Stable Subloop Behavior in Ferroelectric Si-Doped HfO₂

Kyounjun Lee,†,V Hyun-Jae Lee,§,V Tae Yoon Lee,† Hong Heon Lim,‡ Myeong Seop Song,† Hyang Keun Yoo,‖ Dong Ik Suh,‖ Jae Gil Lee,‖ Zhongwei Zhu,‡ Alexander Yoon,‡ Matthew R. MacDonald,‖ Xinjian Lei,‡ Kunwoo Park,‖ Jungwon Park,‡ Jun Hee Lee,*,§‡ and Seung Chul Chae*,†

†Department of Physics Education and ‡School of Chemical and Biological Engineering, Institute of Chemical Process, Seoul National University, Seoul 08826, Korea
§School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Korea
‖SK Hynix Incorporation, Icheon-si, Gyeonggi-do 17336, Korea
Versum Materials Incorporation, Fremont, California 94538, United States
#Versum Materials Incorporation, Carlsbad, California 92011, United States
¶Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul 08826, Korea

Supporting Information

ABSTRACT: The recent demand for analogue devices for neuromorphic applications requires modulation of multiple nonvolatile states. Ferroelectricity with multiple polarization states enables neuromorphic applications with various architectures. However, determinisitic control of ferroelectric polarization states with conventional ferroelectric materials has been met with accessibility issues. Here, we report unprecedented stable accessibility with robust stability of multiple polarization states in ferroelectric HfO₂. Through the combination of conventional voltage measurements, hysteresis temperature dependence analysis, piezoelectric force microscopy, first-principles calculations, and Monte Carlo simulations, we suggest that the unprecedented stability of intermediate states in ferroelectric HfO₂ is due to the small critical volume size for nucleation and the large activation energy for ferroelectric dipole flipping. This work demonstrates the potential of ferroelectric HfO₂ for analogue device applications enabling neuromorphic computing.

KEYWORDS: FeRAM, ferroelectric, multilevel, analogue device, HfO₂

INTRODUCTION

The massive demand for versatile analogue devices in neuromorphic computing is a major issue for artificial intelligence applications. Machine learning and deep learning, based on both discriminative and generative models, require a neural network that includes memory, a memory-read/write head, state register, and memory write rules with analogue weight and bias parameters. From an analogue perspective, conceptual devices with multiple nonvolatile states for multiply-accumulate operations have been proposed through hardware implementation that replaces the data transfer of weight and bias values with a bus between the physical memory and processor. To this end, various architectures can be constructed based on a ferroelectric framework, in which partial polarization switching is possible. For example, variable ferroelectric polarization in conventional devices involving stacked ultrathin films can be used for tunneling junctions with multiple resistance states. In addition, modulation of the physical properties of matter by the ferroelectric field effect with analogue polarization values has been proposed for single-transistor architectures in nonvolatile memory. Irrespective of the mechanisms used for data storage modulation, explicit control of ferroelectric polarization switching, especially unsaturated ferroelectric polarization hysteresis subloops, is a key factor in achieving the desired properties in these analogue devices.

Recently, diverse approaches to achieve stable subloop polarization states have been demonstrated through the external circuit element and material’s internal or external factors. The external circuit elements such as transistors which limit undergoing current control the portion of the ferroelectric domain flipping via restraint of the ferroelectric domain wall motion and/or nucleation processes. However, the compliance level of transistors is beyond the contemporary
specification of memory device applications, in which scaling problems and additional resistive–capacitance delay (e.g., in memory cell transistors) present complications with respect to achieving optimal device performance. On the other hand, although the mediation of the material’s external factors such as interfacial layer or defect dipoles enabled the multilevel polarization states, the artifacts raised the fatigue and imprint problems. The control of the material’s internal structural variants through multilayer heterostructure, structural instability or ferroelastic twin domains achieved multilevel polarization states. However, these approaches are constrained by the limited number of switching states or uncontrollable twin domains due to the predefined electrostatic energies.

