Wake-Up Mechanisms in Ferroelectric Lanthanum-Doped Hf$_{0.5}$Zr$_{0.5}$O$_2$ Thin Films

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Since the discovery of ferroelectricity in thin doped hafnium oxide layers, there is a rapidly growing interest in the implementation of this material into nonvolatile memory devices such as ferroelectric capacitors, transistors, or tunnel junctions. In most cases, a field-cycling-induced change in the remanent polarization is attributed to wake-up and fatigue in ferroelectric HfO$_2$ devices. The lanthanum-doped hafnium/zirconium mixed oxide system is of broad interest due to its high endurance stability and low crystallization temperature which is necessary for low thermal budget, back-end of line devices. Herein, a detailed temperature-dependent field-cycling study is performed in a wide temperature range from liquid nitrogen to room temperature to separate field-cycling-induced charge movements from phase change effects. Results are expected to be relevant for similar doped HfO$_2$ ferroelectric layers.

1. Introduction

The two distinct stable electrical polarization states provided by a ferroelectric material make it a contender to be used for the nonvolatile memory applications. Among the ferroelectric materials, two major classes have emerged as useful choices for the application in ferroelectric random access memories (FeRAM) and ferroelectric field-effect transistors (FeFET): perovskite and HfO$_2$-based ferroelectric materials. Several issues in complementary metal–oxide–semiconductor (CMOS) process integration of perovskite-based ferroelectrics such as contamination caused by lead-based oxides, a high thermal budget required to achieve the ferroelectric phase,[3] and hydrogen sensitivity[2] lead to limited scalability,[3] and therefore hinder the progress of ferroelectric integration into state-of-the-art CMOS technologies. In contrast, HfO$_2$-based ferroelectrics promise to solve the previously mentioned obstacles,[4] but do suffer from defects,[5] a high coercive field leading to high switching voltages and low endurance,[6] and charge trapping.[7]

Among the HfO$_2$-based ferroelectric material class, Hf$_{0.5}$Zr$_{0.5}$O$_2$ exhibits a high remanent polarization ($P_r$) together with a low thermal budget fabrication processes.[8] At the same time, the read/write endurance still needs improvement. In many cases, the endurance is limited by dielectric breakdown. However, the variation of $P_r$ with bipolar field-cycling also needs to be minimized for reliable sensing of the polarization state. The variation of $P_r$ with cycling is usually classified into two regimes. The initial cycles cause an increase in $P_r$. After a time where the polarization is stable, the remanent polarization decreases with further cycling. In the literature, the initial improvement and then degradation of $P_r$ are called wake-up and fatigue, respectively.[17] Lanthanum (La) doping of Hf$_{0.5}$Zr$_{0.5}$O$_2$ improves the cycling behavior for high cycle numbers, but a very pronounced increase in the wake-up effect is reported.[6,8,9] The wake-up effect is not only limited to La: Hf$_{0.5}$Zr$_{0.5}$O$_2$ but is also reported for ferroelectric HfO$_2$ stabilized using other dopants such as La, Si, and Al-doped HfO$_2$.[10,11] Therefore, understanding the cause of these degradation behaviors is an important task for incorporating these materials into reliable memory technologies.

