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On the relationship between field cycling and imprint in ferroelectric $Hf_{0.5}Zr_{0.5}O_2$

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Manifold research has been done to understand the detailed mechanisms behind the performance instabilities of ferroelectric capacitors based on hafnia. The wake-up together with the imprint might be the most controversially discussed phenomena so far. Among crystallographic phase change contributions and oxygen vacancy diffusion, electron trapping as the origin has been discussed recently. In this publication, we provide evidence that the imprint is indeed caused by electron trapping into deep states at oxygen vacancies. This impedes the ferroelectric switching and causes a shift of the hysteresis. Moreover, we show that the wake-up mechanism can be caused by a local imprint of the domains in the pristine state by the very same root cause. The various domain orientations together with an electron trapping can cause a constriction of the hysteresis and an internal bias field in the pristine state. Additionally, we show that this local imprint can even cause almost anti-ferroelectric like behavior in ferroelectric films. *Published by AIP Publishing.*
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I. INTRODUCTION

Ferroelectric random access memories suffer strongly from scaling issues.[1] The most commonly used perovskites such as lanthanum doped lead zirconate titanate are not complementary metal-oxide-semiconductor (CMOS) compatible and need diffusion barriers for their integration.[2] The discovery of ferroelectricity in doped hafnia films,[3] which allows a CMOS compatible 3D deposition via the well-developed ALD technique,[4] has initiated strong research efforts. However, until now, the electric field cycling behavior of this material class is not well understood. After the first cycles, an increase in remanent polarization—the so-called "wake-up" behavior—is often observed which saturates after a certain number of cycles.[5] Further field cycling causes a reduction of the ferroelectric response—the so-called fatigue—which is often terminated by the dielectric breakdown.[6] Manifold ideas were presented explaining all these phenomena such as a change in the crystallographic phase composition during cycling,[7–9] electron trapping,[10,11] and oxygen vacancy diffusion.[7,12] However, most of these approaches are based on a certain experimental result and the interdependencies between all mechanisms seem to be much more complex and require additional data. The field cycling phenomena were recently analyzed by Pešić *et al.*[7] An approach focused on simulation was taken in that work. So far, it seems to be well established that an initial internal bias field caused by unequally distributed charges locally inhibits the ferroelectric domains of both polarities from switching.[13] This causes a constriction of the ferroelectric hysteresis.[14] These local internal bias fields are reduced during field cycling which is caused by a homogenization of the charge distribution.[15] An additional phenomenon observed in all ferroelectrics is the imprint.[16] The imprint results from the increase in the mean internal bias field (averaged over the whole capacitor area) and manifests itself as a time- and temperature-dependent shift of the polarization-voltage (PV) hysteresis along the voltage axis.[17] This can induce a failure of the read out of the opposite state the ferroelectric memory device was stored in.

In this research, for the first time, we show that in hafnia based ferroelectrics, both phenomena—imprint and wake-up—can have the same root cause: The injection of electrons into the ferroelectric and the following trapping at oxygen vacancies into deep trap states. By the *in-situ* measurement of the time and temperature-dependent imprint of the hysteresis, we reveal that electron trapping is an important cause. Furthermore, by using a two-step waveform,[17] we are able to reset the film into a pristine-like state by generating two oppositely biased switching distributions. The field cycling behavior of these films shows wake-up-like behavior again. Charges trapped in defects result in a local shift of the coercive field and are therefore proposed to be the cause of the reduced ferroelectric response in the pristine state. This can be described as a local imprint effect.

II. EXPERIMENTAL

10 nm thick $Hf_{0.5}Zr_{0.5}O_2$ (HZO)-films were deposited in an atomic layer deposition (ALD) reactor using TEMA-Hf and TEMA-Zr at 260 °C and water as an oxygen source. The Hf:Zr pulse ratio was 1:1 to achieve the most homogeneous distribution of hafnia and zirconia in the film. TiN electrodes were deposited before and after ferroelectric deposition using reactive sputtering from a Ti-target as reported before.[18] To achieve crystallization, the metal-ferroelectric-metal capacitors were annealed at 600 °C for 20 s in a nitrogen atmosphere. After annealing, metal contacts consisting of 10 nm Ti as an adhesion layer and 50 nm Pt were deposited via electron beam evaporation through a shadow mask.

The TiN top electrode was etched between the metal contacts afterwards using a SC1 solution.[18]

The X-ray diffraction (XRD) analysis was done using a Bruker D8 Discover XRD tool with a Cu-Kα radiation of 0.154 nm wavelength and a fixed incidence angle of 0.45° for the 2Θ scan. The electrical characterization was performed on a Cascade Microtech RF Probe Station with a Keithley 4200 SCS and an aixACCT TF Analyzer 3000 measurement system.

III. RESULTS AND DISCUSSION

To characterize the crystal structure of the HZO films after annealing, grazing incidence XRD measurements were conducted. The resulting diffraction pattern (see Fig. 1) shows a high peak at about 30°. A closer analysis reveals that the films likely contain a high portion of the orthorhombic or tetragonal phase together with a small fraction of monoclinic grains (compare inset in Fig. 1).

