

**On the origin of wake-up and antiferroelectric-like behavior in**

**ferroelectric hafnium oxide**

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| *Maximilian Lederer\* Ricardo Olivo David Lehninger Sukhrob Abdulazhanov Thomas Kämpfe*  *Sven Kirbach Clemens Mart Konrad Seidel Lukas M. Eng*   Accepted Article  M. Lederer, R. Olivo, Dr. D. Lehninger, S. Abdulazhanov, Dr. T. Kämpfe, S. Kirbach, C. Mart, K.  Seidel  Fraunhofer IPMS, Center Nanoelectronic Technologies, 01099 Dresden, Germany Email Address: maximilian.lederer@ipms.fraunhofer.de  Prof. L. M. Eng  Institut für Angewandte Physik, Technische Universität Dresden, 01069 Dresden, Germany  Keywords: *hafnium oxide, ferroelectric, antiferroelectric, electric field-induced crystallization*  Ferroelectric hafnium oxide ( H fO ) is considered as a very prospective material for applications 2  in integrated devices, due to its considerably large spontaneous polarization and superior thickness scaling. In fact, the evolution of the ferroelectric hysteresis upon field cycling plays the important role in most applications; especially the so-called  *wake-up effect* that describes the increase of  remanent polarization for initial field cycling, needs a profound understanding in H fO . In this 2  article, the discovery of electric field-induced crystallization in hafnium oxide is reported. In addition, differences in the wake-up behavior are addressed that finally can be categorised into five different cases, all being relevant when describing the evolution of ferroelectricity. Moreover, analysis of the temperature dependence and transmission Kikuchi diffraction provide insight into the underlying physical mechanisms of different wake-up behavior scenarios, and prove ferroelastic switching as the origin for the observed antiferroelectric-like behavior. This  knowledge provides clear procedures of (a) how to experimentally quantify, and (b) how to prepare and manufacture hafnium oxide phases for the five different wake-up types.  **1 Introduction**  Since its discovery [1], ferroelectric hafnium oxide has become of interest for a broad range of integrated devices, like ferroelectric field effect transistors (FeFETs), ferroelectric random access memory (FeRAM), ferroelectric tunnel junctions (FTJ), [2-5] as well as piezo- and pyroelectric devices [6, 7], due to its compatibility to standard  complementary-metal-oxide-semiconductor (CMOS) processes [8]. Ferroelectric H fO 2 has  enabled highly scalable devices in 28 nm [9], 22 nm [10], and 14 nm [11] technology due to its coercive field, layer thickness scalability, and other advantages as compared to conventional ferroelectrics like lead titanate zirconate (PZT) [8, 12]. | | | | | |
| The metastable ferroelectric (orthorhombic) | H fO phase of space group 2 | *P ca* | 2 | 1 | [13] can |
| be stabilized by e.g. doping [8, 14], stress [15], specific surface area [16], and thermal quenching [4]. In polycrystalline films, other phases might be found alongside the ferroelectric phase. From | | | | | |

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thermodynamics, the most likely phases are the monoclinic phase of space group *P* 2 / 1 *c*

(ground-state) and the tetragonal phase ( *P* 4 2 / *nm c* ) [15]. In addition, another ferroelectric phase

of rhombohedral symmetry has recently been reported to occur in epitaxial thin films [17]. During the lifetime of the device, the polarisation-voltage (P-V) hysteresis of the ferroelectric thin film is governed by multiple effects. The opening of the initially pinched Accepted Article   
hysteresis loop during electrical field cycling is called  *wake-up effect*. Hereby the remanent

polarization ( P ) increases until reaching saturation. Towards the end of the device lifetime, the

H fO film exhibits fatigue, which usually results in a reduced P and/or an increased leakage R

current [18, 19]. Furthermore, internal bias fields (e.g. due to band alignment) or imprint of the polarization state may affect the hysteresis as well [20].

Especially the wake-up effect is not understood in depth, although many different explanations have been proposed as prospective explanations, however, without giving a concise picture. Most theories can be assigned to one of the following three models:   
 i) Defect redistribution that reduces internal bias fields and assists domain wall depinning within the layer [21, 22]; ii) defect redistribution and subsequent stabilization of the orthorhombic phase [18, 19, 23, 24]; or iii) ferroelastic switching [25-27]. The stabilization of the orthorhombic phase during wake-up is connected to the field-induced phase transition from tetragonal to orthorhombic, as being proposed for explaining the antiferroelectric-like (AFE) behavior in

highly-doped ZrO [1, 28]. 2

In order to clarify the physical origin of the wake-up effect, we analyse in the following

sections the various differences and signatures in the wake-up behavior of H fO , discuss 2

influences resulting from doping, stress, annealing profile, and operating temperature, as well as the resulting implications on the physical origin of the different phenomena.

