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**Structural Changes Underlying Field-Cycling Phenomena in Ferroelectric HfO 2 Thin Films**

*Everett D. Grimley , Tony Schenk , Xiahan Sang , Milan Pešic´ , Uwe Schroeder , \* Thomas Mikolajick , and James M. LeBeau \**

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| **Since 2011, ferroelectric HfO 2 has attracted growing interest in both funda-mental and application oriented groups. In this material, noteworthy wake-up** | of crucial relevance for the performance of ferroelectric memories. [ 12,13 ] The phe-nomenon of wake-up refers to the tran- |
| **and fatigue effects alter the shape of the polarization hysteresis loop during fi eld cycling. Such changes are problematic for application of HfO 2 to fer-roelectric memories, which require stable polarization hystereses. Herein, electrical and structural techniques are implemented to unveil how cyclic** | sition from a pinched hysteresis with a low remanent polarization *P*r to an open (depinched) hysteresis during a certain amount of initial switching cycles. Internal bias fi elds [ 12 ] have recently been shown to |

**switching changes nanoscale fi lm structure, which modifi es the polarization hysteresis. Impedance spectroscopy and scanning transmission electron microscopy identify regions with different dielectric and conductive proper-ties in fi lms at different cycling stages, enabling development of a structural model to explain the wake-up and fatigue phenomena. The wake-up regime arises due to changes in bulk and interfacial structuring: the bulk undergoes a phase transformation from monoclinic to orthorhombic grains, and the interfaces show changes in and diminishment of a nonuniform, defect rich, tetragonal HfO 2 layer near the electrodes. The evolution of these aspects of structuring contributes to the increase in *P*r and the opening of the con-stricted *P* – *V* hysteresis that are known to occur with wake-up. The onset of the fatigue regime is correlated to an increasing concentration of bulk defects, which are proposed to pin domain walls.**

account for this behavior and have been speculated to be caused by charged oxygen vacancies at top and bottom electrodes. [ 5,7 ] The phenomenon of polarization fatigue is characterized by a gradual decrease in *P*r with continued application of switching cycles beyond wake-up. [ 14,15 ] Despite the importance of these phenomena, they have yet to be thoroughly explained for these rather new ferroelectrics. To address this lack of understanding, we chose a combined approach of sophisticated elec-trical and structural analysis. We report the fi rst impedance spectroscopy meas-urements of ferroelectric-doped HfO 2 thin fi lms using TiN-Gd:HfO 2 -TiN metal–fer-roelectric–metal (MFM) capacitors at dif-ferent stages of cycling lifetime. These

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| **1. Introduction** | fi ndings are then correlated to aberration-corrected atomic-resolution scanning transmission electron microscopy (STEM) |

Research on ferroelectric thin-fi lm HfO 2[ 1 ] continues to mature with details of its rich science and functionality beginning to emerge. Though many recent studies have sought to examine general principles of ferroelectricity and stability of various

measurements. Direct evidence for the evolution of multiple aspects of fi lm structure during fi eld cycling is shown to underlie the observed electrical behavior.

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| HfO 2 phases, [ 2,3 ] perhaps preeminent among the current research efforts of HfO 2 thin fi lms is the investigation of the “wake-up” and “fatigue” effects, [ 4–11 ] as both phenomena are | **2. Results** |

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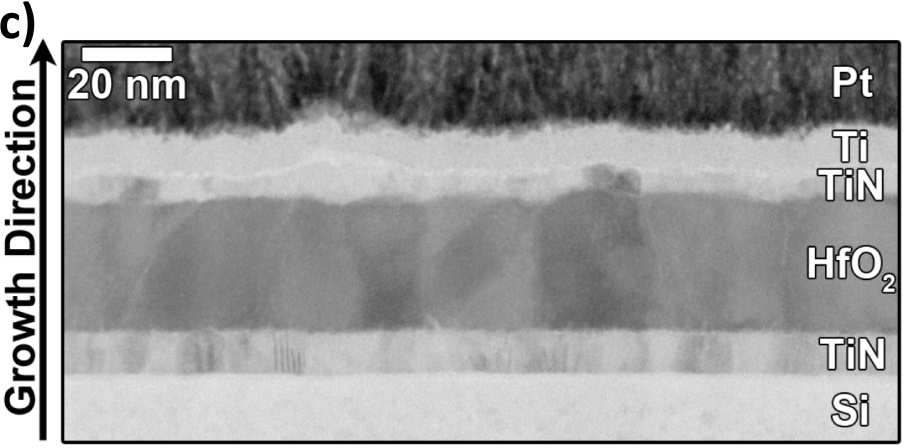
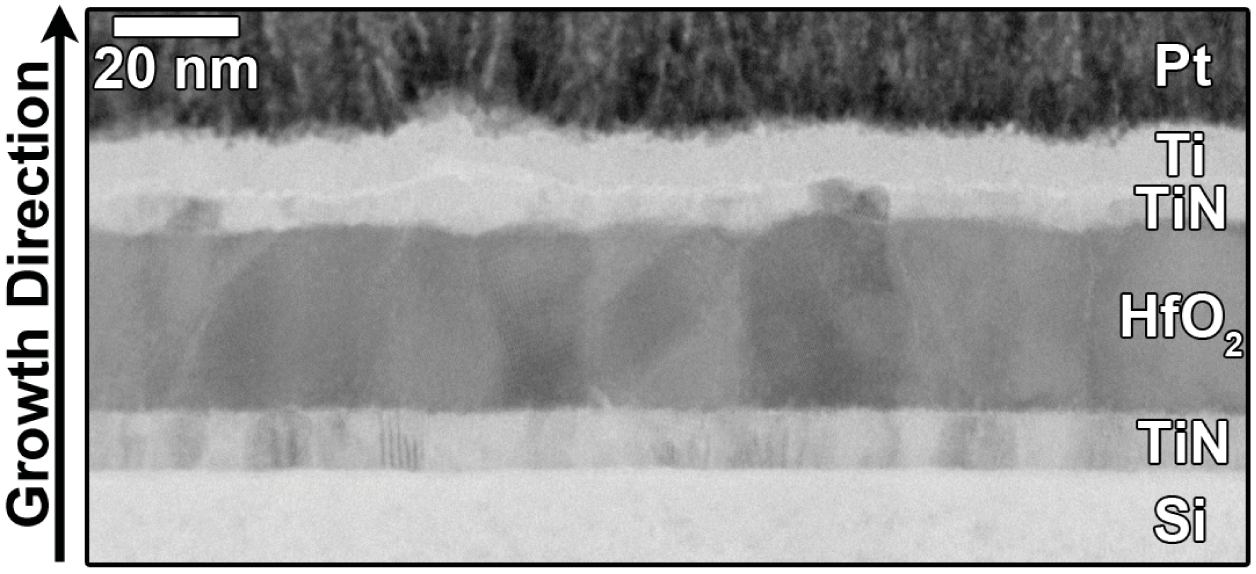
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The electrical response of the Gd:HfO 2 MFM capacitors exhibits typical behavior of HfO 2 ferroelectrics. **Figure1** a shows the manifestation of both wake-up and fatigue in the polari-zation hysteresis whereas Figure 1 b depicts the evolution of *P*r throughout the course of continuous fi eld cycling. Besides the aforementioned changes in the polarization–voltage ( *P* – *V* ) hysteresis (loop opening and *P*r increase followed by a decrease in *P*r ), the slopes of the saturated hysteresis branches hint at changes in relative permittivity of the fi lm. These changes become even more apparent when measuring the small-signal capacitance as a function of applied bias voltage. As expected from the *P* – *V* hysteresis, the peaks in the butterfl y-like hyster-esis in relative permittivity εr that result from additional domain wall capacitance during polarization switching [ 16 ] fi rst increase