Considering the broken inversion symmetry of ionic configurations, an external electric field is a direct external stimulus for macroscopic ferroelectric switching. With respect to the magnitude of the external electric bias, systematic variation of the ferroelectric polarization can be achieved, leaving behind many or continuous intermediate polarization states. To control the polarization precisely, active modulation of the amplitude, duration, and/or repetition of an external stimulus has been considered. However, because of the complicated switching mechanism of ferroelectrics and/or defect-induced uncertainties, multiple attempts using the aforementioned stimuli have yet to reach finite analogue states with the desired accuracy without the cost of delayed switching, fatigue, or imprint problem. In addition, this instability of multilevel polarization states is worsened in small material volumes, inhibiting practical downscaled device application. Recently, hafnium (Hf)-based ferroelectrics have attracted much attention, due not only to their compatibility with current complementary metal–oxide–semiconductor (CMOS) technology but also their use as an alternative to perovskite ferroelectrics. Despite having a large spontaneous polarization, perovskite materials have struggled with poor compatibility with CMOS technology and switching limitations of hydrogen's small band gap and oxygen instability. However, since the discovery of ferroelectricity in HfO₂, subsequent investigations have revealed the robust switching behavior of this material. In tunneling junction devices and ferroelectric field-effect transistors, polarization switching stability has been investigated extensively, with regard to the structural integrity of the material and its switching mechanism. Prior results have shown a large polarization in HfO₂, comparable to those of Pb(ZrₓTi₁₋ₓ)O₃ (PZT) and BaTiO₃; additionally, HfO₂ has shown the ability to maintain polarization under retention and fatigue testing. In addition, the subloop polarization in ferroelectric HfO₂-based memory architectures demonstrated empirical deterministic control of memory states with advantages for neuromorphic applications such as low-power consumption. Considering thin-film thickness (~10 nm) and polycrystalline structure-induced defects of ferroelectric HfO₂, deterministic control of multilevel polarization states is remarkable. However, the direct study of stability in multilevel polarization states in ferroelectric HfO₂ capacitors and the origin of deterministic control is insufficient (i.e., reproducibility and retention of multilevel polarization states). Prior to analogue device application, direct investigation of the subloop behavior in ferroelectric HfO₂ is urgently required.

In this study, we report unprecedented stability in the subloop switching behavior and accessibility to intermediate polarization states in ferroelectric Si-doped HfO₂. We suggest that the enhanced stability of the intermediate states is due to the small critical volume for ferroelectric nucleation in HfO₂ and the large activation energy for flipping the polarization dipole. Conventional voltage pulse measurements, an analysis of the temperature dependence of hysteresis, and piezoresponsiveness were conducted to confirm the small volume for ferroelectric nucleation with large activation energy per unit volume. Theoretical calculations were used to investigate the switching energy landscape of ferroelectric HfO₂. Monte Carlo simulation results confirmed the existence of stable multilevel states, with accessibility facilitated by the small nucleation volume.

**EXPERIMENTAL SECTION**

Sample Fabrication. The 4.2 mol% Si-doped HfO₂ films (thickness: 8 nm) were stacked on the TiN bottom electrode, using the atomic layer deposition process based on tetraethyl(dimethylamido)hafnium (TDMAH), tetraethyl(dimethylamido)silane (4MAM), and ozone. For the electrical measurements, the Pt/TiN top electrode was patterned with a circular shape radius of 100 μm. To crystallize the Si-doped HfO₂, post annealing was conducted at 600 °C for 20 s in N₂ ambient conditions after the deposition of the top electrode known as the post metallization annealing.

Electric Measurement. Polarization–voltage (P–V) curves and time-dependent dynamic polarization switching P(t) were assessed using a ferroelectric tester (TF Analyzer 3000, aixACCT Systems GmbH, Aachen, Germany) and a rapid data acquisition system (4200-SCS; Keithley Instruments, Cleveland, OH, USA). All electric measurements were performed after the wake-up process, by inducing 10 000 voltage pulse cycles of 3 V at a frequency of 10 kHz.

Ferroelectric Domain Imaging. Local polarization switching was measured via PFM (Cypher; Asylum Research, Santa Barbara, CA, USA) with a conventional platinum/iridium-coated tip (PPP-EFM; NANOSENSORS, Neuchatel, Switzerland).

**RESULTS AND DISCUSSION**

Ferroelectric HfO₂ exhibits manifold polarization states, applicable for use in analogue devices. Figure 1a shows the multilevel polarization states through the positive region of the polarization–voltage (P–V) hysteresis loops. These intermediate states can be manipulated by simply varying the amplitude of the external bias. We controlled the multilevel polarization states of our HfO₂ sample by applying voltage pulses of different magnitudes over the range of 0.9–3 V, within a fixed window of 2 μs. The voltage pulses were applied initially to a negatively polarized sample, in which the intermediate polarization states were measured with a triangular pulse of 3 V and a frequency of 2 kHz. The term ΔP in Figure 1a refers to the difference between the remnant polarization value of intermediate states and the fully negatively polarized state. ΔP increased systematically with the voltage. These results suggest that voltage variation can be used to control the intermediate states of ferroelectric HfO₂, in which the analogue behavior of ΔP can be used as a synaptic weight in neuromorphic computing (Supporting Information, Section S3).