To assess the ferroelectric endurance properties, the capacitor structures were cycled with 3 MV/cm using rectangular voltage pulses with 100 kHz. In between, the remanent polarization was measured using triangular voltage pulses with 10 kHz [see Fig. 2(a)]. The positive polarization state was achieved by applying a positive voltage to the top electrode, whereas the negative polarization state was achieved by applying a negative voltage to the top electrode while the bottom electrode remained grounded. Typical ferroelectric properties of the film were observed. The positive and negative remanent polarization of 10 μC/cm^2 in the pristine state increased during the first 10^4 cycles to 13 μC/cm^2. Further field cycling led to a reduction of the ferroelectric response, which corresponds to the fatigue phenomenon.

For the pristine state, the woken up state (after 10^4 cycles), and the fatigued state (after 10^8 cycles), capacitance-voltage (CV) measurements were conducted using an ac-signal of 70 mV and a dc bias ranging from −3 V to 3 V. As can be seen in Fig. 2(b), an asymmetry in the CV-hysteresis is

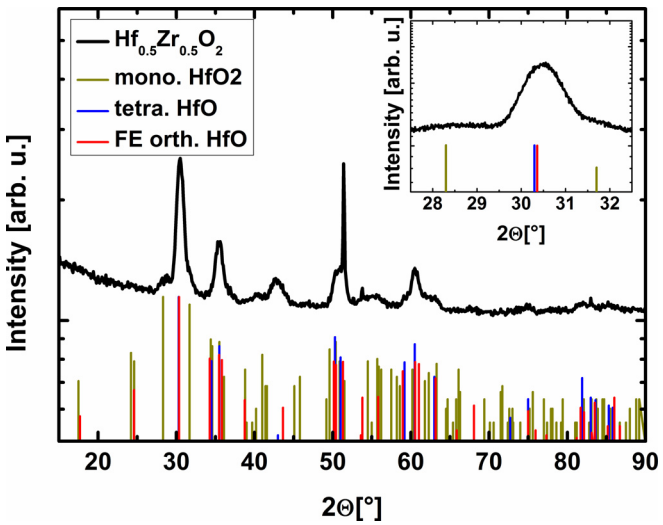

FIG. 1. Grazing incidence X-ray diffraction results for a 10 nm thick $Hf_{0.5}Zr_{0.5}O_2$ thin film capacitor. The inset shows a magnification of the peak at 30.5° including reference patterns. The abbreviation FE (ferroelectric) refers to the observed polarization behavior.

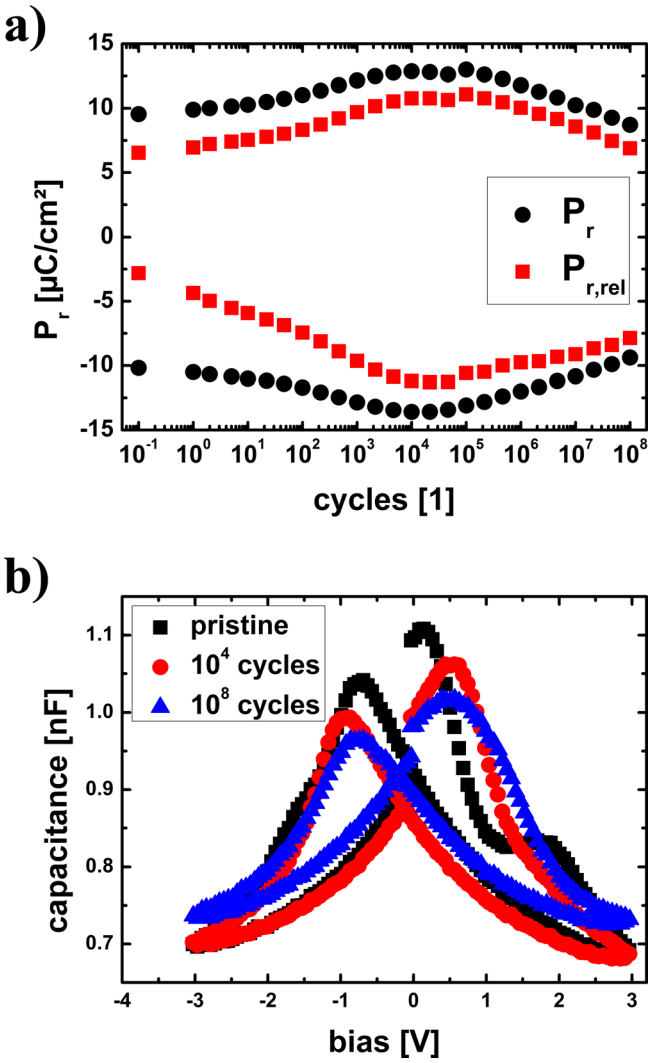

FIG. 2. (a) Evolution of the positive and negative remanent polarization (P_r) with electric field cycling using rectangular pulses with 3 MV/cm and 100 kHz for a 10 nm thick $Hf_{0.5}Zr_{0.5}O_2$ thin film capacitor. The hysteresis measurements in between cycling pulses were performed at 10 kHz. (b) Capacitance-voltage measurement in the pristine state, after 10^4 and 10^8 cycles as shown in (a) using 10 kHz with an ac-amplitude of 70 mV. Each data point represents the average of 100 single measurements.

