Ferroelectric Polarization-Switching Dynamics and Wake-Up Effect in Si-Doped HfO₂

Tae Yoon Lee,‡ Kyoungjun Lee,† Hong Heon Lim,‡ Myeong Seop Song,† Sang Mo Yang,§ Hyang Keun Yoo,† Dong Ik Suh,∥ Zhongwei Zhu,† Alexander Yoon,⊥ Matthew R. MacDonald,# Xinjian Lei,# Hu Young Jeong,† Donghoon Lee,‡ O Kunwoo Park,‡ O Jungwon Park,‡,† and Seung Chul Chae‡,*

‡Department of Physics Education and †School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University, Seoul 08826, Korea
§Department of Physics, SooMyung Women’s University, Seoul 04310, Korea
∥SK Hynix Inc., Icheon-si, Gyeonggi-do 17336, Korea
#Lam Research Corp., Fremont, California 94538, United States
#Versum Materials, Inc., Carlsbad, California 92011, United States
⊥UNIST Central Research Facilities (UCRF), Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Korea
‡Center for Nanoparticle Research, Institute for Basic Science (IBS), Seoul 08826, Korea

Supporting Information

ABSTRACT: The ferroelectricity in ultrathin HfO₂ offers a viable alternative to ferroelectric memory. A reliable switching behavior is required for commercial applications; however, many intriguing features of this material have not been resolved. Herein, we report an increase in the remnant polarization after electric field cycling, known as the “wake-up” effect, in terms of the change in the polarization-switching dynamics of a Si-doped HfO₂ thin film. Compared with a pristine specimen, the Si-doped HfO₂ thin film exhibited a partial increase in polarization after a finite number of ferroelectric switching behaviors. The polarization-switching behavior was analyzed using the nucleation-limited switching model characterized by a Lorentzian distribution of logarithmic domain-switching times. The polarization switching was simulated using the Monte Carlo method with respect to the effect of defects. Comparing the experimental results with the simulations revealed that the wake-up effect in the HfO₂ thin film is accompanied by the suppression of disorder.

KEYWORDS: ferroelectricity, HfO₂, FeRAM, defects, thin films, domain switching

INTRODUCTION

Extensive research has been conducted on the binary oxide HfO₂ and its ferroelectric behavior. 1,2 The unprecedented feasibility of ferroelectric memory using HfO₂ is due to its simple structure and compatibility with current complementary metal oxide semiconductor technologies. 3 The orthorhombic HfO₂ structure can be formed into nanometer-thick films that can accommodate nonvolatile switchable spontaneous polarization. 4 Many studies have reported robust ferroelectricity with a remnant polarization of 10–40 μC/cm² and a form factor appropriate for high-density memory. 5,6,23 Newly discovered ferroelectricity in HfO₂ is of particular interest for applications such as ferroelectric memory and field-effect transistors with negative capacitance. 7,8

Elucidation of the underlying mechanism governing the overall ferroelectric behavior of HfO₂ thin films is crucial for memory applications. The ferroelectric behavior of ultrathin HfO₂ films (less than 10 nm thick) is attributed to a structural distortion that enables the non-centrosymmetric Pca2₁ structural phase. 9,10 Oxygen ion movements are believed to be the origin of ferroelectricity in orthorhombic HfO₂ films (Figure 1a). Ferroelectric HfO₂ exhibits increased remnant polarization against external field cycling, known as the “wake-up” effect. Its origin has been investigated by various methods including simple current–voltage (I–V) curves, first-principles calculations, transmission electron microscopy (TEM), and phenomenological free-energy modeling for first-order phase transitions. 11–13 With regard to the origin of the wake-up
The focus has been on structural transitions in terms of ferroelectric phase according to domain switching during the wake-up process of the Si-doped HfO₂ thin films. Counterintuitively, the disorders seem to decrease during the wake-up process of the Si-doped HfO₂ thin films, whereas the disorders are commonly believed to increase during ferroelectric switching, that is, with fatigue behavior. We investigated the ferroelectric polarization-switching kinetics to gain insight into the correlation between the disorder and the wake-up effect. Ferroelectric switching dynamics, in terms of both ferroelectric domain-wall motion and nucleation, should be considered when studying the role of defects in the switching dynamics of HfO₂ films. Experimental ferroelectric polarization switching of polycrystalline Si-doped HfO₂ films revealed that NLS with the Lorentzian distribution of the logarithmic characteristic switching time governs domain switching during the first two decades of ferroelectric switching. During this period, the wake-up effect induced by external bias cycling resulted in a retardation of the characteristic switching time distribution. Monte Carlo simulations, including interactions between ferroelectric dipoles and nonswitchable randomly oriented dipole defects, indicated that retardation of the characteristic switching time is associated with a reduction in the disorder.