The inherent multiplicity of HfO₂ ferroelectric polarization states was maintained with discernible accuracy with repeated application of external voltage pulses. The reliability of an intermediate polarization state was determined by its reproducibility and retention properties. To confirm reproduci...
intermediate polarization states in terms of Weibull exponent value and the standard deviation to mean ratio orange-shaded 95% confidence interval.

Figure 1. Multilevel states and reliability of Si-doped HfO₂ thin films. (a) Intermediate polarization states of ferroelectric HfO₂ using 2 μs voltage pulses. (b) Histogram of each intermediate polarization state repeated 100 times. (c) Weibull statistic fitting reliability results of the intermediate polarization states using 2.1 V, 2 μs voltage pulses with orange-shaded 95% confidence interval. (d) Statistic results of each intermediate polarization states in terms or Weibull exponent value k and the standard deviation to mean ratio Δ/μ.

For the detailed analysis of the reproducibility of each intermediate states, we analyzed the statistics in terms of the Weibull distribution as shown in Figure 1c by the following equation

\[ F(x) = 1 - \exp[-(x/x_0)^k] \]  \hspace{1cm} (1)

where \( F(x) \) is the cumulative probability of randomly distributed variable (\( \Delta P/2P_s \) value in this work), x is the random variable, \( x_0 \) is the scale parameter, and k is the Weibull exponent. The Weibull exponent value k is correlated with the standard deviation to mean ratio \( \Delta/\mu \) as follows

\[ \Delta/\mu = \frac{\Gamma(1 + 2/k) - \Gamma^2(1 + 1/k)^{1/2}}{\Gamma(1 + 1/k)} \]  \hspace{1cm} (2)

where \( \Gamma \) is the Gamma function. Each intermediate polarization states exhibited a large k value ranging from 37.1 to 338 as shown in Figure 1d. Note that our results exhibited a large k value with small \( \Delta/\mu \) compared to the reported ferroelectric tunnel junction devices \(^{39}\) and even comparable with the contemporary other mersister devices \(^{40}\) indicating superior reproducibility.

The robust stability of each manifold state of ferroelectric HfO₂ was observed under high-temperature and is considered as the device operation environment. To confirm the retention properties of the material, we examined the time evolution of \( \Delta P/2P_s \). Figure 2a shows the retention of intermediate polarization states at room temperature; the polarization was sustained, with only a slight loss after 1000 s. Figure 2b shows the intermediate state retention with 2.4 V, 2 μs pulses at room temperature, 50, and 85 °C. The polarization loss observed at 50 and 85 °C showed only a slight difference with respect to the pristine state after 1000 s, as shown in Figure 2b. The time evolution of intermediate polarization under voltage pulse application exhibited long-term stability, a requirement for practical applications.

The unprecedented stability of the polarization states in HfO₂ can be understood in terms of ferroelectric switching dynamics and the underlying mechanism responsible for deterministic control of the polarization via a large coercive field. Figure 3a shows the time and voltage dependences of ferroelectric polarization in the Si:HfO₂ thin film; the solid dots represent the experimental polarization switching with different applied voltages ranging from 0.9 to 3.0 V. To estimate the time evolution of polarization switching, the portion of switched polarization was measured after applying a positive pulse to the top electrode, with a subsequent increase in the pulse width and height. Before inducing a positive pulse, a negative pulse was introduced with a height and width of ~3 V and 125 μs, respectively, at the top electrode for full saturation (Supporting Information, Section S5). The solid lines in Figure 3a represent the fitting results obtained using a nucleation-limited switching (NLS) model, with a Lorentzian distribution for the characteristic switching time as below

\[ \frac{\Delta P(t)}{2P_s} = \int_{-\infty}^{\infty} \left[ 1 - \exp\left(-\left(\frac{t}{t_0}\right)^2\right)\right] F(\log t_0) d(\log t_0) \]  \hspace{1cm} (3)

where

\[ F(\log t_0) = \frac{A}{\bar{\sigma}} \left(\frac{\bar{\omega}}{(\log t_0 - \log t_1)^2 + \bar{\omega}^2}\right) \]  \hspace{1cm} (4)

\( A, \bar{\omega}, \) and \( \log t_1 \) indicate a normalization constant, the half width at half-maximum of the distribution, and the mean value of the distribution, respectively.
Figure 3. Ferroelectric switching dynamics and temperature dependence of ferroelectric hysteresis. (a) Time and voltage dependence of the switched polarization $\Delta P(t)$ measured at room temperature. The solid lines represent the fitting results using the NLS model, considering the Lorentzian distribution of the characteristic switching time for ferroelectric nucleation. (b) External voltage dependence of the characteristic switching time. (c) Temperature dependence of ferroelectric hysteresis. (d) Temperature dependence of the coercive field.