present, which hints at the existence of an asymmetry in the stack as well. No significant change in capacitance for high fields at 3 MV/cm was observed during wake-up. The missing change in capacitance shows that either the contribution of the phase change to the increased polarization is very low or the involved phases have similar permittivities. Unlike for films doped, e.g., with Gd,[19] a strong contribution of the phase change is not expected for hafnia zirconia due to the wider process concentration window and the higher stability of the orthorhombic phase compared to other doped HfO_2 films. However, for the fatigued state, a clear increase in the capacitance can be seen. Two different mechanisms could be responsible: A partial phase change to the tetragonal phase[20] or the domain wall pinning mechanism.[21] During field cycling, the concentration of charged oxygen vacancies increases,[10] which can stabilize higher symmetry phases of hafnia.[22–24] This would lead to a higher permittivity, which increases the capacitance of the stack. However, it is also suggested that oxygen

vacancies accumulate at the grain boundaries in the fatigued state,[25] which might lead to domain wall pinning. These pinned domain walls bend during application of an external field causing an increase in capacitance as well.[21] Both mechanisms would reduce the ferroelectric switching density and could play a role during fatigue. More research has to be done, e.g., by a TEM analysis or microspot XRD to distinguish both effects.

With respect to the imprint mechanism, it is known that the shift of the hysteresis while storing in a specific polarization state is enhanced for woken up films.[17] During electric field cycling, the unpinned domains are oriented into one switching direction. The subsequent storage causes a shift of the whole hysteresis along the voltage axis—the imprint.[26] The reported dependence of the imprint on the temperature and time[17] showed a different slope of the hysteresis shift along the voltage axis as a function of time for room temperature compared to higher temperatures. However, the published extracted activation energy for the imprint in ferroelectric hafnia-zirconia films[17] contained an additional relaxation process and is therefore misleading: Since the sample was measured at room temperature after exposure to high temperature to determine the imprint, the thermal relaxation of defects also played a role. The extracted activation energy of about 1 eV therefore represents more likely the thermal relaxation activation energy for an electron in a doubly positively charged oxygen vacancy which has a similar value.[27]

To be able to extract the activation energy that is characteristic purely for the imprint process itself, we measured the shift of the coercive voltage V_C *in situ* at the respective temperature. To reach this result, TiN/HZO/TiN capacitors were preconditioned with 10^6 cycles at room temperature at 100 kHz and 3 MV/cm to achieve a woken-up state (compare Fig. 2). Subsequently, the sample was heated up to the desired temperature and then cycled again for 10^4 cycles to reset the already started imprint and shift the PV-hysteresis back into its initial position. Directly after cycling, a PV hysteresis measurement was conducted and repeated after a certain time delay. The imprint was then calculated from the shift of the PV hysteresis using the difference in coercive voltage of both measurements. This procedure was repeated for various times and temperatures. The corresponding measurement results are plotted in Fig. 3(a).

A clear shift of the hysteresis was observed for all temperatures. The direction of the shift to more negative voltages is typical for the sample in the positive polarization state while the shift towards more positive voltages would be expected for negatively polarized samples. Moreover, the slopes of the shift as a function of time in the Arrhenius plot of all temperatures were quite similar. Solely for room temperature, a slight remaining difference was observed. The obtained activation energies for the imprint were extracted as 0.099 ± 0.01 eV including the 25 °C data point and as 0.079 ± 0.003 eV excluding it [see Fig. 3(b)]. This points towards electrons as responsible charge carriers since activation energy is too low for ion diffusion.[28,29] This is in good agreement with thermally stimulated depolarization current (TSDC) results[10] which indicate that no oxygen vacancy