### EXPERIMENTAL PROCEDURES

All measurements were conducted using metal–ferroelectric–metal (MFM) planar capacitors with a radius of 50 μm grown on silicon substrates. The TiN/Si/HfO₂/TiN capacitors were deposited on a Si(001) substrate. Si-doped HfO₂ was fabricated using an atomic layer deposition process based on tetrakis(dimethylamido)hafnium (TDMAH), tetrakis(dimethylamino)silane (4DMS), and ozone.
The TiN top and bottom electrodes were deposited by a chemical vapor deposition process. Specimens were postannealed at 600 °C for 20 s in ambient N₂ to crystallize the Si:HfO₂ film. The cation composition and crystallographic phases of the films were examined using X-ray photoemission spectroscopy, grazing-incidence X-ray diffraction (GIXRD; PANalytical X-pert Pro), and TEM. For electrical characterization, polarization–voltage hysteresis and time-dependent dynamic polarization switching ΔP(t) were measured at room temperature using a ferroelectric tester with an accuracy of 1% (TF Analyzer 3000; aixACCT Systems).

**RESULTS AND DISCUSSION**

The coexistence of monoclinic and ferroelectric orthorhombic phases was observed in the Si-doped HfO₂ thin film. Figure 1b shows the GIXRD spectra of a 4.2% Si-doped HfO₂ thin film, which is a pristine state. This XRD pattern is consistent with mixed monoclinic and orthorhombic phases. The peaks at \( \sim 28.4 \) and \( \sim 30.6° \) are assigned to the monoclinic (111) and orthorhombic (111) phases, respectively. Decomposition of the phases was conducted by refining the diffraction pattern using Gaussian peak shapes for each structural phase. The green and red peaks in the inset of Figure 1b correspond to monoclinic (111) and orthorhombic (111) phases, respectively. However, because the orthorhombic and tetragonal phases are nearly indistinguishable by XRD analysis, the tetragonal phase may be present in the films.

TEM imaging with domain structure analysis also indicated that both orthorhombic and monoclinic phases were present in the pristine cell of the 4.2% Si-doped HfO₂ film. TEM cross-sectional images of the film capped with TiN electrodes are presented in Figure 1c. Domains were defined by geometrical phase analysis (GPA). The details of this technique are provided in Section 1 of the Supporting Information. An average domain size of a few nanometers was observed. Phase analysis was conducted using interplanar spacings and angles obtained for different lattice vectors in the reciprocal space. Domains with orthorhombic and monoclinic phases occupied 71.6 and 15.2%, respectively, of the Si:HfO₂ layer in the TEM image. Some domains showed both the orthorhombic and monoclinic phases simultaneously, presumably due to the coexistence of multiple domains in the TEM specimen in the out-of-plane direction. However, TEM analysis showed only a small area with the tetragonal phase in the 4.2% Si:HfO₂ layer. It seems that the tetragonal-phase fraction can be quite low for Si:HfO₂ thin films fabricated under specific conditions. A few domains had insufficient crystallographic information to identify the phase; these are indicated without color. Although the tetragonal phase was not clearly visible in our TEM image, the tetragonal phase and its phase transition contribute partly to the enhancement of remnant polarization. The ferroelectricity of HfO₂ is due to an intermediate orthorhombic structure having broken the inversion symmetry, other structural phases and their variations should be evaluated with respect to their effect on the ferroelectric property of HfO₂ films.