Figure 3b shows the characteristic switching time estimated from the position of the Lorentzian peak. The linear dependence in Figure 3b reveals the ferroelectric properties associated with nucleation and domain wall propagation. The activation field was estimated to be 1.9 MV/cm, which is similar to a recently reported value in a Zr-doped ferroelectric HfO$_2$ film. It is worth noting that the activation field for ferroelectric switching in HfO$_2$ is larger than that for other perovskite ferroelectrics, enabling long-term stability of intermediate states due to the high coercive field.

To understand the large activation field associated with the nucleation energy per unit volume and the critical volume size of nucleation, we examined the temperature dependence of the coercive field, with a focus on the barrier height for ferroelectric switching in HfO$_2$ films. Figure 3c shows the temperature dependence of the ferroelectric hysteresis from 300 to 480 K, with the application of 3 V pulses at a frequency of 2 kHz. Because of the different concentrations of trap sites and/or oxygen vacancies at the bottom and top electrode ferroelectric interfaces, the imprint effects were enhanced as the temperature increased. Also, as the measurement temperature increased, the remnant polarization and coercive field decreased. In the classical Landau–Devonshire free-energy model, the variation of the coercive field under varying temperature can be associated with the critical volume and activation energy. The free-energy model can be used to derive the coercive field, barrier height, and critical nucleation volume, as given below:

$$E_c = \frac{W_B}{P_s} - \frac{k_B T}{V^* P_s} \ln \left( \frac{\nu_0}{\nu_f} \right) \left( \ln(2) \right)$$

where $W_B$, $P_s$, $k_B$, $T$, $V^*$, $\nu_0$, and $\nu_f$ are the energy barrier per unit volume, spontaneous polarization, Boltzmann’s constant, temperature, critical volume for nucleation, phonon frequency, and measurement time, respectively. We used the soft-mode phonon frequency and the spontaneous polarization value of $1.16 \times 10^{13}$ Hz and 41 $\mu$C/cm$^2$, respectively. Figure 3d shows the experimental temperature dependence of the coercive field and the fitting results obtained with eq 1. For the ferroelectric HfO$_2$ film, we obtained $4.1 \times 10^{26}$ eV/m$^2$ for the energy barrier per unit volume ($W_B$) and $4.0 \times 10^{-27}$ m$^3$ for the critical volume for nucleation ($V^*$); both are similar to the values obtained in a previous study of Si-doped HfO$_2$. Note that $W_B$ is larger than that for PZT ($W_B = 0.38 \times 10^{26}$ eV/m$^3$, $V^* = 2.5 \times 10^{-27}$ m$^3$), which can be attributed to the large coercive field of HfO$_2$: $V^*$ was much smaller than that for PZT. However, although $V^*$ is small, the energy barrier per critical volume for nucleation ($W_B \times V^*$) of HfO$_2$ is still larger than that of PZT.

Scanning probe microscopy demonstrated the influence of critical volume size on ferroelectric switching, in terms of the domain wall speed and size. The stable and small critical volume for ferroelectric nucleation is due to the weak interaction between ferroelectric dipoles. There should be little movement of the domain wall with weak interaction and a high activation barrier. To confirm the domain wall motion of ferroelectric HfO$_2$, we used PFM to estimate the domain wall velocity and its activation field. Figure 4a shows piezoresponse spectroscopy results observed in the HfO$_2$ thin film; the results showed a clear hysteresis in amplitude and phase, with a local coercivity of $\sim$3 V and phase responses that corresponded to upward/downward polarization, as indicated by the blue circles. Figure 3b–e show out-of-plane directional phase images along the external bias, at different temperatures.

Figure 4. Piezoresponse properties and the speed of ferroelectric domain wall propagation in a Si-HfO$_2$ thin film using local PFM. (a) Amplitude (empty red square) and phase (empty blue circle) hysteresis of local PFM. (b–e) PFM phase images after positive poling with a pulse height of 6 V and widths of 100 ms, 20 ms, 100 ms, and 1 s, respectively. Before the measurement, the sample was poled with a negative bias of −6 V. (f) Voltage pulse width dependence of the equivalent domain radius for the switched region. The dashed gray line represents the minimum domain size resolution (~20 nm). (g) Electric field dependence of the domain wall velocity.
polarization state was investigated in terms of the critical unit size and the derivation of subloop polarization by Monte Carlo simulations. To elucidate the small domain size effect on multilevel switching, we conducted Monte Carlo simulations of long-range dipole–dipole interactions with a random magnitude of dipole–defect interactions, considering polycrystalline ferroelectric HfO$_2$.$^{38,61–63}$ Figure 6a shows a schematic diagram of the simulation lattice, in which the total length $L$ was fixed and each unit length $L/N$ was varied by the number of mesh grids $N$. As the number of mesh grids increased, the