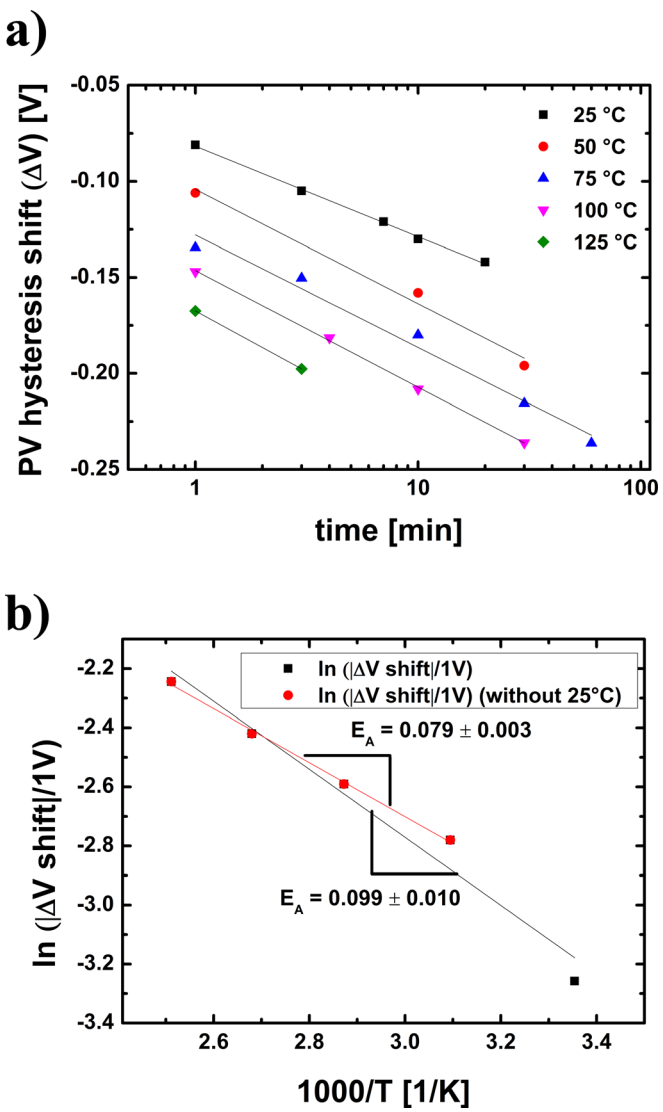

FIG. 3. (a) Voltage shift of the hysteresis as a function of temperature and time after pre-cycling the 10 nm thick $Hf_{0.5}Zr_{0.5}O_2$ film with 3 MV/cm at 100 kHz for 10^6 cycles. (b) Arrhenius plot of the hysteresis voltage shift after 10 min using the linear fits for the different temperatures from (a). The activation energies are extracted from the slope of the curves.

movement is present for temperatures below 100 °C even after application of high fields at room temperature.

Three possible main mechanisms are discussed in the literature as a cause for pinning of domains as it occurs during imprint: Volume effects, domain wall pinning, and seed inhibition. Volume effects describe the suppression of polarization in the ferroelectric by reorientation of polar lattice defects.[30] On the contrary, domain wall pinning and seed inhibition both describe the suppression of ferroelectric switching by blocking single domains. This occurs either at domain seeds (seed inhibition)[31] or at the domains walls (domain wall pinning).[21] Colla *et al.*[21] showed that it is possible to cause a strong reduction of polarization of PZT by cycling a sample with a two-step waveform [see Fig. 4(a)] that applies a voltage for 300 s which is close to the coercive field prior to switching. This method allowed distinguishing between domain wall pinning and the other two effects since it maximizes the number of domain walls. The same