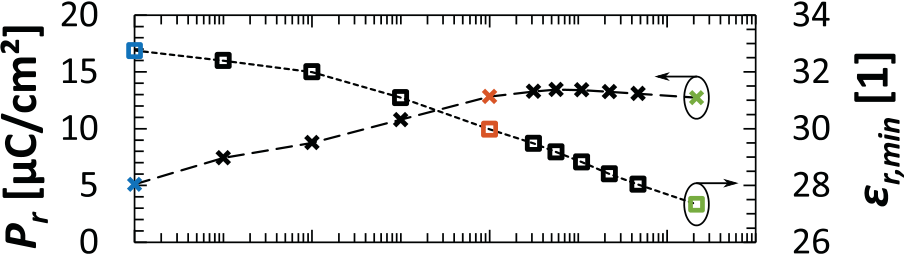
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|  | during wake-up before decreasing upon further cycling. Inter- |
| estingly, the minimal relative permittivity εr*,*min outside these |
| regions, which represents only the dielectric contributions (no |
| domain walls present), exhibits a steady decline from around |
| 33 to 27. Since this value is coupled to the phases present in |
| the polycrystalline fi lm (Figure 1 c), the question arises whether |
| phase fractions in the bulk and/or at the electrode interfaces are |
| subject to a continuous change during fi eld cycling. For com- |
| parison with the data in Figure 1 a,b, different hafnia phases |
| with their corresponding relative permittivities are shown in |
| Figure 1 d. From the change in these values, the trend in rela- |
| tive permittivity seems to suggest a change from predominantly |
| tetragonal/cubic phases toward predominantly orthorhombic/ |
|  |  | monoclinic phases. It should be noted, however, that a signifi - |
| cant polarization is still present in the fi lm even after the εr*,*min |
|  | dropped to 27. Moreover, judging solely from published X-ray |







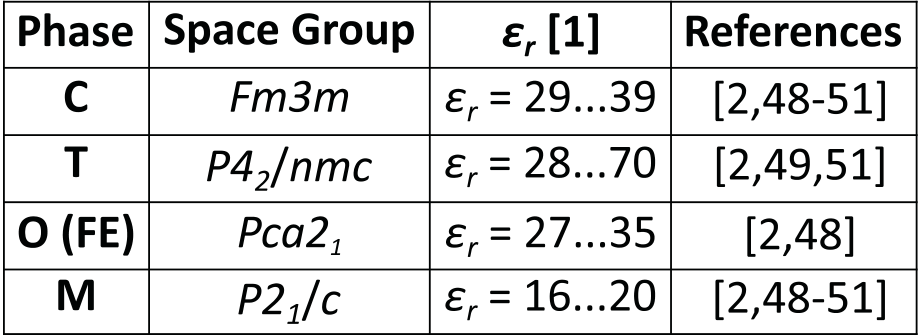


diffractograms of this sample, [ 3,17 ] a predominantly monoclinic to orthorhombic character can be inferred for the pristine case. This seems to partially contradict the electrical results and man-dates clarifi cation.

