ACS APPLIED MATERIALS & INTERFACES
Research Article
Cite This: ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX
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Ferroelectric Polarization-Switching Dynamics and Wake-Up Effect in Si-Doped HfO_2

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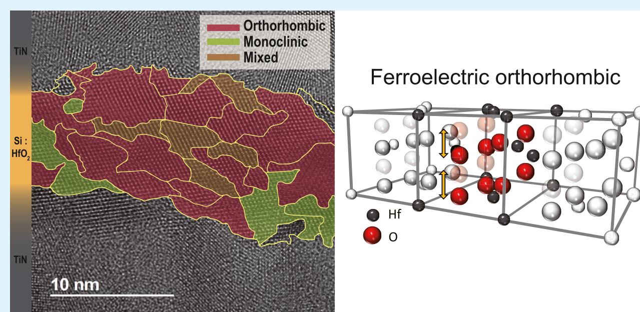
Supporting Information

ABSTRACT: The ferroelectricity in ultrathin HfO_2 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 HfO_2 thin film. Compared with a pristine specimen, the Si-doped HfO_2 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 HfO_2 thin film is accompanied by the suppression of disorder.



KEYWORDS: *ferroelectricity, HfO_2, FeRAM, defects, thin films, domain switching*

INTRODUCTION

Extensive research has been conducted on the binary oxide HfO_2 and its ferroelectric behavior.[1,2] The unprecedented feasibility of ferroelectric memory using HfO_2 is due to its simple structure and compatibility with current complementary metal oxide semiconductor technologies.[3] The orthorhombic HfO_2 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 $\mu C/cm^2$ and a form factor appropriate for high-density memory.[5,6,23] Newly discovered ferroelectricity in HfO_2 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 HfO_2 thin films is crucial for memory applications. The ferroelectric behavior of ultrathin HfO_2 films (less than 10 nm thick) is attributed to a structural distortion that enables the non-centrosymmetric $Pca2_1$ structural phase.[9,10] Oxygen ion movements are believed to be the origin of ferroelectricity in orthorhombic HfO_2 films (Figure 1a). Ferroelectric HfO_2 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

Received: July 12, 2018
Accepted: December 28, 2018
Published: December 28, 2018

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DOI: 10.1021/acsami.8b11681
ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX

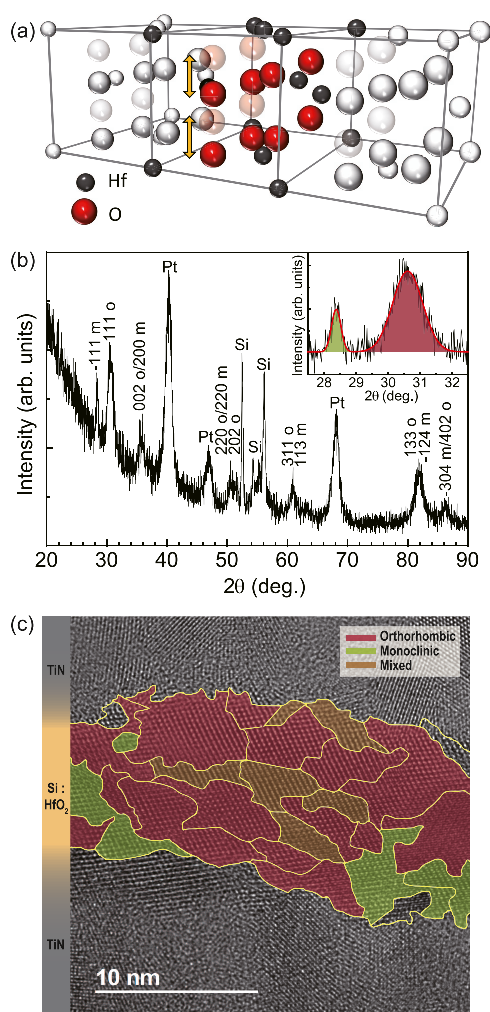

Figure 1. (a) Schematic diagram of the crystal structure of ferroelectric orthorhombic HfO_2 with the displacement of oxygen ions for spontaneous polarization. (b) Grazing-incidence X-ray diffraction (GIXRD) scans for the 8 nm-thick Si:HfO_2 film containing 4.2 mol % Si after annealing at 600 °C for 20 s. The inset shows the fitting result for the GIXRD peaks over the 27.5−32.5° region using Gaussian functions. The green and red peaks correspond to monoclinic and orthorhombic phases, respectively. The sum of their intensities is indicated by a red solid line. (c) Transmission electron microscopy (TEM) image of the cross-section of the Si-doped HfO_2 film. Domain boundaries are indicated by yellow lines. Orthorhombic and monoclinic phases are colored red and green, respectively.