The field-cycling-induced wake-up effect leads to a transformation from a pinched antiferroelectric-like hysteresis to a fully opened ferroelectric hysteresis loop. To understand this transition, mechanisms which cause a pinching of the hysteresis loop need to be revisited. Different effects found in the literature to explain the pinching of pristine hysteresis loop are summarized later. For a HfO$_2$-based ferroelectric material, a ferroelectric phase stabilization was reported for an optimal concentration of silicon (Si) and zirconium in Si-doped HfO$_2$ and Hf$_{0.5}$Zr$_{0.5}$O$_2$, respectively. Park et al.[12] and Bösecke et al.[13] reported the depinning of the hysteresis loop with decreasing ambient temperature for Si-doped HfO$_2$. To explain this depinning of the hysteresis loop, a phase analysis was conducted with decreasing temperatures using grazing incidence X-ray diffraction (GIXRD) measurements.[12] Here, a clear phase transition from a tetragonal to orthorhombic phase was observed through an enhancement of higher order diffraction peaks. It was reported that with decreasing temperature the polar orthorhombic phase is stabilized which leads to depinning of the hysteresis loop. Müller et al.[14] also described the electrical and structural properties of Hf$_{0.5}$Zr$_{0.5}$O$_2$ as a function of temperature, observing a similar trend of depinning of the
hysteresis loop due to ferroelectric phase stabilization. Furthermore, in situ temperature-dependent XRD measurements on epitaxially grown yttrium-doped HfO$_2$ reveal that the peaks related to the orthorhombic phase disappear for temperatures above 475 °C. Therefore, the transformation from the orthorhombic to the tetragonal phase is also observed in epitaxial films with increasing temperature.\[13\]

As a similar kind of pinched to fully open hysteresis loop is also observed during the field-cycling wake-up effect, a field-cycling-induced phase transformation could be the origin. Grimley et al. showed in transmission electron microscopy measurements conducted after different numbers of field cycles that in pristine films a nonpolar tetragonal phase is found at the metal–ferroelectric interface and in the bulk of the film\[16,17\] which transforms into polar orthorhombic phase portions with field-cycling. But as measurements were performed on different capacitors, a clear statistical relevance is debatable due to the small sampling areas observed via local transmission electron microscopy (TEM) measurements. In the literature, synchrotron-based in situ XRD measurements during field-cycling show measured phase changes typically in the sub 5% range even though $P_r$ increases more than 20–100% are reported.\[18–21\] Accordingly, phase changes during field-cycling are present, but not the main mechanism to understand the wake-up effect.

Apart from the nonpolar-to-polar phase transition, there are several other mechanisms proposed to explain the changes observed with field-cycling in the wake-up phase such as the depinning of domains,\[22\] a polarization orientation change,\[23\] or cycling-induced changes in the depolarization field.\[24,25\] During depinning of domains, charges at domain walls and grain boundaries are redistributed during field-cycling which can enhance switching performance of these domains or grains. As reported by Shimizu et al.,\[19\] an in-plane-to-out-of-plane polarization change can be found in epitaxial grown Y: HfO$_2$ films, but again orientation changes seem to be small (<5%) compared with the polarization change.

According to the depolarization field model, a nonpolar film portion in series with polar regions imposes a depolarization field $E_{dep}$ according to Equation (1)

$$E_{dep} = \frac{-P_r}{\varepsilon_0 \varepsilon_p} \left( 1 + \frac{\varepsilon_{np} \varepsilon_p}{\varepsilon_{np} \varepsilon_p + \varepsilon_{tp}} \right)^{-1}$$

where $P_r$ is the remanent polarization, $\varepsilon_0$ is the vacuum permittivity, and $\varepsilon_p$, $\varepsilon_{np}$, $\varepsilon_{tp}$ and $\varepsilon_{hp}$ are permittivity and thickness of polar and nonpolar film portions, respectively. Due to the high electric field across the interfacial nonpolar layers close to the electrodes, charge injection across the interface layer can occur during field-cycling which reduces the depolarization field. In addition, a partial breakdown of the interface layer might follow. Both effects result in a $P_r$ increase.\[24,25\] Details on the effect of depolarization fields on the hysteresis loop and field-cycling can be found in ref. [24].

As mentioned earlier, so far, the depinning of hysteresis loop was reported with decreasing ambient temperature or field-cycling of the pristine films. In this work, a detailed field-cycling characterization at different ambient temperatures is performed to understand the impact of different physical mechanisms which can cause the wake-up effect.

