Substrate-dependent differences in ferroelectric behavior and phase diagram of Si-doped hafnium oxide

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Non-volatile memories based on ferroelectric hafnium oxide, especially the ferroelectric field-effect transistor (FeFET), have outstanding properties, e.g. for the application in neuromorphic circuits. However, material development has focused so far mainly on metal–ferroelectric–metal (MFM) capacitors, while FeFETs are based on metal–ferroelectric–insulator–semiconductor (MFIS) capacitors. Here, the influence of the interface properties, annealing temperature and Si-doping content are investigated. Antiferroelectric-like behavior is strongly suppressed with a thicker interface layer and high annealing temperature. In addition, high-k interface dielectrics allow for thicker interface layers without retention penalty. Moreover, the process window for ferroelectric behavior is much larger in MFIS capacitors compared to MFM-based films. This does not only highlight the substrate dependence of ferroelectric hafnium oxide films, but also gives evidence that the phase diagram of ferroelectric hafnium oxide is defined by the mechanical stress.

Introduction

The discovery of ferroelectricity in hafnium oxide [1], which is a gate material in the high-k metal gate complementary metal oxide semiconductor (CMOS) process technology, enabled the development of highly scaled ferroelectric field-effect transistors (FeFETs) for non-volatile memory application, e.g. in the 28 nm [2], 22 nm [3], or even smaller technology nodes [4]. The possibility for n- and p-type FeFETs [5] enables in addition a larger freedom for novel circuit designs. Moreover, this material system has spurred attention in other applications, like neuromorphic devices [6–8], energy harvesting [9, 10], sensors and actuators [11, 12].

The origin for the presence of ferroelectricity in HfO₂ has been linked to the orthorhombic phase of space group *Pca*2₁ [13]. However, a monoclinic phase is the thermodynamic ground state [14], which is suppressed kinetically, e.g. due to the presence of a capping layer [1, 15]. Other contributing factors are, e.g. film thickness [16] and doping with elements like Si, Zr or La [1, 17, 18]. Since most thin films are of polycrystalline nature, the presence of small amounts of monoclinic grains in the microstructure cannot be excluded, as recently shown by

transmission Kikuchi diffraction [19]. In addition, a tetragonal phase is present for temperatures above the Curie temperature or in a super-cooled state for very high doping concentrations [20, 21].

As demonstrated recently, due to residual mechanical stresses, from, e.g. thermal expansion mismatch, ferroelastic switching, also known as 90°-domain wall movement, leads to an antiferroelectric-like (AFE-like) response of the HfO₂ thin film [22, 23]. Upon electric field-cycling the stress can be reduced, e.g. by defect generation [22], leading to a transition to ferroelectric behavior. This effect is known as (AFE-like) wake-up [22]. This has also been demonstrated in epitaxial and polycrystalline layers, showing a ferroelastic-mediated wake-up which leads to a permanent reorientation of the polarization axis [22–24].

Besides ferroelastic switching, other theories for the AFE-like behavior have been proposed: (i) electric field-induced phase transition of the tetragonal to orthorhombic phase, [1, 25, 26], (ii) internal bias fields and domain wall pinning, [27, 28] and (iii) antiferroelectric orthorhombic phases [29, 30]. However, the phase transition from tetragonal phase appears

unlikely as an origin for AFE-like behavior, since the operating temperature is far below the Curie temperature [31, 32] and recent investigations demonstrated the irreversible nature of this phase transition [20, 21]. Internal bias fields and domain wall pinning on the other side would require diffusion/drift processes during wake-up, which are not observed [22]. Moreover, internal bias fields, domain wall pinning and a phase transition from the tetragonal phase do not agree with the recently reported displacement measurements, which fit nicely to the expected values for ferroelastic switching [12]. Finally, antiferroelectric orthorhombic phases would not explain the observed reorientation of the polarization axis by 90° [22] and recent density functional theory calculations coupled with X-ray diffraction data does suggest that this is not the dominating mechanism [30].