Repeatead polarization switching of the Si-doped HfO₂ thin film resulted in the wake-up effect. We prepared pristine, preset, and woken-up cells to investigate the effect of repeated electrical stimulation on ferroelectric switching. The pristine cell showed a wake-up behavior that was too rapid for measuring stable ferroelectric switching dynamics. It has been reported that most of the phase transformation occurs during the initial voltage pulse. Therefore, the preset cell and woken-up cell were prepared by applying 10 and 10,000 cycles of pulses, respectively, to the pristine specimen, with a frequency and voltage of 10 kHz and ±3 V, respectively. Figure 2a shows the ferroelectric polarization hysteresis loops of the pristine, preset, and woken-up cells as indicated by gray dashed, orange solid, and blue solid lines, respectively. For the preset case, peaks near 0.84 and 1.46 V are colored green and orange, respectively. For the woken-up cell, the green peak position remained at 0.84 V, whereas the orange peak shifted to the lower value of 1.24 V. The intensities of the two peaks increased after the wake-up process. Notably, the

Figure 2. (a) Polarization–voltage measurements performed on pristine, preset, and woken-up cells having a Pt/TiN/Si:HfO₂/TiN capacitor structure. The switching current was measured during the polarization-switching process from downward to upward domains, and the current data were fitted by the sum (red solid line) of two Lorentzian distributions (orange and green regions) for (b) preset and (c) woken-up cells.
intensity of the green peak increased by about 10%. The presence of double switching and its disappearance in oxide thin films have been explained by nonuniform dipole defects and domain pinning. The dipole defects or pinning sites caused by oxygen vacancies and trapped charges can exist in ferroelectric doped HfO₂ thin films deposited on a TiN electrode. Their nonlinear contribution to the I–V characteristics can result in additional hysteresis in P–E measurements, that is, switching-current peak splitting. Also, we confirmed that the ferroelectric switching behavior of Si:HfO₂ thin films exhibits NLS due to the polycrystallinity of specimens. Figure 3a,b show the ΔP(t)/2Pₒ values of the preset and woken-up specimens, respectively, as a function of Vext at room temperature. Details of the experimental method are provided in Supporting Information, Section 2. Also, we confirmed that the unintentional migration of traps in the thin film and the current due to charge trapping and detrapping at the trap sites have less of an effect on the switching dynamics (Supporting Information, Section 3). The ΔP(t)/2Pₒ curves under a high external bias ranging from 2.0 to 3.0 V (much larger than the coercive field) saturated at about 1.0. On the other hand, the ΔP(t)/2Pₒ curves at a low external bias, ranging from 1.0 to 1.6 V, did not saturate at the maximum value of 1.0 within the experimental limits. Although the applied external bias from 1.0 to 1.6 V is comparable to the coercive field observed in Figure 2a, the voltage width/frequency can modulate the coercive field in the polarization–voltage hysteresis loop and result in different saturation behaviors between the slow voltage sweep and fast voltage pulse with high frequency. ΔP(t)/2Pₒ values are fitted using the NLS model with a Lorentzian distribution of the characteristic switching time according to eqs 1 and 2.

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

where

\[
F(\log t_0) = \frac{A}{\pi} \frac{w}{(\log t_0 - \log t_0^{\circ})^2 + w^2}
\]

The wake-up effect of the Si-doped HfO₂ film was accompanied by a sharpening of the defect density distribution and a delay in the ferroelectric characteristic switching time. Figure 4 shows the Lorentzian distribution functions, which are the fitting results of eq 2. The solid lines correspond to the Lorentzian distributions for preset and woken-up cells, respectively.

![Figure 3](image-url)  
**Figure 3.** Time-dependent switched polarization [ΔP(t)] as a function of the external voltage (Vext) at room temperature for (a) preset and (b) woken-up cells. The solid lines correspond to the fitting results using the nucleation-limited switching (NLS) model with a Lorentzian distribution of the characteristic switching time.

![Figure 4](image-url)  
**Figure 4.** Solid lines and dashed lines correspond to Lorentzian distributions of the fitting functions for preset and woken-up cells, respectively.
2.0 V were about 356, 535, and 771 ns, respectively; the wake-up process caused these values to increase by 5.0, 4.7, and 5.7%, respectively. We also performed a polarization-switching dynamics analysis using negative switching voltages, because the polarity-dependent kinetics of ferroelectric polarization switching can be caused by an asymmetric $V_e$ and the asymmetry of the change due to the wake-up process (Figure 2a). However, the experimental results showed that this asymmetry does not change the polarization-switching dynamics mechanism or the tendency of the change due to the wake-up process (Supporting Information, Section 5).