![Figure 6](https://example.com/figure6.png)

**Figure 6.** Monte Carlo simulation results with different critical volumes for ferroelectric nucleation. (a) Schematic diagram of the ferroelectric nucleation size at a fixed length divided into a given mesh grid size. (b) Fitted distribution profiles of an intermediate polarization state repeated 100 times for different mesh grid sizes.

The causality between the small critical volume for ferroelectric nucleation and the discernible accuracy of the pulse widths and with a fixed voltage of 6 V on the negatively pre-poled area. Without any thermally nucleated domains in the scan area, clear domain growth was observed, with dominant domain wall motion, at $\sim$20 nm resolution.

The domain wall velocity and activation energy for the propagation of the domain wall can be estimated using the external pulse width. Figure 4f shows the domain radius as a function of the external pulse width; the domain size was seemingly unchanged along with the external bias, with a width of less than 10 ms. The domain radius increased with the domain wall motion as the bias exceeded 10 ms. This may be due to the minimum size of the domain radius of $\sim$20 nm for the resolution limit. During the estimation of the effective velocity of domain wall propagation, the effective electric field under the tip was calculated from a first-order approximation,$^{56,57}$ $E = V a/r d$ where $V$, $a$, $r$, and $d$ represent the voltage, tip radius, domain radius, and film thickness, respectively.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** First-principles calculations of a single ferroelectric dipole flip. Schematic diagram of ferroelectric HfO$_2$ with (a) all upward dipoles and (b) one opposite dipole. (c) Energy landscapes of HfO$_2$ and PbTiO$_3$ for a single dipole flip.

Note that the domain wall velocity of other perovskite and poly thin film ferroelectrics such as poly(vinylidene fluoride-co-trifluoroethylene) thin films is approximately 4 orders of magnitude faster than that required for switching activation ($\sim$1.9 MV/cm). Note that the domain wall velocity of other perovskite and poly thin film ferroelectrics such as poly(vinylidene fluoride-co-trifluoroethylene) thin films is approximately 4 orders of magnitude faster than that required for switching activation ($\sim$1.9 MV/cm).
**CONCLUSIONS**

Considering the complicated switching mechanism and defect-mediated uncertainty, the stable subloop behavior of ferroelectric HfO2 with conventional voltage pulses was remarkable. The switching dynamics indicated a large activation field for ferroelectric switching. This large activation field provides robust stability, even at high temperatures, as shown in Figure 2a,b. The temperature dependence of hysteresis and PFM measurements are good indicators of the small size of ferroelectric domains and high activation energy. Theoretical calculations confirmed the large activation energy for a single dipole flip. The stabilization of small-size ferroelectric domain was attributed to the intrinsic stability of a single opposite ferroelectric dipole. Based on the extraordinary stability of small nucleation, the macroscopic discernible accuracy of partial switching of ferroelectricity can be achieved in HfO2, as shown in Monte Carlo simulation results. Even considering contemporary scaled down device (i.e., 7 nm technology), the small critical volume for nucleation in ferroelectric Si-doped HfO2 enables diverse multilevel polarization states (more than 32) can be achieved.

In summary, we demonstrated the unprecedented stability of multilevel switching properties in ferroelectric HfO2. The ferroelectric switching dynamics and temperature dependence of hysteresis elucidate the small activation energy for switching due to the stable and small nucleation size. The associated slow domain wall motion because stable small-sized domains was confirmed by PFM measurements. Monte Carlo simulations demonstrated that the small nucleation size induces stable intermediate polarization states.

**ASSOCIATED CONTENT**

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b12878.

Effects of Si-doping concentration, grain size estimation, synaptic behavior of polarization, details of the experimental method for time-dependent switched polarization, the fitting for polarization switching dynamics, details of theoretical calculation, details of Monte Carlo simulation, supporting results, and figures (PDF)

**AUTHOR INFORMATION**

Corresponding Authors
*E-mail: junhees@unist.ac.kr (J.H.L.).
*E-mail: scchae@snu.ac.kr (S.C.C.).

**ORCID**

Kyoungjin Lee: 0000-0003-0472-3583
Tae Yoon Lee: 0000-0003-1754-8657
Jungwon Park: 0000-0003-2927-4331

**Author Contributions**

K.L. and H.-J.L contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

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