### 2. Results and Discussion

#### 2.1. Results

As the basis for the electrical characterization, the structural properties of the La-doped Hf$_{0.5}$Zr$_{0.5}$O$_2$ sample were determined. As visible in the GIXRD pattern (Figure 1), no monoclinic phase is found for the dielectric layer with 2.3 mol% La because characteristic peaks at $2\theta$ of 28.3° and 31.6° are missing. An exact extraction of the tetragonal/orthorhombic phase composition is difficult due to overlapping peak positions for both structures. As different La contents are discussed in a former publication,\[6\] here, only the result for the Hf$_{0.5}$Zr$_{0.5}$O$_2$ doped with 2.3 mol% La is reported. The main GIXRD 2θ peak close to 30.6° belongs to a superimposed orthorhombic/tetragonal (111)$_{O}/$(011)$_T$ peak. As the peak position 30.6° is roughly in between the orthorhombic (30.8°) and the tetragonal peak (30.4°), the layer is expected to consist of a mixture of tetragonal and orthorhombic phase at room temperature (RT). In addition to diffraction peaks of related ferroelectric layer, the measurements also contains TiN (200) peak at $2\theta \approx 42.5°$.

The electrical results and discussion section are further divided into two subsections: the temperature-dependent hysteresis loop measurements which will be proceeded by temperature-dependent field-cycling.

#### 2.1.1. Temperature-Dependent Hysteresis Loop Measurements

Dynamic hysteresis measurements (DHM) are performed at ambient temperatures ranging from 80 to 380 K to study the temperature impact on the ferroelectric hysteresis loop. For each measurement, first a pristine capacitor structure is measured to determine the polarization behavior before field-cycling. As shown in Figure 2A, a decreasing ambient temperature results in a 1) depinning of the hysteresis loop causing an increase in the remanent polarization ($P_r$) and 2) a decrease in the saturation polarization ($P_{sat}$) at the maximum applied field of 3 MV cm$^{-1}$. To further explore the impact of decreasing temperature,
the switching current as a function of the applied electrical field is plotted in Figure 2B. Two distinct current peaks are visible which can be separated into two cases: 1) I, II as switching current and 2) I′, II′ as back-switching current peaks. To experimentally verify the assignment of the back-switching peak to a corresponding forward switching peak, the triangular voltage pulses were applied on pristine films (Supporting information). In Figure S1, Supporting Information, it can be seen that the back-switching peaks are only measured in case the capacitor was poled in the corresponding switching polarization direction before. Such as the back-switching current peak II′ (back-switching current peak I′) is missing during the very first positive (negative) voltage ramp. The decreasing ambient temperature has a strong impact on the back-switching current peaks, while the switching current peaks mostly remain unaffected. With decreasing temperature, the back-switching current peaks shift to merge with the forward switching current peaks and the resulting integration leads to a higher calculated \( P_r \).

As a second step, films are field-cycled at different ambient temperatures to analyze the impact on the woken-up hysteresis loop. The woken-up films showed clockwise tilting of the hysteresis loop with decreasing temperature. The tilting of the hysteresis loop has negligible impact on \( 2P_r \), while \( P_{sat} \) increases with increasing temperature as shown in Figure 2C. This tilting is caused by a broader switching current peak related to a wider distribution of the coercive field \( (E_c) \) at lower temperatures, as shown in Figure 2D. In Figure 2E,F, the impacts on \( P_r \) and \( P_{sat} \) are quantified as a function of temperature. A linear increase
in $2P_r$ from 19 to 34 $\mu$C cm$^{-2}$ with decreasing temperature is measured for pristine films, while woken-up films after field-cycling at different temperatures have a negligible temperature dependence of $2P_r$. The $P_{sat}$ for the woken-up films is lower than for pristine films and in both cases the $P_{sat}$ value increases with increasing temperature.