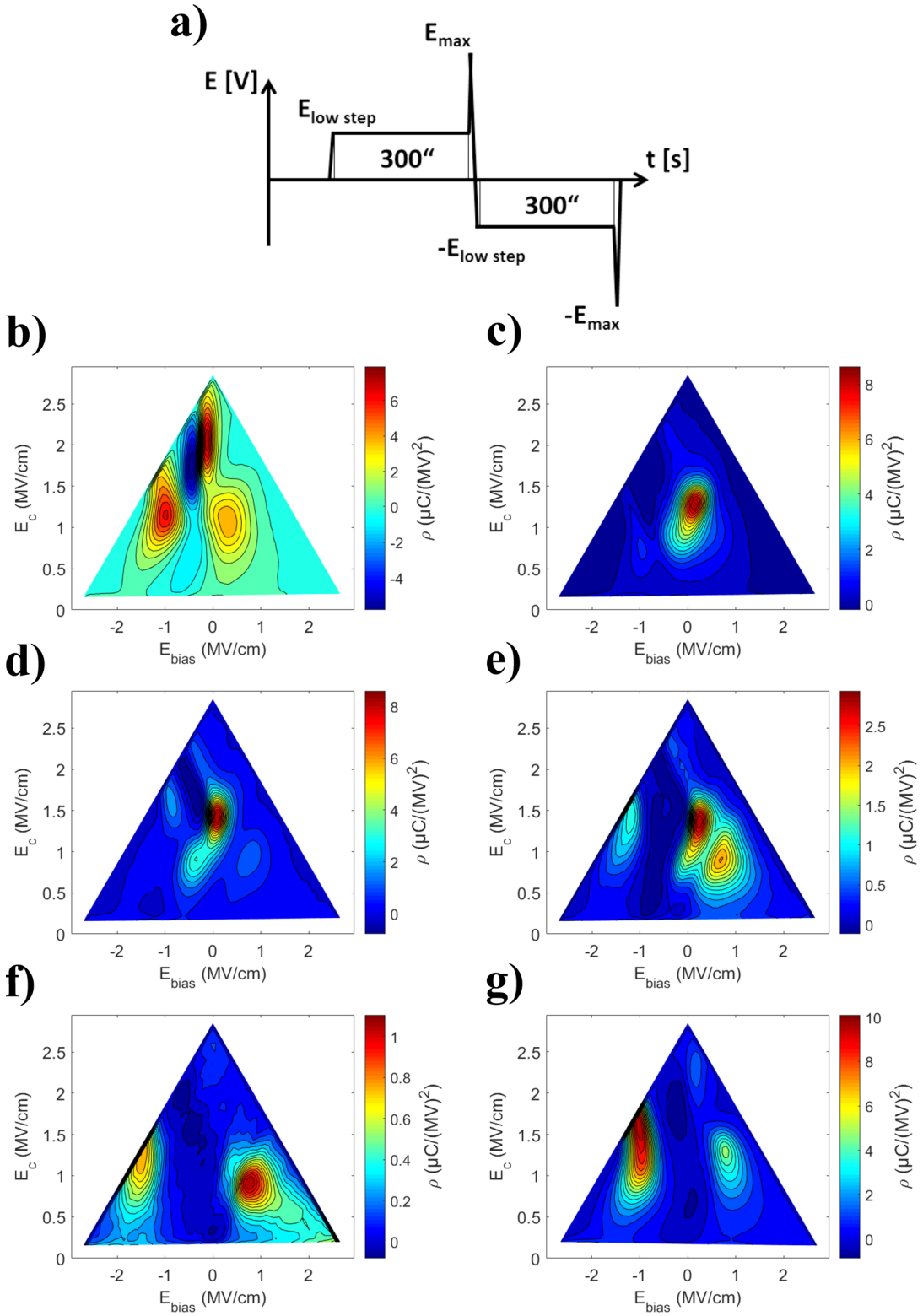

FIG. 4. Switching density distribution determined by FORC in a 10 nm thick $Hf_{0.5}Zr_{0.5}O_2$ film for the (b) pristine state and (c) woken up state after 10^6 cycles at 100 kHz with 3 MV/cm and 40 additional two-step cycles as shown in (a) and a 30 min bake at (d) 25 °C, (e) 125 °C, and (f) 200 °C. (g) Internal bias field distribution determined by FORC in the 10 nm thick $Hf_{0.5}Zr_{0.5}O_2$ film in the woken up state after 10^6 cycles at 100 kHz with 3 MV/cm and a single pulse with 3 MV/cm for 100 μs and with −1.2 MV/cm for 100 μs followed by a 30 min bake at 125 °C.

approach was recently applied to hafnia zirconia films by Fengler *et al.*[17] By using first order reversal curves (FORCs), which are related to the Preisach switching density,[32] it was possible to show that a split up of the switching density occurs which is caused by local internal bias fields. Due to the missing change in capacitance,[17] it can be assumed that seed inhibition or volume effects rather than domain wall pinning are dominating. Since the seeds can be located close to the electrodes or within a grain at inter-grain phase boundaries,[33] it is not possible to distinguish the effects further.

Considering the extracted activation energy of the imprint and the fact that both phenomena—the imprint and the wake-up—already occur at room temperature, it seems possible that the same mechanism can be responsible for both of them. During application of the low voltage step close to the coercive field, the domains with lower coercive field values are switched. This increases the chance to pin the domains in opposite directions. A local bias field is caused which shifts one half of the hysteresis towards negative and the other half towards positive fields resulting in the observed split up of the switching density. However, due to the applied field during the low voltage step, some domains remain unpinned or are sequentially unpinned, which explains the remaining portion of domains without bias field in the FORC distribution.[17]

To further analyze this assumption, the pristine films were pre-cycled for 10^6 cycles at 100 kHz with 3 MV/cm as shown in Fig. 2 to reach the woken up state. Subsequently, the two-step waveform as shown in Fig. 4(a) was applied 40 times using 3 MV/cm for the maximum field and 1.2 MV/cm for the low field step. In the last cycle, only the low positive field was applied to the capacitor to switch a portion of the domains into the opposite direction. The films were stored for 30 min at different temperatures, cooled down quickly to room temperature to measure the FORC distribution that can be compared to the one obtained before the treatment.

From Fig. 4(b), it is visible how the local internal bias fields of the pristine film diminish due to the electric field cycling into the woken up state [Fig. 4(c)]. The negative switching density and the positive values right next to them in the FORC distribution ($E_C \sim 2$ MV/cm) in Fig. 4(b) are a measurement artifact caused by a shift of one of the switching current peaks during the FORC measurement. The reason for this is that in the calculation of the FORC distribution, it is assumed that the switching current peaks do not shift during the measurement itself (see Ref. 15 for a detailed discussion of the FORC method). Nevertheless, all other FORC distribution peaks shown in Fig. 4 are related to the real response of the ferroelectric sample. After application of the two-step waveform, two local bias fields emerge [as shown in Fig. 4(d)]. These bias fields are strongly increasing with higher temperature during the bake [compare Figs. 4(d)–4(f)]. Clearly, it is visible how the remaining unpinned domains without bias field are imprinted with increasing temperature. Additionally, a capacitor was pre-cycled for 10^6 cycles at 100 kHz with 3 MV/cm as before. Instead of a two-step waveform, just a single sub-cycling pulse was applied: First, all domains were switched with 3 MV/cm for 100 μs in one direction and subsequently a portion was switched with −1.2 MV/cm for 100 μs into the opposite polarization state. Afterwards, the sample was baked as before for 30 min at 125 °C. Similar bias field distributions as for the case with the two-step waveform cycled capacitor were achieved. Due to the opposite polarity of the poling voltages, opposite portions of peak maxima for the negative and positive bias fields were achieved compared to the two-step measurements before. Since no additional pulses were applied (in contrast to the two-step cycling), the split up was much clearer and almost no domains without bias field were present, as can be seen in Fig. 4(g). The overall dependence of the bias fields on the baking temperature due to imprint shows strong similarities to the wake-up phenomenon. Using a bake at 200 °C for 30 min even causes the unpinned domain portions to merge with the already imprinted portion with positive bias [see Fig. 4(f)]. This bias field distribution is similar to the pristine distribution. However, it is not fully possible to go back into a truly pristine state due to the possibility that during field cycling, 90° domains might re-orientate.[33] This is possible since the *a*-axis and the *c*-axis of the unit cell have a similar length.[20] Therefore, a reorientation of domains without a significant volume change of the unit cell seems to be possible. In contrast, the local bias fields after the two-step waveform and the bake should contain highly oriented domains which are more strongly pinned.