effect, the focus has been on structural transitions in terms of nonferroelectric phases and the ferroelectric orthorhombic phase[14] induced by oxygen vacancies and their redistribution.[12,15] Oxygen vacancy redistribution and charge injection within the structural phase have been used to model wake-up phenomena and retention properties. However, a fundamental understanding of the ferroelectric characteristics is essential for reliable device operation.

Ferroelectric switching dynamics can be used to investigate the underlying mechanism of the wake-up effect according to key features such as oxygen vacancies and dipolar defects on ferroelectric polarization switching. By analyzing the time dependence of polarization switching, we can understand the forms and roles of defects, which are essential to characterize the wake-up effect. In particular, the distribution of the characteristic switching time provides some indication of the defect type. For example, Jo et al. reported the presence of dipole defects, and their effect on ferroelectric polycrystalline $Pb(Zr_xTi_{1-x})O_3$ (poly-PZT) films, by analyzing the critical time for ferroelectric switching in terms of the nucleation-limited switching (NLS) model with a Lorentzian distribution of the characteristic switching time.[16] On the other hand, So et al. reported that the epitaxial PZT film with fewer defects has a constant characteristic switching time corresponding to the Dirac delta function.[17] Furthermore, Kim et al. reported that the epitaxial BFO film has an asymmetric characteristic switching time distribution due to asymmetric interfacial defects.[18]

Recently, there have been many studies on the ferroelectric polarization-switching kinetics of HfO_2 thin films doped with various dopants, such as Si, La, Al, and Zr.[19−22] The characteristic features of NLS in HfO_2, such as the nucleation rate and critical nucleation number for domain switching, have been reported in ferroelectric domain-switching dynamics investigations.[19−21] These reports showed that ferroelectric domain switching in HfO_2 thin films is heavily influenced by the inhomogeneous distribution of the local field.[20,22] The nonuniform, localized built-in field results in domain pinning and a broad distribution of the characteristic switching time. However, the class of disorders in ferroelectric HfO_2 thin films is not well understood, and further study is necessary.

We report herein the polarization-switching behaviors of preset and woken-up 4.2% Si-doped poly-HfO_2 films. The silicon dopant was used in semiconductor mass production with process maturity and contamination control.[2] With variations in the dopant ratio, we observed the most enhanced ferroelectricity of Si-doped HfO_2 at a doping concentration of 4.2%.[24] We suggest that the wake-up effect in the Si-doped HfO_2 thin film is due to a reduction in the disorder that leads to disturbances in homogeneous ferroelectric polarization switching. Counterintuitively, the disorders seem to decrease during the wake-up process of the Si-doped HfO_2 thin films, whereas the disorders are commonly believed to increase during ferroelectric switching, that is, with fatigue behavior.[25] 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 HfO_2 films. Experimental ferroelectric polarization switching of polycrystalline Si-doped HfO_2 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:HfO_2/TiN capacitors were deposited on a Si(001) substrate. Si-doped HfO_2 was fabricated using an atomic layer deposition process based on tetrakis(dimethylamido)hafnium (TDMAH), tetrakis(dimethylamino)silane (4DMAS), and ozone.

DOI: 10.1021/acsami.8b11681
ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX

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 N_2 to crystallize the Si:HfO_2 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 $\Delta P(t)$ 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 HfO_2 thin film. Figure 1b shows the GIXRD spectra of a 4.2% Si-doped HfO_2 thin film, which is a pristine state. This XRD pattern is consistent with mixed monoclinic and orthorhombic phases. The peaks at ∼28.4 and ∼30.6° are assigned to the monoclinic $(\bar{1}11)$ and orthorhombic (111) phases, respectively. Decomposition of the phases was conducted by refining the diffraction pattern using Gaussian peak shapes for each structural phase.[26] The green and red peaks in the inset of Figure 1b correspond to monoclinic $(\bar{1}11)$ 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.[27,28]

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 HfO_2 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:HfO_2 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:HfO_2 layer. It seems that the tetragonal-phase fraction can be quite low for Si:HfO_2 thin films fabricated under specific conditions.[4] 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.[27,28] Because the ferroelectricity of HfO_2 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 HfO_2 films.