### 2.1.2. Temperature-Dependent Field-Cycling Measurements

The wake-up effect during field-cycling at different ambient temperatures is shown in Figure 3A. As the ambient temperature decreases, the wake-up effect also reduces. At 380 K a very strong wake-up effect is measured, while at 80 K field-cycling results in a stable $P_r$. For most temperatures, a slow change in polarization up to $\approx 10^4$ cycles is followed by an enhanced wake-up for a higher cycle counts. The saturation polarization extracted from the hysteresis loop at the maximum applied field of 3 MV cm$^{-1}$ is shown in Figure 3B. The magnitude is an indication of the relative amount of switchable domains and the dielectric constant. Decreasing the temperature and field-cycling both results in a decrease in $P_{sat}$. The dielectric constant ($k$) is extracted from the polarization-field hysteresis loop in the linear region close to saturation to analyze the impact of ambient temperature and field-cycling. A relatively high $k$-value of 36.5 is measured at 380 K, while decreasing the temperature to 80 K results into a drop to 30 as shown in Figure 3C. A similar but weaker trend of decreasing $k$-value is also observed with field-cycling. To compare the relative impact of temperature and cycling on $P_r$ and $P_{sat}$, the change in $2P_r$ and $2P_{sat}$ from pristine to $10^8$ cycled film is plotted against the ambient temperature in Figure 3D. A very strong impact on $P_r$ is observed as compared with the low impact on $P_{sat}$.

### 2.2. Discussion

Looking at the effects visible in Figure 2 and 3, temperature- and field-cycling-dependent changes are visible, which could be either attributed to a phase change\cite{26} or a reduction in depolarization field\cite{24,25} or a combination of both.\cite{26} The increasing doping concentration of La into Hf$_{0.5}$Zr$_{0.5}$O$_2$ tends to stabilize the nonpolar tetragonal phase,\cite{6} and as shown by the GIXRD measurements above, the 2.3 mol% La-doped Hf$_{0.5}$Zr$_{0.5}$O$_2$ film consists of a mixture of nonpolar tetragonal and polar orthorhombic phases. For the RT case, a dielectric constant $k$ of about 37 is determined which indicates again a certain tetragonal phase portion compared with a $k$-value of 30 for the orthorhombic and more than 40 for the pure tetragonal case. Following the equation

$$P_{sat} = E_{max} \times k \times \epsilon_0 + P_s$$  \hspace{1cm} (2)

where $P_s$ is the spontaneous polarization,\cite{27} $E_{max}$ is the maximum applied field of 3 MV cm$^{-1}$, and $\epsilon_0$ is the vacuum permittivity. With a maximum applied field $E_{max}$ of 3 MV cm$^{-1}$,
the dielectric contribution to \( P_{\text{sat}} \) can be determined as about 10 \( \mu \text{C} \cdot \text{cm}^{-2} \) which is about 25% of \( P_{\text{sat}} \) at RT. Assuming a field-induced phase change\(^{28,29} \) for the tetragonal phase portion to the orthorhombic phase, a pinched hysteresis loop can easily be explained. On the contrary, the nonpolar tetragonal phase induces a depolarization field. This depolarization field is oriented in opposite direction to the applied field and back-switching of dipoles would occur at a different applied field. Without the depolarization field, back-switching and switching would take place almost at the same absolute value of applied field. With increasing depolarization field, both switching events separate and back-switching happens at lower fields reflecting a pinched hysteresis loop. Accordingly, the pinched hysteresis loop for La-doped \( \text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_{2} \) films at RT can either be observed by a field-induced phase change and/or a depolarization field. It is important to mention here that the field-induced and field-cycling-induced phase changes are two different mechanisms. The first is a reversible mechanism that will disappear when the field is reduced to zero again, while the later will irreversibly change the phase composition of the film at a given temperature and remain after the field-cycling ends. Therefore, both effects need to be treated separately.