To further assess the similarity between wake-up and imprint, capacitors that were backed for 30 min at 125 °C and 200 °C [as shown in Figs. 4(e)–4(g)] were cycled with 3 MV/cm at 100 kHz and the PV hysteresis was measured in

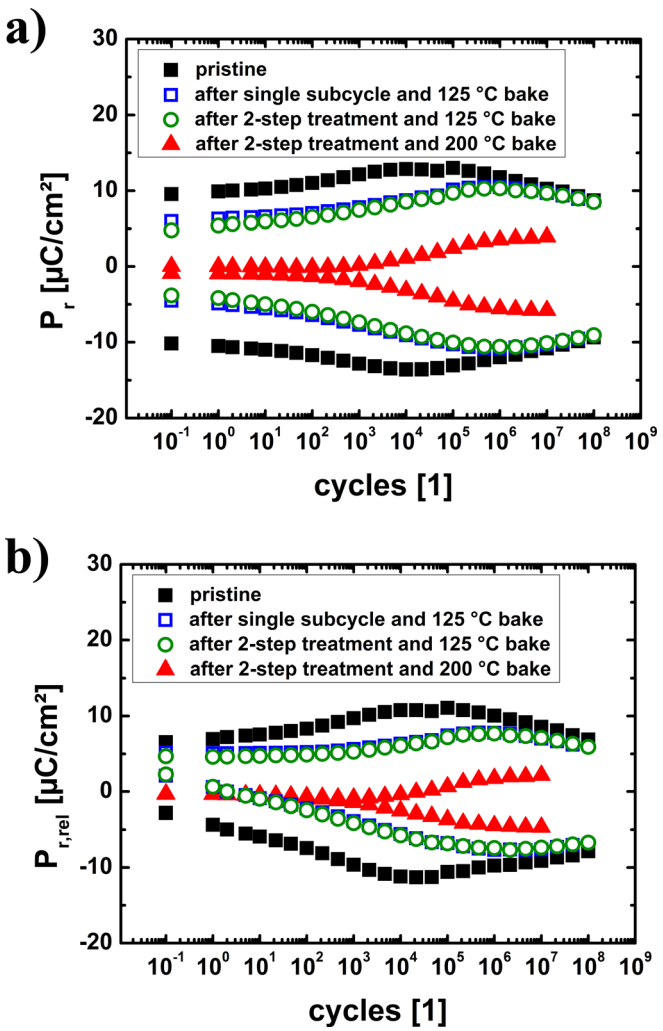

FIG. 5. (a) Evolution of positive and negative remanent polarization P_r and (b) of positive and negative remanent polarization after one second relaxation time $P_{r,rel}$ with electric field cycling using rectangular pulses with 100 kHz for 10 nm thick $Hf_{0.5}Zr_{0.5}O_2$ thin film capacitors and 10 kHz for hysteresis measurements in between cycling pulses of a prior pristine state and after 2-step treatment and subsequent bake for 30 min at 125 °C, 200 °C, and after single sub-cycling pulse and a subsequent bake for 30 min at 125 °C as shown in Fig. 4.