For characterization and application, two different H fO material stacks are commonly 2

used **Figure**  **1a**), namely metal-ferroelectric-metal (MFM) and metal-ferroelectric-insulator-semiconductor (MFIS) stacks. Due to the symmetry and absence of parasitic capacitances or semiconductor-based non-linearities, MFM capacitors are generally used to characterize the ferroelectric behavior, directly paving the way to FeRAM and back-end of line (BEoL) integration in FeFETs [29, 30]. On the other hand, MFIS stacks resemble the integration of hafnium oxide based FeFETs in the front-end of line (FEoL).

**2 Differences in the wake-up behavior of hafnium oxide**

In this article, MFM structures with H fO films of 5 nm and 10 nm thickness doped with 2

various elements (Si, Zr, La) of different concentrations were analysed. In addition Si-doped

H fO -based MFIS structures were inspected, with the goal to investigate the impact of the layer

stack on wake-up behavior. Electrical and structural analysis showed, that the wake-up effect does not follow the same trend for all samples. Instead, they showed either one of the five different wake-up effects presented in the following paragraphs, or a superposition of those. Since these effects have all been tagged  *wake-up effect* before, an extended nomenclature is introduced to improve the readability of this article and to clearly classify the different wake-up scenarios.

Typically, the wake-up behavior in a MFM capacitor is described by an initially fully pinched or AFE-like hysteresis loop that opens during cycling, as shown in Figure 1b.

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Furthermore, it can be described by two current peaks popping up at either direction of the current-voltage (I-V) curve, that might even merge to a single peak then resembling the standard

distribution of coercive fields ( E ), as depicted in Figure 1b. This behavior has been reported C

already by multiple groups [6, 18, 22, 26, 29, 31-34] and will be referenced to as the  *classical wake-up effect*.

Furthermore, four additional types of wake-up behavior could be identified in this study.

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They are referred to as  *textured* (Figure 1c),  *non-split* (Figure 1d),  *sudden* (Figure 1e), and *asymmetric* (Figure 1f) wake-up.

Compared to the classical wake-up,  *textured wake-up* exhibits a faint asymmetry in the initial current peaks, and the resulting merged peak does not follow a normal distribution but is of

asymmetric shape (see Figure 1c). Consequently, the E distribution has a preferred value, and C

the P-V loop appears in a more square-like behavior. A similar observation was also witnessed by other groups [21, 27, 35].

*Asymmetric wake-up* is defined by an asymmetry between forward and backward bias direction. While in one direction, initially strong peak splitting can be observed, the other direction displays merged peaks. Upon wake-up, the peaks merge further, but a slight asymmetry remains even for post-cycled curves.

Under some conditions, the absence of initially split peaks can be observed; this type therefore is referred to as  *non-split wake-up* (see Figure 1d). For this case, the magnitude of the I-V peak increases, while the width of the peak decreases slightly. This behavior has also been reported before [24, 29].

Additionally, we report the emergence of ferroelectric properties from an initial approximately dielectric and amorphous film (see Figure 1e) in a MFM device. In contrast to the wake-up types discussed above, there is no initial presence of AFE or ferroelectric behavior in this last wake-up scenario, and a single peak emerges and increases in magnitude upon cycling. Thus, this type is referred to as  *sudden wake-up*, as polarization emerges unexpectedly.

Classical, textured, and asymmetric wake-up initially show antiferroelectric-like behavior, while sudden and non-split wake-up initially exhibit a dielectric or ferroelectric behavior, respectively. This provides already a valuable hint that the number of underlying physical mechanisms is actually lower and further influenced by some other factors, e.g. microstructure and/or adjacent layers.