### 2.2.1. Temperature-Dependent Hysteresis Loop Measurements

As reported by Park et al.,\(^{32} \) a mixed composition of a tetragonal/orthorhombic phase undergoes a temperature-dependent phase change leading to a higher orthorhombic phase portion when cooling to liquid nitrogen temperatures. Decreasing the temperature results in a decrease in \( P_{\text{sat}} \), indicating a reduction of switched domains, possibly due to stronger pinning of domains\(^{30} \) and/or an increase in the coercive field. In addition, changes in \( P_{\text{sat}} \) by about 2 \( \mu \text{C} \cdot \text{cm}^{-2} \) can also be due to phase changes related to decrease in the dielectric constant from 37 to 30 from room to liquid nitrogen temperature. From the thermodynamic perspective, Landau–Devonshire (LD) theory explains the temperature-induced phase change in terms of free energy of the material. Using LD theory, the shape of the hysteresis loop can be explained by the free energy curve of the material. At higher temperatures, the material has a triple well energy landscape with an energy minimum at zero polarization. The energy minima at nonzero polarization magnitudes can be obtained by application of an electric field, but once the field is removed, the lowest energy minimum again shifts to zero polarization. The reversible shifting of energy minima with applied electric fields explain the pinched hysteresis loops which have close-to-zero remanent polarization. In contrast, open ferroelectric hysteresis loops have a double well energy landscape with energy minima at nonzero polarization values. Therefore, even after the removal of external electric field the material retains the switched polarization. To observe the impact of temperature, LD free energy calculations were performed for different temperatures, which shows the transformation of triple well energy landscape to double well with decreasing temperature and explains depinning of hysteresis loop (supporting information). Independent of the discussed field-induced phase change/depolarization model earlier, a reduction of the temperature causes a depinning (Figure 2A).

Looking at the switching current in Figure 2B, the switching and back-switching current peak positions would behave similar for the two models. For the depolarization field model, as discussed earlier according to Equation (1), the depolarization field would reduce for lower temperatures due to a reduction of \( t_{\text{tip}} \). Consequently, the switching and back-switching current peaks would merge, which is consistent with the experimental results. In case of the field-induced tetragonal-to-orthorhombic phase change at RT, a reduction in temperature would cause a higher orthorhombic phase portion and a reduced field-induced phase change would be the consequence. Therefore, a field-induced transition from triple well to double well is expected, resulting also in a shift and merge of the switching peak positions. If the energy barrier for the field-induced phase change is independent of temperature, the back-switching peak position should not shift along the field axis for reduced temperatures, but temperature-dependent changes in the energy barrier are also expected. As synchrotron XRD results discussed in the literature indicate only very minor field-induced phase changes for various doped \( \text{HfO}_2 \) and mixed \( \text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2 \) layers,\(^{21} \) the depolarization field model might be more consistent with our results than the field-induced phase change model. But neither effect can be completely excluded based on these trends.

In the woken-up case (Figure 2C), regardless of the temperature range, the switching and back-switching peaks can no longer be readily distinguished. Only the peak width is changing with temperature. Here, a different local charge distribution can slightly change the switching field for different domains, resulting in a broadening of the switching current peak. At higher sample temperature, a charge redistribution is initiated causing a better distribution of the charges after wake-up cycling and sharper switching peaks. This charge redistribution is reduced at 80 K and the broad peak width of the pristine switching peak is not changing much with field-cycling. This effect would be similar for the two discussed models. Summarizing the findings for temperature-dependent hysteresis measurements, a phase change can be attributable to a mixed tetragonal/orthorhombic phase at RT where a higher orthorhombic phase portion occurs at 80 K and the initial pinching of the hysteresis loop is most likely related to depolarization fields caused by the nonpolar tetragonal phase portion.

### 2.2.2. Temperature-Dependent Field-Cycling Measurements

In a next step, effects caused by field-cycling are discussed which are strongest at RT. Following the discussion in the former section, the pinched hysteresis loop is caused by depolarization fields. Again, two different mechanisms could be possible during field-cycling. Grimley et al. reported a transformation of the nonpolar tetragonal phase portion to polar orthorhombic regions during cycling as determined by TEM together with a higher conductivity of the interfacial layer after cycling as measured by impedance spectroscopy.\(^{16} \) From both effects, Lomenzo et al. proposed a possible wake-up scenario with two different cycling phases.\(^{24,25} \) In the initial phase, charge injection and charge redistribution within the dielectric/metal interface layer cause a depinning of domains and shielding of depolarization...
fields. In the second phase, closely related to the reduction of the interface resistivity, a partial breakdown of the interface layer is proposed. Accordingly, first a slow and later a faster wake-up process occurs. These two regions are clearly visible also in the La-doped regions (see green layers in Figure 3A). As a reduced amount of the tetragonal phase is assumed for liquid nitrogen temperature, here the wake-up would be reduced. Changes in the interfacial properties would also cause a decrease in the overall dielectric constant of the capacitor structure (Figure 3C). Again, almost no k-value change is visible in the first cycles and a stronger reduction is determined beyond $10^6$ cycles.