To elucidate the origin of these changes in permittivity, impedance spectroscopy was performed. Impedance spectros-copy provides the potential to identify structural inhomogenei-ties and their evolution via frequency-dependent small-signal measurements of the complex impedance *Z* (*Z* = *Z*′ −*Z*′′). [ 18 ]

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|  |  |  |  | Bulk ceramics, for which this technique is frequently used, are |
|  | | often represented by parallel arrangements of a capacitance *C* |
| and a resistance *R* (an *RC* element) to account for the dielec- |



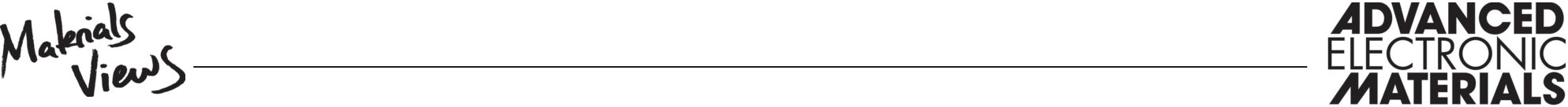
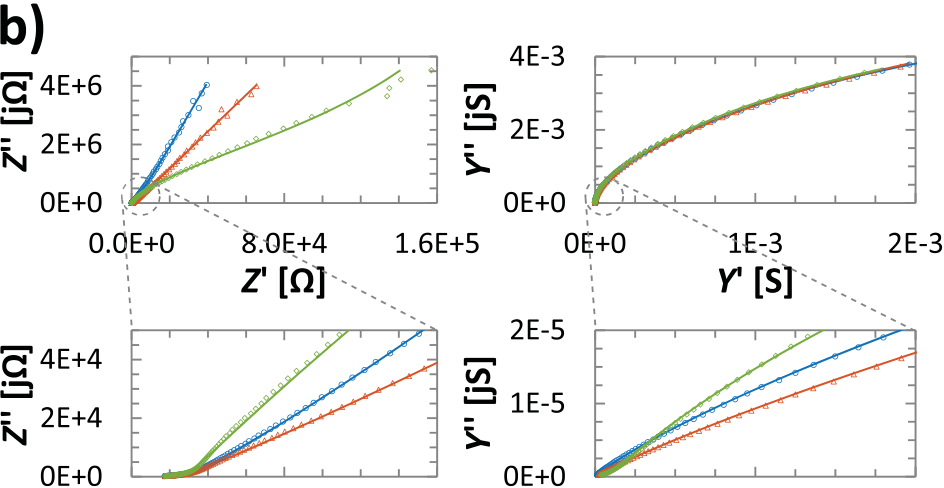


**Figure 1.**  a) Hystereses of polarization *P* (dotted lines) and relative permittivity εr (solid lines) for the three different regimes: pristine (0 cycles), during wake-up (1000 cycles), and during fatigue (215 000 cycles); b) the evolution of remanent polarization *P*r and minimum rela-tive permittivity εr*,*min versus number of switching cycles; c) a bright-fi eld STEM image of the complete fi lm stack; and d) literature values of εr for the ferroelectric (FE) orthorhombic (O) *Pca2* 1and the paraelectric mono-clinic (M) *P2* 1 */c* , tetragonal (T) *P4* 2 */nmc* , and cubic (C) *Fm3m* phases. The corresponding εr spans derived from the data in (d) are marked in (a) for comparison.

tric properties and fi nite conductivity (i.e., nonideal insulating capabilities), respectively. In series with this *RC* element, an additional resistance contribution is usually included to rep-resent uneliminated resistances of the electrodes, the elec-trode interfaces, the cables/contacts, and parasitic elements of the measurement setup. In the Supporting Information S1, a more exhaustive description of this very basic equivalent cir-cuit and its refl ection in the frequency-dependent behavior of the measured impedance is provided. In contrast to mm-thick ceramics, [ 18 ] grain boundaries are not expected to necessitate a second *RC* element in series to the fi rst one. As Figure 1 c shows, grains span the whole fi lm thickness and should, from a physical point of view, give rise to an *RC* element in parallel to the *RC* element of the grains. However, from a mathematical point of view, the two parallel resistances and two capacitances could be condensed into one *R* and one *C* , respectively. A unique best fi t for the two *R* and two *C* elements is impossible as it is an underdetermined system. Thus, also for thin fi lms, the mod-elling strategy does not change and series arrangements of *RC* elements are primarily used and then later on assigned a phys-ical meaning in all conscience. Differences in interface and bulk properties, for example, can explain the necessity of two or more *RC* elements in series. The sample studied in this work requires an equivalent circuit of three *RC* -like elements and one series resistance *R 4*to adequately fi t the measured imped-ance results shown in **Figure2** a,b (for a mathematical descrip-tion: see Supporting Information S2). These *RC* elements and the parts of the fi lm stack they represent are derived in the fol-lowing. The fi rst *RC* element consists of an ideal capacitance *C*1 and a resistance *R*1 , with the latter being orders of magni-tude too large to be properly fi t within the accessible frequency

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| **www.MaterialsViews.com** | **www.advelectronicmat.de**  the TiN itself. It can be explained by a TiO *x*N *y*interfacial layer formed during the deposition and subsequent annealing pro-cess [ 25–27 ] or a partial oxidation of the Ti adhesion layer below the Pt pad. Despite the high ratio of roughness to thickness anticipated for an interfacial TiO *x*N *y*, this electrode-like layer does not require a CPE for a proper fi t. Existence of an interfa-cial TiO *x*N *y*electrode interfacial layer of ≈1 nm thickness would result in εr≈ 6 for all three stages of fi eld cycling. The scenario of an interfacial layer with such a low permittivity combined with a high uniformity in dielectric and resistive properties is, thus, unlikely. Instead, assuming a layer thickness of ≈10 nm as would be the case for a partially but uniformly oxidized TiN or Ti layer, the permittivity would be around 60, which is in the |
|  | range of what has been reported for TiO 2 . [ 28 ] Comparing the remaining parameters to the actual fi lm, we see that the high resistance *R*1 together with a capacitance *C*1≈ 1 nF (resulting εr≈ 30) is exactly expected from the capacitor geometry and the bulk of the thin fi lm. Thus, the second *RC* -like element has also  to be in a thickness range of an interfacial-like layer, but still possesses notable insulating properties with *R*2≈ 10 5 –10 7Ω. Assuming ≈1 nm interface thickness, *Q*2 results in a relative permittivity on the order of that of the bulk dielectric layer for |







a frequency of 10 kHz. **Figure3** summarizes the equivalent circuit with extracted fi t parameters at different stages of fi eld cycling and the concluded counterparts for each element in the physical fi lm stack. From this overview, some trends can be identifi ed:

1. The resistance of the electrode-like layer ( *R*3 , *C*3 , *R*4 ) does not change substantially. A drop of the capacitance occurs during the wake-up stage. No CPE was needed to fi t the data.