Repeated polarization switching of the Si-doped HfO_2 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.[14,29] 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. Figure 2a shows that the wake-up effect was clearly observed with an increase in remnant polarization. Electric field cycling caused the double-hysteresis-like pinched hysteresis loop of the pristine sample to change into a clear hysteresis loop, with an increase in both remnant polarization and coercive voltage (V_c). The hysteresis loop of the pristine cell showed polarity asymmetry with respect to the V_c values: specifically, V_{c+} and V_{c-} were 0.82 and −0.67 V, respectively. Comparing the woken-up cell with the preset cell, the V_{c-} and remnant polarization were higher by about 15 and 18%, respectively; however, V_{c+} did not change significantly. Both the asymmetric V_c and asymmetric shift of V_c can be attributed to the highly different concentrations of trap sites and/or oxygen vacancies at the bottom and top electrode−ferroelectric interfaces.[25]

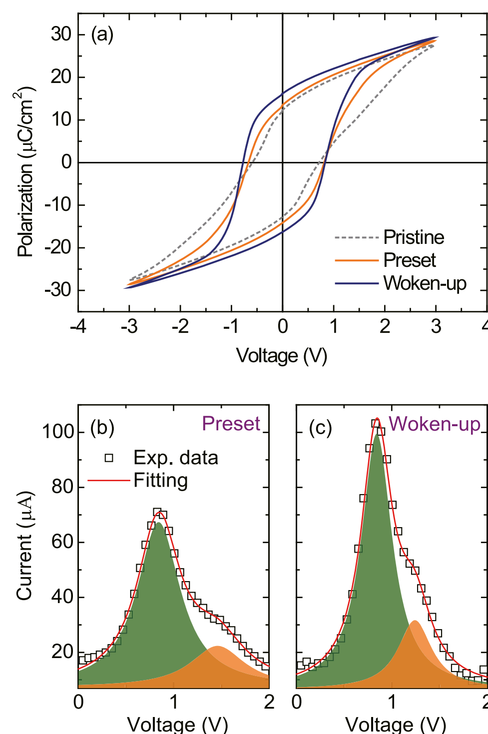

Figure 2. (a) Polarization−voltage measurements performed on pristine, preset, and woken-up cells having a Pt/TiN/Si:HfO_2/TiN capacitor structure. The switching current was measured during the polarization-switching process from downward to upward domains, and the current data were fitted by the sum (red solid line) of two Lorentzian distributions (orange and green regions) for (b) preset and (c) woken-up cells.

The switching current during the ferroelectric polarization reversal exhibited the characteristic changes associated with the wake-up effect. Figure 2b,c show the switching-current curves of the preset and woken-up cells measured during polarization switching from downward to upward polarization, 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

DOI: 10.1021/acsami.8b11681
ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX

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.[30] The dipole defects or pinning sites caused by oxygen vacancies and trapped charges can exist in ferroelectric doped HfO_2 thin films deposited on a TiN electrode.[11,31] Their nonlinear contribution to the $I-V$ characteristics can result in additional hysteresis in $P-E$ measurements, that is, switching-current peak splitting.[12,32] Therefore, the change in switching-current behavior caused by the wake-up effect indicates an adjustment of the disorder by the external electric field.