The retarded $t_1$ value after the wake-up process is attributable to the annihilation of a disorder-inducing localized built-in field associated with the ferroelectric polarization switching. Various defects, such as oxygen vacancies, charged defects, depletion layers, interfacial defects, other structural phases, and domain orientations, can be regarded as disorders. Therefore, the annihilation of the disorder can be attributed to the redistribution of oxygen vacancies or charged defects, a decrease in the depletion layer or interfacial defects, and improved uniformity of the structural phase or domain orientation.12,22,31 Figure 4 illustrates how the $t_1$ value increased after the wake-up process. The mean value of the characteristic switching time $t_1$ can be controlled by the degree of disorder as this governs the domain-wall velocity, the time needed for nucleation, and the average ferroelectric domain size.35,36 During the wake-up process, the reduction in local fields produced by charged defects increases the time required for nucleation and the average domain size via domain-wall motion.37,38 The local fields can induce a reduction in nucleation bias.39 Additionally, during sideways domain growth, the ferroelectric dipoles can be pinned to quenched defects whose charge or dipole is opposite to that of the ferroelectric polarization, such that domain-wall propagation can be prevented.40 The reductions in both the nucleation and pinning centers induce an increase in the effective domain size. On the other hand, the domain-wall velocity may increase slightly after the wake-up process, due to the annihilation of domain-wall pinning centers.41 Thus, in the case of the woken-up cell, $t_1$ increased because of the increase in both the radius of the effective domain and the wait time for nucleation.

To elucidate the role of defects in the ferroelectric switching dynamics and the wake-up effect, we investigated the defect ratio dependence of ferroelectricity using Monte Carlo simulations. The Hamiltonian for a long-range dipole–dipole interaction is as follows:

$$H = \sum_{ij} \frac{P_i P_j - 3(P_i n)(P_j n)}{r^3} - P_i E_{\text{ext}}$$

(3)

where $P_i$, $r_i$, and $E_{\text{ext}}$ represent the ferroelectric dipole moment at the lattice site $i$, the distance between dipoles, and the external electric field, respectively. During the simulation, defect sites were assigned to be randomly oriented and fixed against the external electric field, and dipole interactions with other ferroelectric dipoles were included. In the simulation, the defects represent the existence of the local field that may be caused by various disorders, such as oxygen vacancies, charged defects, the depletion layer, interfacial defects, and different orientations of domains in ferroelectric doped HfO$_2$ polycrystalline films.12,22,31 The magnitude of the potential defects in Si-doped HfO$_2$ thin films has not been reported. We used an arbitrary magnitude of dipole defects for the simulation, with regard to defect density. Thus, the defect density used in the simulation does not represent the exact density of the disorders in the actual film. However, the tendency of ferroelectricity to change by adjusting the disorder is meaningful. We used the value of $K_{\text{eff}} = 1$ in the simulations, which were performed with a two-dimensional squared lattice of size 100 × 100, imposed with periodic boundary conditions. The density of the defects used in the simulation varied from 0 to 36%. In our domain-switching simulation, the 0% defect density corresponded to an ideal epitaxial film; thus, polycrystalline HfO$_2$ thin films required a higher defect density. The soundness of the parameters in the simulation was confirmed through detailed simulations (Supporting Information, Section 6). The simulation parameters, that is, the system size needed to reduce boundary effects, the truncation distance of the interaction length, and the magnitude dependence of the dipole defect, were checked before the investigation of the defect density dependence of ferroelectric switching dynamics.

The ferroelectric polarization reversal by the Monte Carlo simulation demonstrated the characteristic features of the ferroelectric switching behavior of a Si-doped HfO$_2$ film. Figure 5 shows the Monte Carlo simulation results. Ferroelectric hysteresis with a lower defect ratio exhibited an increase in both spontaneous polarization and the coercive field (Figure 5a), analogous to the experimental results for the Si-doped HfO$_2$ film. Figure 5b shows the Monte Carlo step (MCS) dependence of the $\Delta P(t)/2P_e$ values well-fitted with eqs 1 and 2, except for the case corresponding to a 0% defect density. The case of 0% represents an ideal film and should be analyzed with the KAI model used to represent the switching mechanism with dominant domain wall growth after nucleation.35,36 Note that we did not analyze the defect-free case with the KAI model, the characteristic switching time was identical such that the switching time distribution collapsed into a delta function rather than a Lorentzian distribution. As the defect ratio decreased, the Lorentzian distributions became sharper and the $t_1$ values increased (Figure 5c); this behavior matched the experimental results. Figure 5d,e show ferroelectric domain switching in ferroelectric media with 0 and 4% dipole defect densities, respectively. In both cases, the ferroelectric domains switched through domain-wall motion after nucleation. However, the wait time for initial nucleation was longer in the simulations with a lower defect density than in those with a higher defect density. Also, the effective domain radius was larger in simulations with lower defect densities. The results of Monte Carlo simulations with reduced defects showed the same trend as the experimental results after the wake-up process. However, when the simulation results were compared with the experimental results, the change in the characteristic switching time was exaggerated. This is because we used only the dipole defect as a parameter in the simulations to resolve the effect of the disorder, which may play a role similar to that of the dipole defect for the characteristic switching time. In actual thin films, there are also disorders such as a monoclinic phase that would not act as a dipole defect. A reduction in disorders not associated with dipole defects can also contribute to an increase in remnant polarization.12,14