2. The capacitance *C*1 of the bulk layer remains nearly constant during wake-up, but drops by 20% during fatigue. A look at Figure 1 a reveals the problem arguing with these values: At 0 V, they are superimposed by domain-wall contributions (peaks of the butterfl y like curve). Moreover, impedance

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|  |  |  |  |  |  | spectroscopy is not able to account for the evolution of the |
| exceedingly large *R*1 . However, the static leakage current |
|  |  |
| measurements (see Supporting Information S4) suggest a re- |

**Figure 2.**  Results of impedance spectroscopy: a) logarithmic Bode plots of impedance *Z* with arrows indicating the dominant *RC* elements in the respective *f* range and admittance *Y* (inset); b) Nyquist plots of imped-ance as well as admittance in both full scale and magnifi ed sections to demonstrate the high quality of the fi t throughout the whole frequency spectrum.

range. The second *RC* -like element consists of a fi nite resistance *R*2 and a constant-phase element (CPE) *Q*2 , which can be con-sidered as a nonideal capacitance. A wealth of potential sources for such nonideal capacitance behavior have been found previ-ously including fi lm roughness [ 18 ] as well as inhomogeneities in resistivity and/or permittivity (distributed in-plane and/or normal to it), [ 19–24 ] which are all possible explanations for pre-sent sample. Finally, the third *RC* element is given by another ideal capacitance *C 3*and a resistance *R 3*on the order of 100 Ω, which is similar to the series resistance *R 4*. Thus, it is likely that this third *RC* element is more refl ective of a nonideal electrode than of a real capacitance, and it therefore likely stems from the interface of TiN to HfO 2 or imperfect electrode-behavior of

sistance degradation of this thickest layer by at least one order of magnitude for the fatigued sample.

3. The dielectric interfacial layer is subject to notable changes of both resistance and permittivity. Its resistance (both the *R*2 and the real *Q*2 contribution) increases during wake-up, which hints on a reduction in the number of defects, but it then drops by two orders of magnitude during fatigue.

Interestingly, *n* (exponent of the constant phase element) in-creases continuously from about 0.87 via 0.91 to 0.93, which represents a decrease in inhomogeneity.

These results also highlight the importance of checking a broad frequency spectrum when arguing with permittivity data, i.e., for temperature-dependent measurements to inves-tigate phase transitions. In the present case, the frequency of 10 kHz falls in a range which does not predominantly refl ect the dielectric properties of the ferroelectric bulk.

To help explain the impedance spectroscopy and elec-trical measurements, aberration-corrected STEM was con-ducted on Gd:HfO 2 capacitors in pristine (0 cycles), woken-up

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|  | by the increased probability of including defects that result in |
| dielectric breakdown after only a few cycles or a short of the |
|  | capacitor from the start. Furthermore, the spatial resolution of |
| STEM enables direct interrogation of the interfacial structure, |
| which is critical to help interpret the impedance spectroscopy |
| results. |
| Through observation of multiple regions in each sample, |
| all three samples are found to be polycrystalline containing |
| orthorhombic and monoclinic grains of various sizes, including |
| many grains that span the entire fi lm thickness in the direc- |
| tion of growth (such as in Figure 1 d). Phase fractions are |
| determined by identifying phases in a region with high magni- |
| fi cation images and measuring the grain areas from lower mag- |
|  |  | nifi cation images. An example of this process is included in the |
| Supporting Information S6. Nine regions in both the pristine |
| and woken-up samples and eight for the fatigued are suitable |
| for phase fraction measurement. From pristine to woken-up to |
| fatigued stages of fi eld cycling, the presence of the monoclinic |
| phase decreases from roughly 90% to 20% and fi nally to 10%, |
| respectively. The remaining regions are all orthorhombic. The |
|  | STEM phase measurements have estimated error of ±10% to |
| the reported phase fractions (limited by STEM sampling and |
| challenges in measuring area due to grain overlap, localized |
| tilting, etc.). Hence, the phase fractions of the woken-up and |
| fatigued samples are within error of each other. Measurement |
| of phase fraction using a histogram “counting” method by tal- |
| lying the zone-axis/phase combinations from the different |
| regions yields phase fractions which are in good agreement |
| with the values and trends of the area measurements. Further |
| information on this alternative measurement are presented in |
| Supplementary Information S6. Though the above phase frac- |
| tion assessments approach the limits of what STEM can pro- |
| vide in terms of statistics, it remains a competitive and realistic |
| approach especially without easy alternative at hand. Further- |
| more, the reliability of the phase fraction results is augmented |
| by its good agreement with the fi ndings of the global technique |
| impedance spectroscopy as will be described later. Lastly, it is |
| worth noting that while the polarity of each orthorhombic grain |

**Figure 3.**  Film stack with corresponding equivalent circuit and model parameters used to fi t the impedance spectra presented in Figure 2 . Rela-tive standard deviations of all fi t parameters are 10 −4 or below.