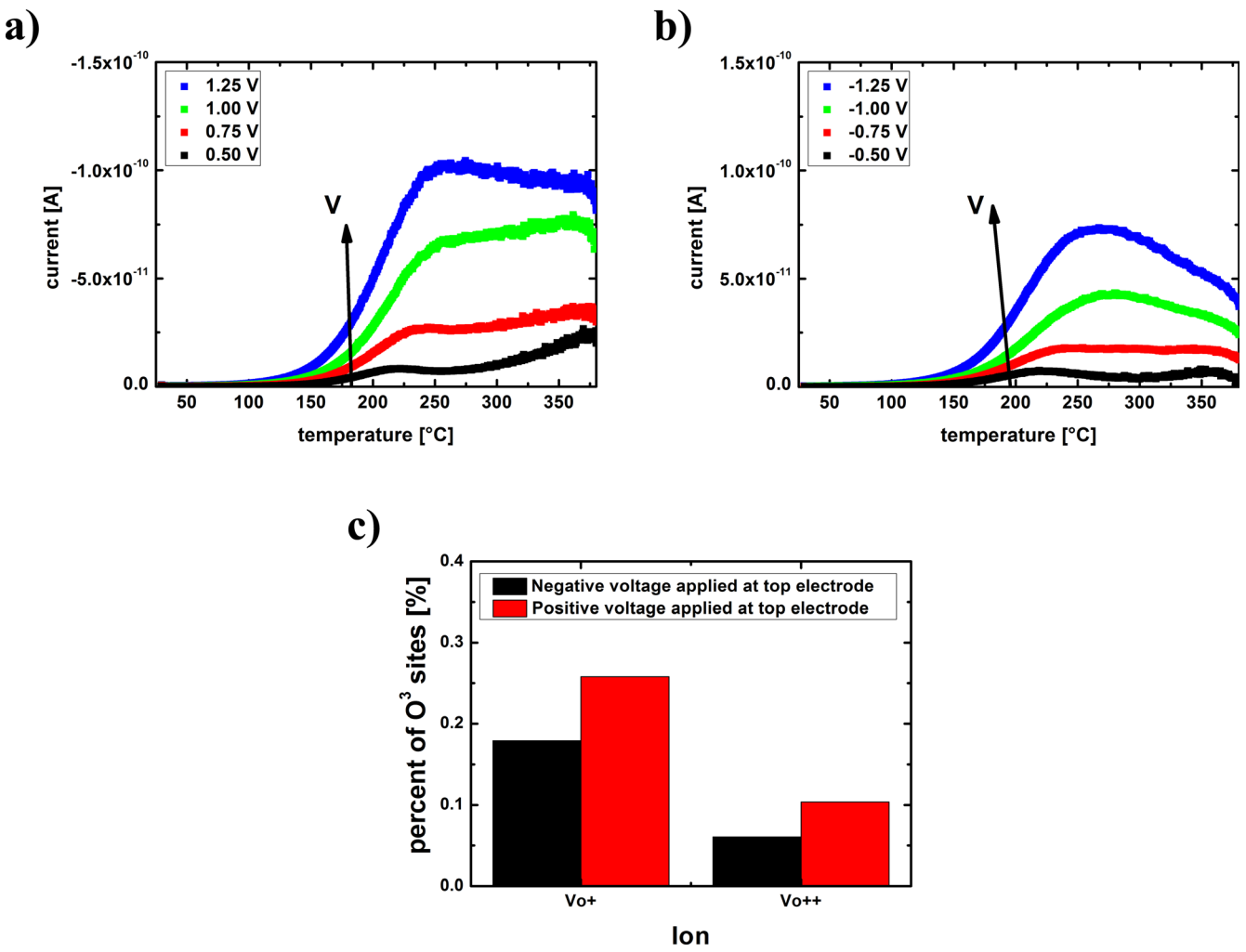

FIG. 6. Thermally stimulated depolarization current measurement of 10 nm thick TiN-$Hf_{0.5}Zr_{0.5}O_2$-TiN capacitors using a ramp rate of 0.2 K/s after poling with (a) voltages between 0.5 V and 1.25 V in steps of 0.25 V for 800 s at 380 °C and (b) voltages between −0.5 V and −1.25 V in steps of 0.25 V for 800 s at 380 °C. The different colors indicate the different polling voltages. (c) Extracted charged oxygen vacancies from (a) and (b) as percentage of the threefold coordinated oxygen atoms.

between with 10 kHz. The resulting remanent polarization as a function of the number of cycles is shown in Fig. 5(a).

Clearly, an inhibition of the ferroelectric switching can be observed for all samples. However, the effect is more pronounced for the "artificial" local bias fields generated by the single sub-cycling pulse and two-step treatment compared to the pristine film. The "artificial" wake-up or depinning effect is strongly dependent on the temperature as shown before (see Fig. 3). Almost no difference between the field cycling of the two-step and the single sub-cycling can be observed after a bake at 125 °C. As for the FORC distributions before, a strong temperature dependence of the local bias fields and therefore for the wake-up is observed. After the bake at 200 °C for 30 min, a very stable local internal bias field leading to a constricted hysteresis was observed during the first 10^2 cycles. In the literature, such behavior is sometimes misinterpreted as antiferroelectricity in the film. Here however, the origin clearly is a local internal bias field. The observed trapping mechanism is therefore definitely strong enough to cause a severe constriction of the PV hysteresis and the suppression of ferroelectric switching in the pristine state. Possible ways to distinguish between real anti-ferroelectrics and strongly imprinted ferroelectrics, as shown here, were recently discussed by Hoffmann *et al.*[34]

The remaining question, however, is where the defects are located which are acting as trapping centers for the imprint. To further analyze this, thermally stimulated depolarization measurements were conducted. To polarize the film, different bias voltages were applied ranging from 0.5 V to 1.25 V at 380 °C for 800 s. The sample was subsequently cooled down quickly during application of the same bias. By this procedure, possible diffused ions and charges are trapped into their spatial and energetic positions and permanent dipoles are reoriented. Then, by slowly heating up the sample with a heating rate of 0.2 K/s, the charges are detrapped, dipoles reoriented, and ions diffused back causing a current to flow which depends on energetic positions and concentrations. Although an exchange of oxygen with the atmosphere during the measurement is considered unlikely due to the top metal coating, every single measurement was conducted on a new small piece of the same film and a new capacitor to avoid any influence caused by possible film degradation. To subtract the pyroelectric current components