**2.1 Impact of microstructure and material stack on the wake-up behavior**

While sudden wake-up is obtained by annealing the material at low temperatures for short

time periods (see **Table 1**), e.g. 5 nm thin HZO at 4 0 0 C for 60 s, all other wake-up types require anneals that fully crystallize the film. AFE-like wake-up phenomena can be stabilized by increasing stress or doping [1, 26, 29, 36]. The differences between classical, textured and asymmetric wake-up can be explained by differences in the microstructure and layer stacking. Textured wake-up can be obtained by increasing the in-plane stress or using dopants whose ionic radii differ from hafnium, e.g. La (see supplementary Figure S1) or Si [27]. This suggests that textured wake-up, as previously reported [27], emerges with increasing crystallographic texture and preferred orientation.

When inserting a dielectric interface layer between one of the electrodes and the H fO 2

layer as is the case in MFIS stacks, an asymmetric wake-up is obtained for low temperature

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anneals. This asymmetry of the wake-up behavior in case of MFIS stacks annealed at lower temperatures is yet not fully understood and can even result in a hysteresis, which is behaving AFE only in one direction (see supplementary Figure S2). Possible explanations are likely to be an interplay of the non-linear silicon capacitance, asymmetric stress fields due to the different thermal expansion coefficients of top and bottom layers, charged defects within the interface layer, and effects due to band alignment along the different work functions of the layers. That the interface Accepted Article   
layer itself, similar to a dielectric dead layer, is not causing the antiferroelectric behavior has been recently demonstrated as well, as thicker interfaces resulted in non-split wake-up [37].

Non-split wake-up can be obtained for thicker films [29] or at higher annealing temperatures (see Figure S3 in the supplement) and is the only phenomenological effect, where ferroelectric behavior is observed in the initial cycle. Possible explanations could be the emergence of [001], [011] or [111] out-of-plane textures, relaxation processes during high temperature annealing, or a lower in-plane stress after cool-down. The remaining increase of remanent polarization can be explained by small regions exhibiting classical wake-up and minor domain-wall depinning. Another explanation would be the initial presence of a dead layer [20]. Such a dead layer would increase in addition the coercive field and the depolarization field, which should influence the retention behavior of such stacks.

In order to easily distinguish between the different phenomenological types of wake-up, the trend of some important figures of merit for ferroelectric hysteresis are given in **Figure 2**. Field-induced crystallization can be clearly identified by increasing saturation polarization ( P ) S

and a quite constant P / P ratio. Non-split wake-up does not show strong changes in S P and S P R

(Figure 2a), while the AFE-like wake-up types (classical, textured, and asymmetric) exhibit strong

changes in the P ratio (Figure 2b), due to the de-pinching of the P-V characteristics.The

evolution of this ratio differs in case of asymmetric wake-up for positive and negative remanent polarization.

As mentioned previously, non-split wake-up appears likely to exhibit an initial out-of-plane orientation of the polarization axis. On the other hand, it has recently been suggested that in case of AFE-like wake-up, some grains should have in-plane polarization due to ferroelastic switching (see Figure 2c)[26], as illustrated by Figure 2d.As shown in Figure 2e, the degree of texture visualizes itself in a more square-like hysteresis curve.

In addition, superposition with varying degree of sudden and AFE-like behavior might be present in other samples. These trends are further summarized in Table 1. Additionally, experimental growth strategies and methods in order to achieve all these types either taken from literature or deduced from this article, are given alongside in Table 1.

Consequently, only two physical mechanisms appear likely to govern wake-up in hafnium oxide, one for transitioning from dielectric and another transitioning from AFE-like behavior. As the initial state of the latter is not fully understood, the origin of AFE-like behavior and wake-up is analyzed. As mentioned above, non-split wake-up could be explained by these two mechanisms as well. Nevertheless, an additional mechanism for this effect cannot be ruled out.

**2.2 Origin of antiferroelectric-like behavior**

In case of classical wake-up, measuring the polarization hysteresis at higher operating

temperatures, e.g. for H f 0.5 Zr 0.5 O as shown in **Figure 3a**, showed an increased splitting of the

displacement current peaks as observed for the initial curve. Furthermore, a third peak is emerging

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in-between when lowering the temperature, thus resulting in less cycling to achieve full wake-up with lower temperatures. A similar trend is observed for increased dopant concentration (supplementary Figure S4). Here, the wake-up cannot be completed at higher temperatures. Measuring the wake-up behavior at different frequencies shows a clear cycle dependence (see Figure 3b) instead of a time dependence (see supplementary Figure S4). The minor influence of cycling time might be related to the superimposed fatigue effect for high cycle count.