(1000 cycles), and fatigued (after onset of fatigue, see Figure 1 b; 215 000 cycles) states to gain insight into any changes in struc-ture that occur with fi eld cycling. These numbers of cycles were chosen in compromise between a best possibly saturated hys-teresis (amount of domains taking part in the switching) and low enough fi eld to avoid an early dielectric breakdown of the lab-scale capacitor stack. The incoherent imaging afforded by high-angle annular dark-fi eld (HAADF)-STEM enables direct visualization of atomic arrangements, which is suffi cient to distinguish crystal structures. While STEM is limited in its sampling capabilities, it is uniquely situated over conventional techniques such as X-ray diffraction (XRD) to address changes in HfO 2 structure with fi eld cycling. Since the target regions in the present sample are cycled HfO 2 areas beneath top electrode pad of a few hundred µm width, they are spatially too small for common XRD without special microspot optics. The use of pad-diameters in the millimeter or centimeter range is hampered

was not sampled individually in this work, it is a safe inference that many of the orthorhombic grains generated by fi eld cycling here are polar. The *P*r increased with cycling suggesting genera-tion of polar grains, and polar orthorhombic grains have been previously isolated in these fi lms. [ 17 ]  
 In addition to changes in bulk structure, complex changes particular to the interfacial HfO 2 layers occur with fi eld cycling. For the pristine Gd:HfO 2 , some grains exhibit a noticeable transition into tetragonal phase directly adjacent to TiN elec-trodes ( **Figure4** a). These regions are regularly between half a unit cell to several unit cells thick and they abruptly relax into the bulk monoclinic or orthorhombic phase. These regions are expected to be stabilized by and relate to the defect concentra-tion and strain environment at the interfaces as will be further considered in the discussion. In contrast to the pristine sam-ples, woken-up (Figure 4 b) and fatigued (Figure 4 c) Gd:HfO 2 samples exhibit changed and possibly diminished interfacial tetragonal regions, and their presence is often more subtle as they commonly retain some of the symmetry and spacing of the bulk grains. More STEM images of the interfaces can be found in the Supporting Information S5. Changes in this interface

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| **www.MaterialsViews.com** | **www.advelectronicmat.de**  fi t, which suggests the absence of such a layer. Furthermore,  electron energy-loss spectroscopy (EELS) found oxygen in the ≈10 nm thick Ti adhesion layer beneath the Pt electrode (Sup-porting Information S9), suggesting partial but uniform oxida-  tion of the Ti into TiO *x*. Thus, impedance spectroscopy suggests that the equivalent circuit elements *R*3 , *C*3 do not stem from a thin interfacial TiO *x*N *y*layer and EELS shows oxidation of the Ti adhesion layer into TiO *x*.  More importantly, interfacial changes do occur in the thin  dielectric layer comprising circuit elements *R*2 and *Q*2 , and these changes originate from a strained and defective dielec-  tric interfacial layer of tetragonal HfO 2 . The tetragonal phase and the related strained region appear to change and diminish |
|  | during fi eld cycling. Impedance spectroscopy reveals that the resistance of this layer increases during wake-up (both in *R*2 and *Q*2 contribution), although the thickness decreases. This hints on a reducing number of defects in the layer counter-acting and surpassing the effect of physical thickness reduction. Defects can enhance both the charge carrier transport through and the injection of carriers into the dielectric fi lm. [ 29–31 ] This was shown in earlier studies for similar fi lms. [ 11 ] Adjacent to an oxidized electrode, these defects are likely to be charged oxygen vacancies (O ions scavenged from the HfO 2 fi lm). The nonuni-form lateral distribution of this tetragonal, defect-rich interface layer in the pristine sample, explains the observed constricted hysteresis, which is known to result from internal bias fi elds (for a detailed illustration, see Supporting Information S8). [ 12 ] A uniform charge accumulation at one electrode can result in a so-called imprint, [ 13,32,33 ] as was observed by Lomenzo et al. [ 7 ] for a pristine Si:HfO 2 sample with TaN electrodes. Since oxygen vacancies stabilize the tetragonal compared to the monoclinic bulk phase, [ 3 ] the result of tetragonal regions being defect-rich and thus, charged regions is plausible. A recent simula-tion approach [ 11 ] and other studies on hafnia [ 34,35 ] also support a redistribution of interfacial oxygen vacancies during fi eld |

**Figure 4.**  Tabulated monoclinic (M) and orthorhombic (O) phase frac-tions measured from the pristine, woken-up, and fatigued samples together with corresponding remanent/maximum polarization *P*r / *P*max values. HAADF-STEM images show that the interfacial HfO 2 layer under-goes complex changes in interfacial strain and phase presence with fi eld cycling, including some reduction of the presence of the tetragonal phase in the cycled (woken-up and fatigued) samples compared to the pristine. Lattice parameter maps from these regions further highlight the complex interface environments and assist in visualizing strain and phase pres-ence (color-scale ranges set manually to better visualize details).

structure with cycling is likely driven by defect redistribution and phase change/orientation change of grains which both alter the strain environment and occur with fi eld cycling. [ 11 ]

**3. Discussion**

Combining the electrical and structural fi ndings, the following pictures of interfacial effects and bulk effects that change with fi eld cycling can be identifi ed. Beginning with the electrode-like layer (circuit elements *R*3 , *C*3 , and *R*4 ), existence of an inter-facial TiO *x*N *y*layer with a high ratio of surface to roughness would necessitate inclusion of a CPE element to properly fi t the impedance data. This, however, is not needed for the current