The initial increase in ferroelectric polarization, that is, the wake-up effect, is attributable to the annihilation of the disorder, including oxygen vacancies, charged defects, depletion layer, interfacial defects, and the associated structural
investigations using TEM reported that the structural change can coincide with a redistribution of oxygen vacancies during the wake-up process. The disorder should be controlled by nucleation and domain-wall motion via pinning-depinning processes at the defect sites.43 The defect density variation affects the elastic propagation of the domain walls and nucleation at defect centers having different pinning potentials. The retardation of the Lorentzian peak in Figure 4 is associated with an increase in $t_{ij}$, whose value is determined by the domain size, wait time for nucleation, and domain-wall speed.34,35 Ferroelectric polarization switching can be controlled by nucleation and domain-wall motion via pinning-depinning processes at the defect sites.13 The defect density variation affects the propagation of the domain walls and nucleation at defect centers with different pinning potentials. The retardation of the Lorentzian peak and increased spontaneous polarization should be interpreted as a reduction in disorder and the emergence of ferroelectric dipoles. This defect suppression could also induce a shift of the switching current in the $I$–$V$ curves shown in Figure 2. Investigations using TEM reported that the structural change from the monoclinic phase to the orthorhombic phase of HfO$_2$ thin films can involve intermediate structural phases.44 Such a structural change can coincide with a redistribution of oxygen vacancies. During the wake-up process, the disorder should be considered in light of interactions with ferroelectric dipoles. In doped HfO$_2$ thin films, various chemical and structural defects, such as oxygen vacancies and different domain orientations, can be considered to be responsible for inducing the local field associated with ferroelectric polarization switching. Annihilation of these defects during device cycling is essential for increasing spontaneous polarization and retarding the mean characteristic switching time $t_{ij}$. Schenk et al. suggested that the wake-up effect is caused by the absence of internal bias fields due to the redistribution of charged defects.13 Starschich et al. also showed that the redistribution of oxygen vacancies is the origin of the wake-up effect in an investigation of the temperature dependence of the effect.15 The nonuniform oxygen vacancies are evenly redistributed during the wake-up process; this redistribution reduces the local built-in field due to charged defects or dipole defects. Thus, the phase transition and reduction in the disorder by the redistribution of vacancies into the bulk region occur simultaneously because of external electric field cycling. However, to our knowledge, quantitative investigations of the relation between structural phase transitions and variations in disorder are yet to be reported. We were unable to determine the exact contribution of various types of defects, for example, oxygen vacancies, interfacial defects, and other structural phases and domain orientations, during the wake-up process. Therefore, further study is needed to understand the exact mechanism of the reduction of disorder and the correlation between the phase transition and disorder.

**CONCLUSIONS**

In summary, we investigated the polarization-switching behaviors of both preset and woken-up polycrystalline 4.2% Si-doped HfO$_2$ thin films. Over the entire switching bias, the switching kinetics of both the preset and the woken-up cells could be explained using the NLS model with a Lorentzian distribution of the characteristic switching time. On comparing the switching kinetics between preset and woken-up cells, the characteristic switching time increased due to an increase in both the effective domain radius and the nucleation wait time after the wake-up process. The results of Monte Carlo simulations with reduced defects showed the same trend as the experimental results after the wake-up process. Our results provide an insight into the mechanism of polarization switching and the wake-up phenomena in HfO$_2$-based ferroelectric thin films.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b11681.

Details of the GPA method, high-resolution TEM imaging, and strain-mapping procedure used in GPA; details of the experimental method for time-dependent switched polarization; investigation of charge trapping and traps in Si-doped HfO$_2$ thin films; fitting for polarization switching in the later decades; ferroelectric polarization-switching kinetics using negative switching bias; details of Monte Carlo simulation (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: scchae@snu.ac.kr.