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Consequently, drift and diffusion processes and therefore defect redistribution and domain wall depinning [18, 21, 31] can be ruled out as underlying mechanisms. Even if these processes would happen only during the domain switching, the temperature dependence is opposing the expected trend. Combined with previously-published data [27] we are able to rule out transitions from the monoclinic phase [18, 19, 23] as well. More details on this are given in the supplementary material.

Ferroelastic switching [25-27] and the field-induced phase transition from the tetragonal to the orthorhombic phase [1, 24, 28, 38] would become more pronounced with increasing operating temperature.

ZrO films, density functional theory (DFT) calculations suggest the presence of

a first-order phase transition from the tetragonal to the ferroelectric orthorhombic phase as well as a very low difference of about 1 meV in the energy level of both phases [28]. Due to the kinetically suppressed transition from tetragonal to monoclinic [39], the film exhibits anti-ferroelectric

properties. Furthermore, a more Hf rich film (e.g. H f 0.5 Zr 0.5 O ) is expected to behave more 2

ferroelectric, as the energy level of the orthorhombic phase decreases [28]. As other dopants than Zr as well as surface effects can also stabilize the tetragonal phase, this behaviour can be one of the underlying processes during the AFE-based wake-up. On the other hand, the reported high Curie

to 5 0 0 C ) [40-42] of the phase transition in combination with the almost

constant P observed during cycling in case of AFE-like wake-up, makes the field-induced phase

transition quite unlikely. Furthermore, without redistribution of oxygen vacancies or other defects, common suggestions for the destabilization mechanism of the tetragonal phase are ruled out. On the other hand, transmission Kikuchi diffraction analysis of pristine and post-cycled

regions of Si doped H fO with classical wake-up behavior shows an increased out-of-plane 2

orientation of the polarization axis after cycling, while the ferroelastic axis decreases in out-of-plane orientation density (see Figure 3c). In consequence, this proves initial presence of ferroelastic switching. Pre-existing orthorhombic phase has recently been confirmed by displacement measurements as well [43]. The stabilization of ferroelectric behavior upon field cycling can be attributed to stress relaxation upon cycling, e.g., by formation of defects like dislocations or changes in the electrical and stress field distribution. A more detailed discussion is given in the supplement.

**2.3 Electric field-induced crystallization**

For sudden wake-up, here shown for a 5 nm H f 0.5 Zr 0.5 O sample with a 400 2  C rapid

thermal anneal (RTP), no significant differences with temperature are observed for the initial

curves. Nevertheless upon cycling, a faster increase of P and R P is observed with increasing S

temperature (see supplementary Figure S6). Here, an outstanding P of more than 15 ** C/cm2 is R

found for the 5-nm thin film at 1 2 0 C . Additionally, peak splitting in the I-V hysteresis and

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consequently pinching in the P-V hysteresis appears with increasing temperature, in direct analogy to classical wake-up.

Furthermore, the P increase characteristic for the sudden wake-up also shows a clear R

time dependence (see **Figure 4a**), which is expected for electric-field-induced crystallization processes [44]. Combining time and temperature dependence with the evolution of P , an R Accepted Article   
effective activation energy of 0 .4 50 .0 3   
eV could be extracted by visualizing the data in the form of an Arrhenius plot, as displayed in Figure 4b. This value is lower as compared to the activation energies of other materials ( 1 .3 eV to 3 eV), that are known for

electric-field-induced crystallization, like G e S b T e [44, 45]. Note, that the activation energy 2 2 5

might differ, as the polarization is further influenced by the pinching of the P-V characteristics and the pyroelectric effect.

Since the rapid thermal processing (RTP)-annealed sample is X-ray amorphous (cf. grazing incident X-ray diffraction (GIXRD) pattern in the supplementary Figure S7), and as-deposited samples do not show this effect (see supplementary Figure S8), it can be concluded that the RTP-annealed sample contains nano-crystallites embedded into an amorphous matrix. Upon field cycling, these nuclei grow (see Figure 4c) and ferroelectricity is emerging, thus explaining the sudden wake-up.

**3 Conclusion**

In conclusion, different types of wake-up behavior were found and classified, investigating also their underlying mechanisms. Here, the following major findings are reported:   
 (i) For the first time electric field-induced crystallization of hafnium oxide into a ferroelectric phase was demonstrated, and an effective activation energy of 0.45 eV was determined.