So far, most material optimization has been focused on metal-ferroelectric-metal (MFM) structures, as used in ferroelectric capacitors, or back-end-of-line (BEoL) integration of memories, like ferroelectric random access memory (FeRAM) or FeFETs [33, 34]. Here, a quite narrow doping window for Si is commonly observed, which is in stark contrast to, e.g. Zr, which has a very wide process window for good ferroelectric behavior [1, 17]. These dopants are commonly considered to occupy the Hf lattice position [35, 36]. However, front-end-of-line (FEoL) based FeFETs are based on metal-ferroelectric-insulator-semiconductor (MFIS) stacks, which have only been investigated recently in more detail. Here, strong differences in the electrical and structural properties have been observed [5, 37]. Transmission Kikuchi diffraction studies, which have investigated the microstructure of these films, found much larger grains in the range of 230 nm compared to the rather small grains (around 30 to 50 nm) in MFM structures. Moreover, the crystallographic texture differed strongly by exhibiting an <110> out-of-plane texture and consequently tilted polarization axis. [37] Electrical characterization have highlighted in addition strong differences in the polarization response, ranging from asymmetries induced by the stack structure to differences in the wake-up and AFE-like behavior [5, 22].

In order to gain a deeper understanding on the influence of the layer stack as well as process parameters, the influence of the interface thickness/composition, crystallization temperature and Si-doping concentration are investigated, here. For this, X-ray based techniques as well as electrical characterization are applied to investigate the structural and electrical properties of Si-doped HfO₂ (HSO) layers.

Results and discussion

As shown recently [38], the annealing temperature strongly influences the electrical behavior. While low annealing temperatures, e.g. 800 °C, lead to AFE-like behavior (see Fig. 1a), ferroelectric behavior is observed for higher annealing temperatures, like 1000 °C (see Fig. 1b). This has been suggested to be related to the change in the interface thickness, which is a result of the growth induced by high annealing temperatures [5]. However, different annealing conditions affected the crystallographic texture as well and its impact on the electrical behavior is not fully understood [5]. Nevertheless, recent measurements were able to relate the change in the degree of AFE-like behavior to the interface thickness [38]. Such behavior cannot easily be explained by domain pinning and internal bias fields, as the chemical composition of the hafnium oxide layer and the interfaces did not change, or increased tetragonal phase, since it is not expected for thicker interface layers. Moreover, an increase in interface thickness should result in an increased depolarization field. Nevertheless, ferroelectric behavior is stabilized, highlighting the importance of stress reduction for the material behavior.

First-order reversal curve (FORC) measurements (see Fig. 1c) have revealed that even for the ferroelectric-like wake-up, as observed in Fig. 1b, purely ferroelectric behavior is not present initially [38]. This is indicated by the peak splitting in the extracted Preisach density. In comparison, ferroelectric behavior is expected to be present as a single peak in the Preisach density along the diagonal dotted white line. Bias fields, however, can shift the peak to locations parallel to the central line. Peak splitting on the other hand describes pinching or

Figure 1: Electrical characterization of MFIS stacks annealed at different temperatures. Evolution of the polarization hysteresis upon electric field cycling (number of cycles is given in the legends) for samples annealed at 800 °C (a) and 1000 °C (b). An AFE-like behavior is observed for 800 °C. Preisach density of the sample annealed at 1000 °C (c) extracted from first-order reversal curve (FORC) measurements consists of initially split peaks, which merge upon field cycling. Figure reproduced with permission from: [38].

antiferroelectric-like behavior for peaks inside or outside the region, which is marked by the horizontal/vertical dotted lines, respectively. Upon electric field-cycling, the observed Preisach density transits to 180°-domain wall movement (no peak splitting) and therefore ferroelectric switching. In consequence, the presence of 90°-domain walls, that are able to explain the observed behavior [38], has to be considered for the here investigated samples, which were annealed at 1050 °C, resembling FEoL conditions.