cycling in similar fi lms. Moreover, a templating effect by the pre-deposited crystalline TiN electrode on the anneal of amor-phously deposited Gd:HfO 2 fi lms should be considered. During the subsequent anneal, the HfO 2 likely starts crystallizing beginning at the electrode interfaces with a structure more compatible to the cubic TiN lattice which then relaxes after the strain relaxes away from the interface. Evidence of an orienta-tion relationship was found in STEM, and can even be seen in the pristine sample in Figure 4 . Moreover, fi rst principles studies have explored the nuances of formation of higher sym-metry phases (i.e., orthorhombic, ferroelectric orthorhombic, and or tetragonal), fi nding that strain and surface energy effects play a crucial role in stabilizing them over the monoclinic phase. [ 2,36,37 ] The presence of an interfacial layer that is involved in the wake up process is consistent with recent electrical work on Hf 1-*x*Zr *x*O 2 . [ 9,10,38 ]  
 Finally, for the bulk of the fi lms (circuit elements *C*1 and *R*1 ) a transformation from monoclinic to orthorhombic phase HfO 2 is found. Only 10% of the grains were orthorhombic in the pristine sample, but remanent and maximum polarization are found to be 40% and 70% of the value after 1000 cycles, respectively (see Figure 4 ). This strongly suggests that part of the transfor-mation already took place during the very fi rst *P* – *V* measure-ment (see Supporting Information S7 for further insights into

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| the evolution of the fi rst *P* – *V* hysteresis loops and XRD data). | **4. Conclusion** |
| The similar amount of orthorhombic phase found during wake- |
| To summarize, we present work that synergizes the global |
| up and fatigue is consistent with Figure 1 b indicating that the |
| present domains get stuck after the maximum *P*r was reached | impedance spectroscopy technique with the site specifi c and |
| around 5000 cycles. Of course, besides the mentioned limita- | in-depth structure analysis afforded by HAADF-STEM. Com- |
| tion of sampling of the STEM approach, texture might serve to | bined, the two provide insight into the evolution of structure |
| hamper quantitative statements. Texture also needs to be con- | that underlies wake-up and fatigue in FE HfO 2 thin fi lms. This |
| sidered when interpreting former results of microspot XRD in | evolution was separated into bulk and interface changes. The |
| Bragg-Brentano geometry, which did not give strong indications | wake-up regime is governed by (1) a phase transformation |
| of a structural change during wake-up in a similar sample. [ 3 ] The | from monoclinic to orthorhombic grains (bulk effect) as well |
| tetragonal P4 2 /nmc to the orthorhombic Pca2 1 phase has been calculated to ≈30 meV per ZrO 2 formula unit (f.u.). [ 2,39 ] From a | as (2) changes in and diminishment of a nonuniform, defect |
| rich, tetragonal HfO 2 layer near the electrodes (interface effect). |
| (orthogonalized) monoclinic P2 1 /c phase to the FE phase, sev- | These fi ndings explain the increase in *P*r and the opening of |
| eral 100 meV (per HfO 2 f.u.) are anticipated. [ 40 ] Materlik et al. [ 2 ] reported that 1 MV cm −1 reduces the ground state energy (not | the initially constricted *P* – *V* hysteresis. The fatigue regime is |
| characterized by an increase in the bulk defect concentration, |

the barrier) of the FE phase by around 10 meV. The effect on the barrier can, thus, be expected to be in the same order of magni-tude. The redistribution of oxygen vacancies from the interface into the bulk is expected to result in an additional leverage to surmount the energy barrier. Leakage current measurements indicate an increasing amount of bulk defects in the layer with fi eld cycling. With the applied methods, it cannot be explic-itly determined if these defects act as pinning centers for the domains and consequently induce fatigue, but there is a corre-lation of the onset of fatigue and the leakage current increase similar to what has been demonstrated for Sr:HfO 2 . [ 11 ]  
 As a fi nal note, this work further stresses the importance of optimizing processing conditions to yield interfacial layers that contribute minimally to wake-up and fatigue effects. Previously, Hoffmann et al. [ 3 ] pointed out the structural (certain extent of orientation relationship, lateral grain size confi nement, nuclea-tion sites during crystallization of HfO 2 , maybe strain) and chemical role (oxygen is scavenged from HfO 2 and resulting vacancies destabilizing the monoclinic phase) of the electrode for the stabilization of the ferroelectric phase. Schenk et al. [ 12 ] examined internal bias fi elds similar to what was found in con-ventional ferroelectrics and concluded that similar routes could be used to prevent their formation, which include:

• fi nding proper annealing conditions;   
• carefully adjusting the stoichiometry of HfO 2 regarding O and dopant content;   
• use of inert electrodes.

which is proposed to give rise to domain wall pinning.

**5. Experimental Section**

Gd-doped HfO 2 thin fi lms capacitors between TiN electrodes were deposited and processed by methods previously outlined. [ 3 ] A 650 °C anneal in N 2 ambient for 20 s was used after top electrode deposition. Polarization and small-signal capacitance measurements were performed at different stages of fi eld cycling using a TF Analyzer 3000 (aixACCT Systems). Polarization hystereses were recorded at a frequency of 1 kHz. A triangular large-signal voltage excitation was used with a modulated 10 kHz small signal of 150 mV amplitude to record the capacitance–voltage characteristics. Impedance spectroscopy was conducted with an HP 4294A (Agilent Technologies). Small-signal amplitude was the same as for the *C* – *V* measurements and a point averaging factor of 25 was applied. Details about the choice of the equivalent circuit as well as about the fi tting procedure can be found in the Supporting Information S2 and S3.