(ii) AFE-related wake-up effects are most likely derived from stress relaxation, e.g. defect generation, during field-cycling.

(iii) AFE behavior can be introduced by increased operating temperature.

(iv) Defect redistribution, domain wall depining and field-induced phase transitions from tetragonal or monoclinic phase to the orthorhombic phase can all be excluded as the major underlying mechanisms for AFE and classical wake-up in hafnium oxide.

(v) The presence of ferroelastic switching in polycrystalline hafnium oxide films was proven and identified as the underlying mechanism for antiferroelectric-like behavior in hafnium oxide.

Additionally, means in order to distinguish and to manufacture the various kinds of wake-up, are summarized in Table 1.

These findings highlight the importance of stress engineering in ferroelectric hafnium oxide films. Furthermore, the newly discovered field-induced crystallization as well as ferroelastic switching in hafnium oxide enable novel device concepts, new nano-electro-mechanical applications and give relevant insights for the optimization of current devices and processes.

**4 Experimental Section**   
 *Material preparation:*

The Si and Zr doped H fO MFM capacitors were fabricated on top of 10-nm-thick TiN, 2

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deposited using atomic layer deposition (ALD) on top of the highly p-doped Si wafer, which acts

as a conductor for electrical measurements. Ferroelectric H f Zr *x*  1*x* O 2 thin films of 5 and 10 nm

thickness were deposited by ALD with H fC l 4 / H O and 2 S iC l 4 / H O or 2 ZrC l 4 / H O 2

precursor pulses using the cycle ratio of 1:1 and 3:5 or 16:1 and 20:1, respectively. The thin films were then capped by a 10-nm-thick top TiN electrode by means of physical vapor deposition Accepted Article   
(PVD). Obtained MFM stacks were then annealed by a rapid thermal anneal (RTA) at

temperatures between 3 5 0 C and 1 0 5 0 C for 5 to 70 seconds. La doped MFM samples were prepared in a similar manner, a more detailed description has been reported elsewhere [46]. For MFIS structure, the TiN bottom electrode was substituted by a native oxide layer. An overview of all measured samples is given in Table 2.

*Electrical characterization*   
 I-V and P-V measurements were performed with an aixACCT TF Analyzer 3000. During the temperature measurements, samples were subjected to voltage pulses of triangular shape and 1 kHz or 100 Hz frequency with an amplitude of 2.3 V and 2.6 V for samples with 5 nm and 10 nm HZO, respectively. Amplitudes were chosen to minimize the leakage currents at high temperatures to avoid electrical breakdown. Between our measurements, samples were stressed with a square-shaped pulses of 1 kHz or 20 Hz frequency, respectively. Temperature was varied between

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 To check the frequency dependence, dynamic hysteresis measurements and cycling were performed with frequencies varying from 10 Hz to 1 kHz. The pulse amplitude was set to 2.3 V and 3 V for the 5 nm and 10 nm samples, respectively. Further wake-up analysis at room temperature was conducted at 1 kHz with varying amplitudes.

*Structural characterization*   
 Grazing incidence X-ray diffraction patterns were collected using a Bruker D8 Discover XRD system scanned over the 2** range from 15° to 45° at a fixed incident angle of 0.5Â°. Transmission Kikuchi diffraction was conducted on dimpled samples. An acceleration voltage of 30 keV and a current of 3.2 nA was used. More details on the measurement technique and data analysis can be found in previous work [26].