In a second model, one can follow the second claim in the Grimley et al.’s article. The authors claim that an oxygen vacancy redistribution would initiate a phase change for the interfacial tetragonal regions to the orthorhombic phase. Here, the statistical relevance of the local TEM measurements might be critical. The transformation of the in-series nonpolar tetragonal phase to polar orthorhombic phase with decreasing temperature results into a reduction of depolarization fields and as a consequence switching current peaks merge and wake-up is suppressed. Again, this effect would be lower at reduced temperatures because the amount of the nonpolar tetragonal phase is reduced. Following the discussion earlier, both scenarios seem to be possible and indications, which favor one over the other case, need to be found. In contrast to lower temperatures, at RT the different slopes of wake-up with field-cycling indicate that a field-cycling-induced phase change is less likely. Here, the initial trapping and subsequent breakage of interfacial layer proposed by the depolarization field model can explain the different wake-up slopes. The different impact of temperature and field-cycling on the k-value and the $P_{\text{sat}}$ is another indication that a remnant polarization increase with temperature has a different origin as compared with field-cycling. Apart from the aforementioned indications suggesting that field-cycling-induced phase change is less likely to be the cause of the wake-up effect at RT, the slight decrease in k-value and $P_{\text{sat}}$ with field-cycling can be explained by field-cycling-induced phase change from the nonpolar tetragonal having a higher k-value to the polar orthorhombic phase with lower k-value. To further illuminate the topic, the impact of ambient temperature on the woken-up films is characterized and the following procedure is followed: in the first step, the hysteresis loop of a pristine sample is measured at RT subsequently, wake-up field-cycling at RT is performed for $10^6$ cycles, and finally the wake-up field-cycling is repeated for another $10^6$ cycles at 150 K. The results are shown in Figure 4 where it can be seen that the wake-up procedure results in a $2P_r$ increase from 22 to 35 $\mu$C cm$^{-2}$ by 13 $\mu$C cm$^{-2}$, while measuring the RT woken-up film at 150 K only results in an additional $2P_r$ increase by 2 $\mu$C cm$^{-2}$. This experiment demonstrates that cooling down a pristine film to lower temperature results into substantial increase in $P_r$, while once the film went through the wake-up procedure at RT, decreasing the temperature has a negligible impact on $P_r$. Again, both the oxygen vacancy redistribution-induced tetragonal-to-orthorhombic phase change and breakage of interfacial layer can explain the effect. According to the oxygen vacancy redistribution model, the field-cycling at RT redistributes the interfacial oxygen vacancies which results into transformation of interfacial tetragonal-to-orthorhombic phase; therefore, after this process reducing the temperature will have negligible impact on remanent polarization increase. Similar kind of explanation is also valid for interfacial layer breakage.

In summary, La doping of Hf$_{0.5}$Zr$_{0.5}$O$_2$ results into a stronger stabilization of the nonpolar tetragonal phase by introducing oxygen vacancies in the La-doped regions (see green layers in the middle of the Hf$_{0.5}$Zr$_{0.5}$O$_2$ layer in Figure 5). The creation of oxygen vacancies at metal/ferroelectric interface due to an oxygen scavenging effect of TiN is also reported in the literature and therefore, a formation of nonpolar tetragonal phase at metal/ferroelectric interface is also included into figure (see additional green layers at the ferroelectric/metal interface in Figure 5). The field-cycling at 380 K can result in injection of charges into nonpolar dielectric layer at the metal/ferroelectric interface and into a minor tetragonal to orthorhombic phase change (Figure 5B). Both mechanisms reduce the depolarization field and results into merger of switching current peak. During cooling the pristine sample from 380 to 80 K, a reduction of the depolarization field occurs due to a possible temperature-induced tetragonal-to-orthorhombic phase change. Accordingly, the switching current peaks merge during cool down (Figure 5A, C). Due to a reduced kinetic energy, field-cycling at lower temperatures causes a suppressed amount of injected charges into nonpolar interfacial layers during field-cycling which can be seen as slight sharpening of switching current peak (Figure 5C, D).

