.; Zhu, Y. L.; Wang, Y. J.; Wang, W. Y.; Xu, Y. B.; Ren, W. J.; Zhang, Z. D.; | | | | | | | | | |
| 17 | Ma, X. L. Atomic-Scale Mapping of Dipole Frustration at 90° Charged Domain Walls in | | | | | | | | | |
| 18 | Ferroelectric PbTiO3 Films. *Sci Rep***2015**, *4* (1), 4115. https://doi.org/10.1038/srep04115. | | | | | | | | | |
| 19 |
| (62) Islamov, D. R.; Gritsenko, V. A.; Perevalov, T. V.; Pustovarov, V. A.; Orlov, O. M.; | | | | | | | | | |
| 20 |
| Chernikova, A. G.; Markeev, A. M.; Slesazeck, S.; Schroeder, U.; Mikolajick, T.; | | | | | | | | | |
| 21 |
| Krasnikov, G. Y. Identification of the Nature of Traps Involved in the Field Cycling of | | | | | | | | | |
| 22 |
| Hf0.5Zr0.5O2-Based Ferroelectric Thin Films. *Acta Materialia***2019**, *166*, 47–55. | | | | | | | | | |
| 23 |
| 24 | https://doi.org/10.1016/j.actamat.2018.12.008. | | | | | | | | | |
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