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

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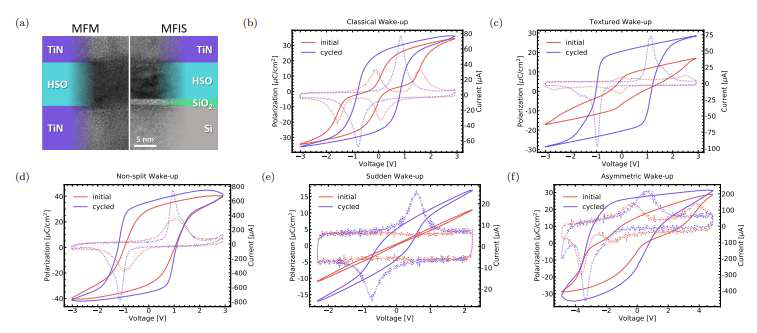
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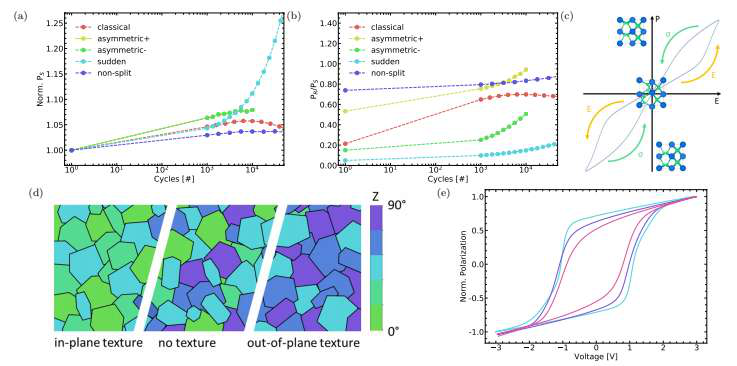
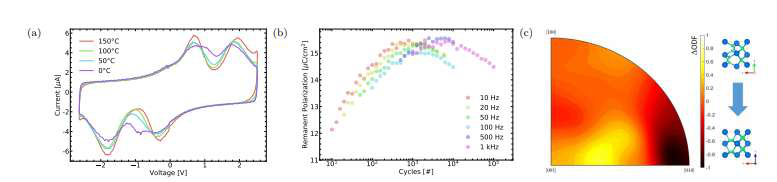
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Figure 1: Differences in the observed wake-up behavior in hafnium oxide. (a) Samples commonly are produced as metal-ferroelectric-metal (MFM) or

metal-ferroelectric-insulator-metal (MFIS) stacks; (b) Classical wake-up in H fO exhibits a clear 2

transition from antiferroelectric-like to ferroelectric behavior; (c) Textured wake-up shows a non-Gaussian coercive field distribution; (d) shows a decrease of the coercive field distribution width, observed as a non-split wake-up; (e) Sudden wake-up describes the emergence of ferroelectricity in a dielectric sample; (f) A strongly asymmetric hysteresis is characteristic for wake-up in MFIS stacks. Note that the displacement current is given as dotted curves in all panels.

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Figure 2: Characteristics of the different wake-up behaviors in the evolution of certain figures of merit for polarization hysteresis. Sudden wake-up shows a significant increase of saturation polarization (a), unique to this wake-up type. Curves of asymmetric wake-up coincide. Opening of

the hysteresis upon cycling can be described by an significant increase of the P / R P ratio (b) in S

case of AFE-like wake-up, here shown for classical and asymmetric wake-up. The latter shows

additional differences in the evolution of P R and P R. The impact of in-plane tensile stress and

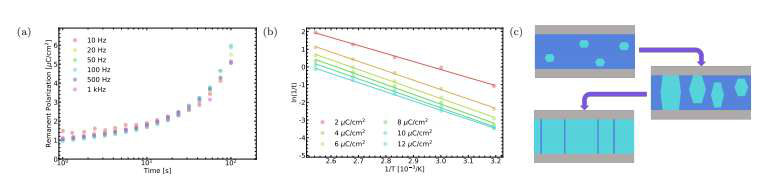
the consequential ferroelastic switching is illustrated in (c). While out-of-plane texture of the polarization axis resembles non-split wake-up, in-plane orientation is responsible for AFE behavior (d). Increased crystallographic texture can be seen by an increasing square-like behavior of the hysteresis (e).

Figure 3: Influence of cycling and temperature on classical wake-up. When inspecting the

hysteresis loop of a H f 0.5 Zr 0.5 O sample at different operating temperatures (a), the emergence of 2

a third peak located in-between the initial two peaks, is observed for lower temperatures. By cycling at different frequencies (b), we observe the wake-up to strongly depend on the number of cycles, and not the time. The difference in the extracted orientation density functions (initial and post-cycling) extracted from transmission Kikuchi diffraction (see supplementary Figure S5) reveals a transition from the ferroelastic [010] axis to the ferroelectric [001] axis in out-of-plane

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direction as shown by the inverse pole figure (c).