Cross-section samples for STEM were prepared using either an FEI Quanta Focused Ion Beam or an FEI Helios nanolab 600i. STEM images were recorded with a probe-corrected FEI Titan G2 60–300 kV operated at 200 kV with a beam current of ≈80 pA, a probe semiconvergence angle of either 13.5 or 19.6 mrad, and an HAADF detector inner semiangle of 77 mrad. STEM images were acquired and processed with the RevSTEM technique including 20–40 1024 × 1024 pixel frames with a 2 µs pixel −1 dwell time and a 90° rotation between each successive frame. [ 47 ]

**Supporting Information**

Supporting Information is available from the Wiley Online Library or

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| Our results confi rm and provide a structural understanding | from the author. |

of these phenomena and serve to further emphasize the impor-

tance of engineering high quality interfaces between HfO 2 and electrodes. First attempts at devices with Pt, [ 8,41 ] Ir, [ 42–44 ] and RuO 2[ 27 ] electrodes exist, but none of them yielded a dramatic improvement of the endurance performance. In fact, in some cases *P*r seemed compromised compared to TiN. Other studies showed the impact of annealing conditions [ 45,46 ] and Hf 1-*x*Zr *x*O 2 stoichiometries [ 38 ] on the wake-up behavior, which proves that the interplay between ferroelectric and electrodes is more com-plex. Simply exchanging the electrode material is not expedient and a careful adjustment of other process parameters is addi-tionally mandated to make HfO 2 fully competitive for memory applications. The present work, thus, provides helpful instru-ments for the route forward.

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| **www.MaterialsViews.com**  stacks, the sample preparation, and introduction to impedance analysis, respectively.  Received: April 27, 2016  Revised: June 3, 2016  Published online: July 29, 2016 | **www.advelectronicmat.de**  [25] W. Weinreich , R. Reiche , M. Lemberger , G. Jegert , J. Müller , L. Wilde , S. Teichert , J. Heitmann , E. Erben , L. Oberbeck , U. Schröder , A. J. Bauer , H. Ryssel , *Microelectron. Eng.* **2009** , *86* , 1826 .  [26] M. H. Park , H. J. Kim , Y. J. Kim , T. Moon , K. D. Kim , C. S. Hwang , *Adv. Energy Mater.* **2014** , *4* , 1400610 .  [27] M. H. Park , H. J. Kim , Y. J. Kim , W. Jeon , T. Moon , C. S. Hwang , |

*Phys. Status Solidi RRL* **2014** , *8* , 532 .

[28] J. Robertson , *Eur. Phys. J.: Appl. Phys.* **2004** , *28* , 265 .

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| [1] T. S. Böscke , J. Müller , D. Bräuhaus , U. Schröder , U. Böttger , *Appl.*  *Phys. Lett.* **2011** , *99* , 102903 .  [2] R. Materlik , C. Künneth , A. Kersch , *J. Appl. Phys.* **2015** , *117* , 134109 . [3] M. Hoffmann , U. Schroeder , T. Schenk , T. Shimizu , H. Funakubo , O. Sakata , D. Pohl , M. Drescher , C. Adelmann , R. Materlik , A. Kersch , T. Mikolajick , *J. Appl. Phys.* **2015** , *118* , 072006 . | [29] L. | Vandelli , | A. | Padovani , | L. | Larcher , | R. | G. | Southwick , |
| W. B. Knowlton , G. Bersuker , *Proc. Eur. Solid-State Device Res. Conf.* **2010** , 388 . | | | | | | | | |
| [30] L. | Vandelli , | A. | Padovani , | L. | Larcher , | R. | G. | Southwick , |
| W. B. Knowlton , G. Bersuker , *IEEE Trans. Electron Devices* **2011** , *58* , 2878 .  [31] O. Pirrotta , L. Larcher , M. Lanza , A. Padovani , M. Porti , M. Nafría , | | | | | | | | |

[4] S. Mueller , C. Adelmann , A. Singh , S. Van Elshocht , U. Schroeder , T. Mikolajick , *ECS J. Solid State Sci. Technol.* **2012** , *1* , N123 .

[5] D. Zhou , J. Xu , Q. Li , Y. Guan , F. Cao , X. Dong , J. Müller , T. Schenk , U. Schröder , *Appl. Phys. Lett.* **2013** , *103* , 192904 .

[6] T. Schenk , U. Schroeder , M. Pešic´ , M. Popovici , Y. V. Pershin ,

G. Bersuker , *J. Appl. Phys.* **2013** , *114* , 134503 .

[32] T. Schenk , E. Yurchuk , S. Mueller , U. Schroeder , S. Starschich , U. Böttger , T. Mikolajick , *Appl. Phys. Rev.* **2014** , *1* , 041103 .

[33] G. Le Rhun , R. Bouregba , G. Poullain , *J. Appl. Phys.* **2004** , *96* , 5712 . [34] C. Li , Y. Yao , X. Shen , Y. Wang , J. Li , C. Gu , R. Yu , Q. Liu , M. Liu ,

T. Mikolajick , *ACS Appl. Mater. Interfaces* **2014** , *6* , 19744 . *Nano Res.* **2015** , *8* , 3571 .

[7] P. D. Lomenzo , Q. Takmeel , C. Zhou , C. M. Fancher , E. Lambers , [35] S. Starschich , S. Menzel , U. Böttger , *Appl. Phys. Lett.* **2016** , *108* ,

N. G. Rudawski , J. L. Jones , S. Moghaddam , T. Nishida , *J. Appl.*  032903.

*Phys.* **2015** , *117* , 134105 . [36] R. Batra , H. D. Tran , R. Ramprasad , *Appl. Phys. Lett.* **2016** , *108* ,

[8] S. Starschich , D. Griesche , T. Schneller , R. Waser , U. Böttger , *Appl.*  172902.

*Phys. Lett.* **2014** , *104* , 202903 . [37] T. D. Huan , V. Sharma , G. A. Rossetti , R. Ramprasad , *Phys. Rev. B*

[9] H. J. Kim , M. H. Park , Y. J. Kim , Y. H. Lee , T. Moon , K. D. Kim ,  **2014** , *90* , 064111 .