The ferroelectric switching behavior of Si:HfO_2 thin films exhibits NLS due to the polycrystallinity of specimens. Figure 3a,b show the $\Delta P(t)/2P_s$ values of the preset and woken-up

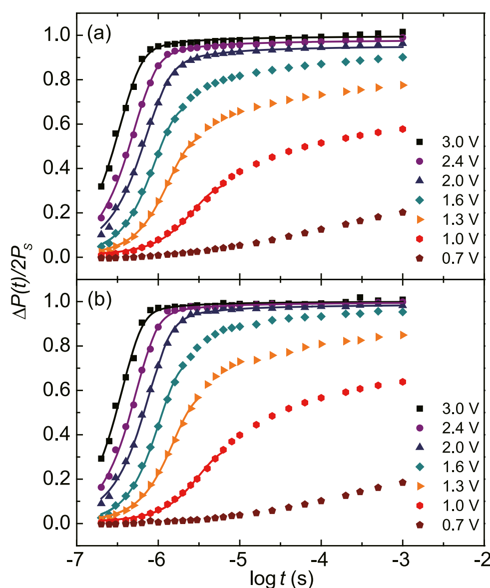

Figure 3. Time-dependent switched polarization [$\Delta P(t)$] as a function of the external voltage (V_{ext}) at room temperature for (a) preset and (b) woken-up cells. The solid lines correspond to the fitting results using the nucleation-limited switching (NLS) model with a Lorentzian distribution of the characteristic switching time.

specimens, respectively, as a function of V_{ext} 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 $\Delta P(t)/2P_s$ 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 $\Delta P(t)/2P_s$ 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.[33] $\Delta P(t)/2P_s$ values were fitted using the NLS model with a Lorentzian distribution of the characteristic switching time according to eqs 1 and 2[16]

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

where

$$F(\log t_0) = \frac{A}{\pi}\left[\frac{w}{(\log t_0 - \log t_1)^2 + w^2}\right] \quad (2)$$

where A, w, and $\log t_1$ are a normalization constant, the half-width at half-maximum of the distribution, and the mean distribution value, respectively. Note that assigning a distribution other than a delta function to $F(\log t_0)$ means that the ferroelectric characteristic switching times of the elementary regions (t_0) are inhomogeneous. The solid lines in Figure 3a,b at the point of initial polarization reversal indicate that the polarization switching was governed by NLS, with a Lorentzian distribution of the local switching times. Jo et al. and others also used a Lorentzian distribution of the ferroelectric characteristic switching time and attributed the broadening of the polarization reversal slope in the early decades to the existence of dipolar defects and their interactions.[16,34] Note that polarization-switching behaviors at later decades were fitted using a Gaussian distribution, which is more intuitive than the case using only the Lorentzian distribution for random defects. The results also indicate that the overall growth is governed by the NLS model (Supporting Information, Section 4).

The wake-up effect of the Si-doped HfO_2 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

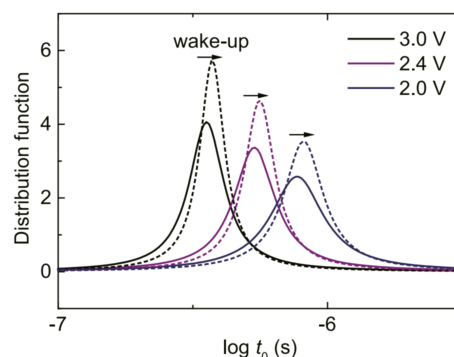

Figure 4. Solid lines and dashed lines correspond to Lorentzian distributions of the fitting functions for preset and woken-up cells, respectively.

are the fitting results of eq 2. The solid lines correspond to the Lorentzian distributions for the preset case, whereas the dashed lines correspond to the situation after wake-up cycling. Figure 4 illustrates the sharpening of the distribution dispersion after the wake-up process. Such a sharpening implies that the characteristic switching time of the HfO_2 films becomes more uniform. Note that if the distribution of t_0 becomes a delta function due to an identical switching characteristic, regardless of the film region, then the switching dynamics follow the Kolmogorov−Avrami−Ishibashi (KAI) model and correspond to polarization reversal via homogeneous nucleation and domain-wall motion.[35,36] The peak positions t_1 for different external electric fields of 3.0, 2.4, and

DOI: 10.1021/acsami.8b11681
ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX

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_c 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[42]

$$H = \sum_j \frac{P_i \cdot P_j - 3(P_i \cdot n)(P_j \cdot n)}{r^3} - P_i \cdot E_{ext} \tag{3}$$

where P_i, r, and E_{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 $K_{BT} = 1$ 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 $\Delta P(t)/2P_s$ 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