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Accepted Article   Figure 4: Influence of cycling and temperature on sudden wake-up. Cycling at different frequencies (a), shows a purely time dependent behavior. Combined with measurements at different temperatures, an Arrhenius plot (b) can be constructed by curve interpolation. The extracted activation energy measures 0 .4 50 .0 3 eV. The growth process in case of field-induced crystallization is shown schematically in (c).  Table 1: Overview of the five different wake-up types. General trends of P and the S P / R P S  ratio are given, as well as differences in the shape of the polarization hysteresis. Finally, the differences in the microstructure and means for obtaining the different kinds of wake-up in respect of process conditions are summarized.   |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | |  | | P S | P / R P S | P-V (I-V) loop | Structural  characterization | Obtainable by: | | field-induced  crystallization | | increas. | const. | initially  dielectric | XRD:  amorphous | short  anneal at  low  temperature | | AFE-like classical | | const. | increas. | initially  pinched P-V loop |  | in-plane  stress [26], doping [1, 29, 36],  ZrO [36] 2 | |  |  | const. | increas. | initially  pinched P-V loop, sharp  transitions | XRD, TKD: texture | increased in-plane  stress,  dopants  with  different  ionic radii [27] | |  | asymmetric | const. | increas. | direction dependent behavior |  | integration in MFIS  stacks | | FE-like | non-split | const. | const. | no peak  splitting in I-V | XRD, TKD: texture | increased layer  thickness | |

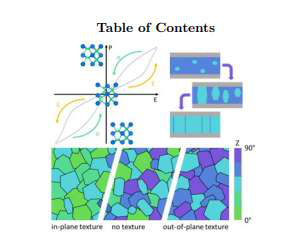
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|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  |  |  |  |  |  | [29], high  annealing  temperature |

Table 2: Process conditions of measured samples.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Precursor   ~~l~~ | | Thickness | Deposition temperature | Annealing temperature | Substrate layer | Figures |
| ~~ic~~ H fC l ,  ZrC l | | 10 nm |  2 5 0 C |  8 0 0 C | ALD TiN | 1b,  2a,b |
| H fC l ,   ~~rt~~ ZrC l | | 10 nm | 3 0 0 C | 8 0 0 C | ALD TiN | 1d,  2a,b, S3 |
| H fC l ,   ~~A~~ ZrC l | | 10 nm | 3 0 0 C | 4 0 0 C | ALD TiN | 3b, S1a, S3 |
| H fC l ,   ZrC l | | 10 nm | 3 0 0 C | 4 5 0 C | ALD TiN | 3a,  S1b |
| ~~d~~ H fC l ,  ZrC l | | 10 nm | 3 0 0 C | 4 5 0 C | ALD TiN | S1c |
| ~~te~~ H fC l ,  ZrC l | | 5 nm | 3 0 0 C | 4 0 0 C  RTP | ALD TiN | 1e, 4, 2a,b,  S2, S4, S5b |
| ~~p~~ H fC l ,  ZrC l | | 5 nm |  3 0 0 C |  4 0 0 C  Furnace | ALD TiN | S4,  S5c |
| ~~e~~ H fC l ,  S iC l | | 10 nm |  2 5 0 C |  8 0 0 C | ALD TiN | 1c,  2a,b,d |
| ~~c~~ H fC l ,  S iC l | | 10 nm | 3 0 0 C | 8 0 0 C | S i/S iO 2 | 1f,  2a,b |
| ~~c~~ H fC l ,  S iC l | | 10 nm | 3 0 0 C | 6 5 0 C | S i/S iO 2 | S8 |
| ~~A~~ TEMAHf,  TEMAZr | | 10 nm | 2 8 3 C | no anneal | ALD TiN | S4,  S5a |
| TEMAHf,  3DMAS (Si) | 25:1 | 10 nm | 2 8 3 C | 6 5 0 C | ALD TiN | 3c, S7 |
| TEMAHf, La(iP rC p) 3 | 2:1 | 10 nm | 2 8 3 C | 6 5 0 C | ALD TiN | S6 |
| TEMAHf, La(iP rC p) 3 | 3:1 | 10 nm |  2 8 3 C |  6 5 0 C | ALD TiN | 2d, S6 |

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|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| TEMAHf, La(iP rC p) 3 | 4:1 | 10 nm | 2 8 3 C | 6 5 0 C | ALD TiN | 2d, S6 |

**Table of Contents**   
 Antiferroelectricity in hafnium oxide is caused by ferroelastic switching due to the in-plane stress ** of the thin film. Additionally, electric field-induced crystallization into the ferroelectric Accepted Article   
phase as well as crystallographic texture affect the ferroelectric response over field-cycling. Multiple process parameters, like annealing temperature, influence this behavior.

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