3. Conclusions

In conclusion, temperature-dependent hysteresis and field-cycling measurements can help to understand field-induced mechanisms in doped HfO$_2$ capacitor structures. Temperature-dependent hysteresis measurements on La-doped Hf$_{0.5}$Zr$_{0.5}$O$_2$-based capacitor structures can support a phase change from tetragonal at RT to a more orthorhombic phase at liquid
The nonpolar tetragonal phase portions in a ferroelectric matrix create depolarization fields, which result in a pinched hysteresis loop as also indicated by a clear separation of switching and back-switching peaks in the switching currents. Additional temperature-dependent field-cycling measurements show a reduced wake-up effect for lower sample temperatures. Our results suggest that the wake-up effect can be separated into two stages: an initial stage where charge redistribution and depinning of ferroelectric domains occur and a second stage after about $10^8$ cycles with a phase change in interfacial regions or an interface degradation. The possibility of both effects was formerly verified by impedance spectroscopy or transmission electron microscopy but further studies will be necessary to verify the effects on a structural level beyond any doubt. As the aforementioned mechanisms are predominantly interface related, interface and electrode engineering can provide a solution to reduce the challenging wake-up effect and take advantage of the increased field-cycling endurance in La-doped Hf$_{0.5}$Zr$_{0.5}$O$_2$. Overall, results are relevant in general for the field-cycling behavior of doped HfO$_2$ ferroelectric layers.

4. Experimental Section

Metal–insulator–metal capacitor structures were fabricated on a silicon substrate. Ten nanometer titanium nitride bottom and top electrodes were deposited at RT using a sputter deposition tool from Bestec. A 10 nm-thick Hf$_{0.5}$Zr$_{0.5}$O$_2$ film doped with 2.3 mol% La was deposited by atomic layer deposition (ALD) at 300 °C deposition temperature. For hafnium, zirconium and lanthanum oxides tetrakis[ethylmethylamino]hafnium (Hf[N(C$_2$H$_5$)C H$_3$]), tris(dimethylamino)cyclopentadienyl-zirconium (C$_5$H$_5$)Zr[N(CH$_3$)$_2$]$_3$ and tris(isopropyl-cyclopentadienyl)lanthanum (La-(iPrCp)$_3$) were used as precursors, respectively. Ozone was the oxidant source for all three oxides mentioned earlier. After the deposition of the top electrode, the samples were annealed at 600 °C for 20 s under nitrogen atmosphere. A 10 nm-thick titanium adhesion layer and a 25 nm-thick platinum layer were deposited through a shadow mask to define the capacitor structure and a subsequent standard clean (solution of H$_2$O, H$_2$O$_2$, and NH$_3$) was used for patterning of the TiN top electrode. For thickness determination X-ray reflectivity measurements and for phase characterization GIXRD measurements were both realized using a Brueker D8 Discover tool (Cu K$_\alpha$ radiation with $\lambda = 0.154$ nm). Electrical characterization was performed using a Keithley parameter analyzer and a cryogenic workstation, while liquid nitrogen was used for cooling the samples down to 80 K. The bottom electrode was kept at ground, while the measurement signal was applied to the top electrode. DHM were performed using triangular pulses with a maximum applied field of 3 MV cm$^{-1}$ and a frequency of 1 kHz, while for cycling rectangular pulses of the same amplitude and 100 kHz frequency were used.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
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