DOI: 10.1021/acsami.8b11681
ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX

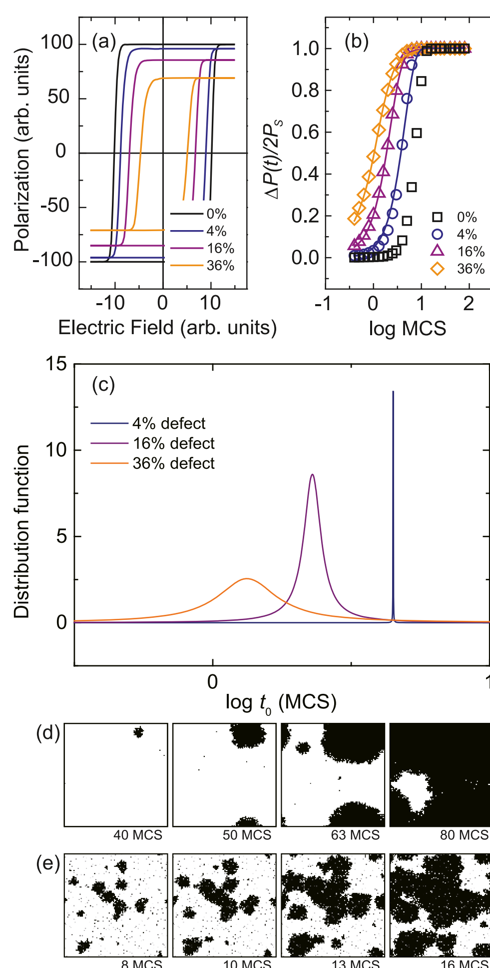

Figure 5. (a) Monte Carlo simulations of the ferroelectric polarization hysteresis loop as a function of the defect ratio. (b) Monte Carlo step (MCS) dependence of ferroelectric polarization switching as a function of the defect ratio under an external field E = 9.0 (a.u.). (c) Lorentzian distributions of fitting functions for 4% (solid navy line), 16% (solid purple line), and 36% (solid orange line) defect ratios, respectively. (d, e) Snapshots of ferroelectric polarization switching for defect ratios of 0 and 4% with E = 7.0 (a.u.), respectively.

phase variation, mainly from the nonferroelectric monoclinic phase to the ferroelectric orthorhombic phase, in the Si-doped HfO_2 film. The retardation of the Lorentzian peak in Figure 4 is associated with an increase in t_1, 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.[43] The defect density variation affects the elastic propagation of the domain walls and nucleation at defect centers having different pinning potentials.[44] 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 satellite 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.[45] 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_1. 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.[11] 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.[12] 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)

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DOI: 10.1021/acsami.8b11681
ACS Appl. Mater. Interfaces XXXX, XXX, XXX−XXX

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Author Contributions

T.Y.L. and S.C.C. designed and initiated the experiments. T.Y.L., K.L., and M.S.S. conducted the electrical measurements. H.H.L. conducted the Monte Carlo simulations. S.M.Y. and H.K.Y. discussed the results, D.I.S., Z.Z., A.Y., M.R.M, and X.L. prepared the specimens. H.Y.J., D.L., K.P., and J.P. conducted the TEM experiments. All authors contributed to writing the manuscript and have approved the final version.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the MOTIE (Ministry of Trade, Industry & Energy) (No. 10080657) and KRSC (Korea Semiconductor Research Consortium) support program for the development of future semiconductor devices. A part of this study was performed using facilities at the IBS Center for Correlated Electron Systems, Seoul National University. S.M.Y. was also supported by a National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIP) (NRF-2017R1C1B2010258). The authors gratefully acknowledge the contributions of all of the joint development (JD) members in Lam Research, Versum Materials and SK Hynix. This paper was a result of the research project supported by SK Hynix Inc. H.Y.J. acknowledges the support from the Creative Materials Discovery Program (NRF-2016M3D1A1900035). D.L., K.P., and J.P. acknowledge support from IBS-R006-D1 and the National Research Foundation of Korea (NRF) grant funded by the Korea Government (MSIT) (NRF-2017R1A5A1015356).

■ ABBREVIATIONS

NLS, nucleation-limited switching
MFM, metal−ferroelectric−metal

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