When comparing the different Si-doping conditions, the polarization hysteresees of these samples behave quite similarly (see Fig. 2a). All of them show no initial pinching and behave therefore ferroelectric. In addition, higher Si-doping (less Hf cycles) increases the remanent polarization (P_R) slightly, which are explainable by differences in crystallographic orientation, which are discussed in the section below. In the displacement current, however, more differences can be observed (see Fig. 2b). Besides the minor presence of leakage currents at high voltages, peak splitting in the positive current peak can be observed for the 10:1 cycling ratio. This suggests, based on the discussion above, the presence of in-plane domains in the pristine device and is in agreement with the aforementioned presence of ferroelastic switching. The domain evolution of this complex switching process is illustrated in Fig. 2c. The here shown process starts most likely from an in-plane configuration in pristine condition as observed previously by transmission Kikuchi diffraction [37]. However, randomly polarized domains or super-cooled tetragonal phase might be present alongside. When applying a positive electric field, the domains are switched with the polarization pointing outwards in respect to the sample surface. Upon field-reversal, a sharp transition is observed, thus suggesting a high fraction of 180°-domain wall movement. The field-reversal in opposite direction however shows peak splitting and is therefore governed by 90°-domain wall movement. Even though the phase transition from tetragonal phase have been suggested previously to be responsible for peak splitting, a non-polar phase cannot explain a behavior dependent on the direction of the voltage

sweep. After wake-up the displacement current peaks merge (see supplementary Fig. S1), and the switching process transits to 180°-domain wall motion as well.

To investigate the origin for the higher polarization values in the Si-rich sample, grazing incident X-ray diffraction (GIXRD) patterns of the samples are compared (see Fig. 3a). No signal at the diffraction line positions of the monoclinic phase around 30° is observed, suggesting insignificant fractions of monoclinic phase in all layers. Moreover, the presence of strong intensities at the diffraction lines around 17° and 24° strongly suggest predominant orthorhombic phase as they should not be present in the case of tetragonal phase. Less (100) and (110) signal is observed for the 10:1 sample. While this might be explainable by increased tetragonal phase, this would not match to the electrical results, as other groups have reported that super-cooled tetragonal phase does not result in AFE-like behavior but reduced P_R and P_S [20, 21]. Moreover, the shape of the {200}-peak is slightly changed for the 10:1 sample, as indicated by the smaller TiN-related shoulder and reduced intensity of the (200) shoulder at smaller angles. This correlates to an increased presence of out-of-plane aligned ferroelastic/-electric axis and therefore higher polarization values. The change in crystallographic texture for higher Si-doping could have multiple origins. One major influence of the higher amount of Si in the HfO₂ film is the change in the crystallization temperature. As HSO has a higher crystallization temperature compared to pure HfO₂, increased doping concentrations are expected to increase the temperature required for crystallization even further. This will directly affect the nucleation and grain growth of the film and is therefore expected to affect the crystallographic texture. Moreover, other material properties might be altered by the doping as well, contributing to the observed changes. Nevertheless, the (111) signal is dominating for all MFIS samples and, consequently, smaller polarization values compared to highly [010] out-of-plane textured MFM samples is expected [19, 37].

Comparing now the X-ray photoelectron spectroscopy (XPS) Si signal intensity between MFM and MFIS (see Fig. 3b),

Figure 2: Dynamic hysteresis measurements of MFIS samples with different Hf:Si cycling ratios. Polarization hysteresees (a) of the pristine samples show similar ferroelectric behavior. The displacement current (b) is indicating a trend to AFE-like behavior for high Si-content due to peak splitting. A schematic description of the domain evolution in a pristine MFIS device is given in (c).

Figure 3: (a) Depicting the XRD patterns of the corresponding MFIS samples. In (b) the cycling ratio of Hf and Si pulses is related to the silicon content measured by X-ray photoelectron spectroscopy (XPS). Colored areas indicate the confidence interval. An exemplary survey scan of the Si 2p peak is shown in (c) for MFIS and MFM samples. No significant difference is found in the peak shape for the two sample stacks. The small shift in position is likely an artifact due to, e.g. charging effects, as the substrate layer differs (SiO₂ or TiN).

similar trends are observed in dependence of the cycling ratio. However, the MFIS samples exhibit slightly higher values compared to MFM. This might be a result of the SiO₂ layer present in MFIS, which could increase the Si signal during XPS measurement, whereas in MFM there is a TiN layer present. Besides the very similar doping concentrations, the shape of the XPS Si signal is similar for the two stack configurations as well (see Fig. 3c). This confirms that there are no significant changes in the binding behavior of Si for MFM and MFIS stacks.