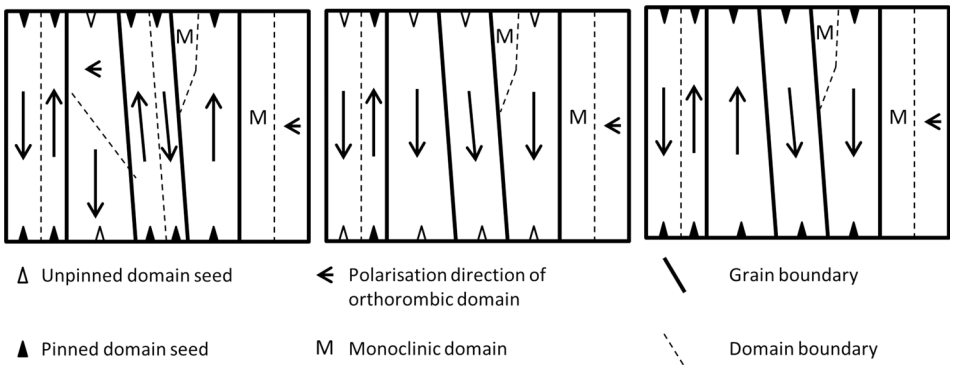

FIG. 7. Model for the different cycling states in hafnia-zirconia thin films: (a) pristine state—monoclinic phase portions present, which are not ferroelectric. Most domains are randomly oriented and domain seeds are pinned (b) woken up state—some monoclinic phase portions are still present. Domains are now more aligned, mostly unpinned, and poled into one direction as a result of the last switching. (c) Biased by imprint after wake-up due to sub-cycling. The domains are pinned again and oriented depending on their coercive voltage.

and disturbing signals caused by the heating circuit, this step was additionally repeated without prior poling. The resulting thermally induced current was subtracted from all shown results. The resulting thermally stimulated depolarization current as a function of the temperature [see Figs. 6(a) and 6(b)] reveals two strongly overlapping peaks with maxima at about 250 °C and 350 °C. Fengler *et al.*[10] already showed that the diffusion of singly and doubly positively charged oxygen vacancies can cause these peaks, whereas dipole reorientation or trapped charges as cause were excluded. It was also presented how to use the thermal cleaning method and estimate the amount of charged oxygen vacancies by fitting the dependence of the integrated charges on the applied poling voltage to a sinh function.[10]

The same method was applied to the 10 nm HZO films investigated here. Oxygen vacancy concentrations in a similar range of ∼0.2% for the singly and ∼0.1% for the doubly positively charged oxygen vacancies as a portion of the threefold coordinated oxygen atoms O^3 in the film were extracted as in Ref. 10. The fact that no significant oxygen vacancy diffusion was observed for temperatures below 100 °C under the measurement conditions [compare Figs. 6(a) and 6(b)] corroborates the assumption that ion migration is not the dominating factor for wake-up and imprint which occurs already at room temperature.[10]

Additionally, we measured the concentration of defects for both polarities of the poling voltage using the TSDC method and the described approach by utilizing a sinh fitting function. A higher amount of diffused charges was observed for positive voltage at the top electrode compared to a negative voltage. Since a positive voltage should repel the positively charged oxygen vacancies, this might hint at a higher concentration of the oxygen vacancies at the top electrode.

This is in good agreement with the observed asymmetry in the CV-measurements [compare Fig. 2(b)] and earlier publications claiming that an asymmetry should be caused by a stronger oxidation of the bottom electrode during the ALD compared to a minimal oxidation of the TiN top electrode during the crystallization anneal process.[35] During the high temperature anneal, the chemical reduction of the HZO is expected to generate a lower amount of oxygen vacancies at the bottom interface compared to the top interface.[36]

To describe our experimental results, the model illustrated in Fig. 7 is suggested for the imprint and wake-up phenomenon in hafnia zirconia thin films.

Pristine State: The ferroelectric phase portion contains 90° and 180° domains with partly pinned domain seeds depending on the fabrication conditions like anneal, etc.[6,10] Due to the different orientations of grains, different orientations of domains within the sample are present. Different phases coexist depending on the processing conditions.[6,23]

Woken up: With electric field cycling, the domain orientations align and the domains are unpinned.

Imprinted: The aligned domains are pinned again due to pinned domain seeds and local internal bias fields emerge. Depending on the pinned domain orientation, the bias field can be positive or negative.

IV. CONCLUSION

The field cycling behavior of ferroelectric hafnia zirconia films was analyzed. During field cycling, typical wake-up and fatigue behavior was observed. The negligible change in the dielectric constant of the films with cycling suggests that during the wake-up, no pronounced phase change into a phase with a significantly different permittivity occurs. On the other hand, the capacitance change during fatigue remains unclear making the interpretation of the capacitance values without further structural or electrical data rather speculative. Due to an increased capacitance of the film, a phase change or a domain wall pinning is suspected. However, an asymmetry was observed in the capacitance-voltage curves, which hints towards an electrode dependent asymmetry in the capacitor stack. The analysis of the dependence of the thermally stimulated depolarization currents might point to a higher oxygen vacancy concentration at the top electrode compared to the bottom electrode; however, further analyses with other characterization techniques are necessary to confirm these data. An improved approach to investigate the cause of imprint showed, however, that electron trapping at the defect sites—most likely oxygen vacancies—takes place. By application of a two-step waveform and a subsequent bake, we show that a similar state as the pristine one can be caused by just splitting up the domains

and imprinting them into different directions. A similar situation is most likely the cause of the constricted hysteresis in the pristine state. Additionally, it was shown that the anti-ferroelectricity of hafnia films must be analyzed in detail to not confuse it with a strong imprint mechanism.

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