S. D. Hyun , C. S. Hwang , *Nanoscale* **2016** , *8* , 1383 . [38] M. H. Park , H. J. Kim , Y. J. Kim , Y. H. Lee , T. Moon , K. D. Kim ,

[10] M. H. Park , H. J. Kim , Y. J. Kim , Y. H. Lee , T. Moon , K. D. Kim , S. D. Hyun , F. Fengler , U. Schroeder , C. S. Hwang , *ACS Appl. Mater.*

S. D. Hyun , C. S. Hwang , *Appl. Phys. Lett.* **2015** , *107* , 192907 . *Interfaces* **2016** , *8* , 15466 .

[11] M. Pešic´ , F. P. G. Fengler , L. Larcher , A. Padovani , T. Schenk , [39] S. E. Reyes-Lillo , K. F. Garrity , K. M. Rabe , *Phys. Rev. B* **2014** , *90* ,

E. D. Grimley , X. Sang , J. M. LeBeau , S. Slesazeck , U. Schroeder , 140103(R) .

T. Mikolajick , *Adv. Funct. Mater.* **2016** , *26* , 4601 .

[12] T. Schenk , M. Hoffmann , J. Ocker , M. Pešic´ , T. Mikolajick , U. Schroeder , *ACS Appl. Mater. Interfaces* **2015** , *7* , 20224 .

[13] J. F. Scott , *Ferroelectric Memories* , Springer-Verlag , Berlin  **2000** . [14] A. K. Tagantsev , I. Stolichnov , E. L. Colla , N. Setter , *J. Appl. Phys.*

[40] S. Clima , D. J. Wouters , C. Adelmann , T. Schenk , U. Schroeder , M. Jurczak , G. Pourtois , *Appl. Phys. Lett.* **2014** , *104* , 092906 .

[41] M. H. Park , H. J. Kim , Y. J. Kim , W. Lee , H. K. Kim , C. S. Hwang , *Appl. Phys. Lett.* **2013** , *102* , 112914 .

[42] M. H. Park , H. J. Kim , Y. J. Kim , W. Lee , T. Moon , K. D. Kim ,

**2001** , *90* , 1387 . C. S. Hwang , *Appl. Phys. Lett.* **2014** , *105* , 072902 .

[15] X. J. Lou , *J. Appl. Phys.* **2009** , *105* , 024101 .

[16] D. Damjanovic , *Rep. Prog. Phys.* **1998** , *61* , 1267 .

[17] X. Sang , E. D. Grimley , T. Schenk , U. Schroeder , J. M. LeBeau , *Appl.*  *Phys. Lett.* **2015** , *106* , 162905 .

[18] E. Barsoukov , J. R. Macdonald , *Impedance Spectroscopy: Theory,*

[43] P. D. Lomenzo , P. Zhao , Q. Takmeel , S. Moghaddam , T. Nishida , *J.*  *Vac. Sci. Technol., B* **2014** , *32* , 03D123 .

[44] T. Shimizu , T. Yokouchi , T. Shiraishi , T. Oikawa , P. S. Sankara Rama Krishnan , H. Funakubo , *Jpn. J. Appl. Phys.* **2014** , *53* , 09PA04 .

[45] P. D. Lomenzo , Q. Takmeel , S. Moghaddam , T. Nishida , *Thin Solid*

*Experiment, and Applications* , John Wiley & Sons, Inc ., Hoboken, NJ *Films* **2016** , *615* , 139 .

**2005** . [46] M. H. Park , H. J. Kim , Y. J. Kim , W. Lee , T. Moon , C. S. Hwang , *Appl.*

[19] C.-H. Kim , S.-I. Pyun , J.-H. Kim , *Electrochim. Acta* **2003** , *48* , 3455 . *Phys. Lett.* **2013** , *102* , 242905 .

[20] J.-B. Jorcin , M. E. Orazem , N. Pébère , B. Tribollet , *Electrochim. Acta*  [47] X. Sang , J. M. LeBeau , *Ultramicroscopy* **2014** , *138* , 28 .

**2006** , *51* , 1473 . [48] J. Müller , U. Schröder , T. S. Böscke , I. Müller , U. Böttger , L. Wilde ,

[21] B. Hirschorn , M. E. Orazem , B. Tribollet , V. Vivier , I. Frateur , J. Sundqvist , M. Lemberger , P. Kücher , T. Mikolajick , L. Frey , *J. Appl.*

M. Musiani , *J. Electrochem. Soc.* **2010** , *157* , C452 . *Phys.* **2011** , *110* , 114113 .

[22] B. Hirschorn , M. E. Orazem , B. Tribollet , V. Vivier , I. Frateur , M. Musiani , *J. Electrochem. Soc.* **2010** , *157* , C458 .

[23] M. Musiani , M. E. Orazem , N. Pébère , B. Tribollet , V. Vivier , *J. Elec-*

[49] X. Zhao , D. Vanderbilt , *Phys. Rev. B* **2002** , *65* , 233106 .

[50] Y. Watanabe , H. Ota , S. Migita , Y. Kamimuta , K. Iwamoto , M. Takahashi , A. Ogawa , H. Ito , T. Nabatame , A. Toriumi , *ECS*

*trochem. Soc.* **2011** , *158* , C424 . *Trans.* **2007** , *11* , 35 .

[24] M. E. Orazem , I. Frateur , B. Tribollet , V. Vivier , S. Marcelin , N. Pébère , A. L. Bunge , E. A.White , D. P. Riemer , M. Musiani , *J. Electrochem. Soc.* **2013** , *160* , C215 .

[51] C. Adelmann , H. Tielens , D. Dewulf , A. Hardy , D. Pierreux , J. Swerts , E. Rosseel , X. Shi , M. K. Van Bael , J. A. Kittl , S. Van Elshocht , *J. Electrochem. Soc.* **2010** , *157* , G105 .

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| --- | --- | --- | --- |
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