While similar Si-doping concentrations are observable in the XPS results, the electrical behavior differs strongly. For the MFM samples, a strong difference in the polarization hysteresis is observable in pristine state (see supplementary Fig. S2) and after 1000 cycles (see Fig. 4a). Here, strong pinching and therefore AFE-like behavior is observed for high Si-concentrations. Moreover, fully pinched and strongly AFE-like behavior persists even after cycling for the 10:1 MFM sample. In consequence,

based on the discussion above, ferroelastic switching is most likely the dominating mechanism at these concentrations. The discrepancy between MFM and MFIS is highlighted by the extracted 2P_R (Fig. 4b). Here, a quite sharp transition is observable for MFM, forming a peak with a maximum around 2 at.% and reaching full AFE-like behavior (2P_R ≈ 0) for the highest measured Si-concentration. The decrease in 2P_R at low Si-concentrations has been related to increased monoclinic phase. For MFIS, on the other hand, only an increase with higher Si-content is observed forming no maximum. However, an decrease is expected for even higher Si-concentrations, as the measured sample with the highest Si-concentration showed peak splitting and therefore a trend to AFE-like behavior. Nevertheless, the region for stable ferroelectric behavior is much larger in MFIS stack configuration.

Similar trends are observable in the saturation polarization (2P_S) in Fig. 4c. Here, the MFM samples again reach a maximum

Figure 4: MFM samples exhibit polarization hystereses (a) with high values and show a clear trend to AFE-like behavior with increasing Si-content, as indicated by the Hf:Si cycling ratio. Extracted 2P_R (b) and 2P_S (c) for MFIS and MFM samples show strong differences, indicating a larger process window for ferroelectric properties in MFIS stacks. Colored areas indicate the confidence interval.

$2P_S$ before decreasing and the influence of monoclinic phase fraction appears more clearly, as $2P_S$ is influenced less by AFE-like behavior. This explains the shift of the peak position to higher Si-content, compared to the $2P_R$ values, as well. Moreover, the decrease in $2P_S$ is likely an artifact, resulting from the transition to sub-loop behavior due to the very high fields required for switching the sample with strong AFE-like behavior. In consequence, the $2P_S$ trend correlates with the amount of orthorhombic phase and degree of out-of-plane texture of the ferroelastic/-electric axes.

For MFIS the $2P_S$ values are slightly lower. Nevertheless, an increase with Si-content is observable as well. Like for $2P_R$, the MFIS behavior appears to be shifted to higher Si-concentrations. The lower values are in line with the previous reports on the crystallographic texture of MFIS [37] and MFM [19] samples. While MFM samples commonly show an out-of-plane texture of the three $\langle 100 \rangle$ -axes [19], MFIS samples show a $\langle 110 \rangle$ and $[111]$ out-of-plane texture instead [37]. This is in agreement with the here reported GIXRD patterns (Fig. 3a). Since the $[010]$ - and $[001]$ -axis resemble the ferroelastic and -electric axis, respectively, higher P_R and P_R values are expected. Lower $2P_S$ values may also arise due to the lower permittivity of the stack due to the presence of the interface layer. Further, the voltage drop across the ferroelectric layer might differ slightly for MFIS due to the presence of the interface layer, which will act as a voltage divider. To compensate the interface layer, values were extracted at higher voltages for MFIS (4.5 V) compared to MFM (3 V). Moreover, the decrease in (100) and (110) signal in the GIXRD patterns with increasing Si-doping, as mentioned before, nicely match with the here observed trends for the $2P_R$ and $2P_S$ values. It should be noted here that the P_R values are slightly overestimated in case of the MFIS samples due to the presence of a small leakage current.

While this explains most of the observed behavior, it raises the question for origin of the shift to higher Si-concentrations in case of the MFIS samples. Recent studies have investigated the

impact of the interface layer on the behavior of HSO [5, 37, 38]. Comparing the hysteresis of the samples with different interface layer thickness, a clear trend to ferroelectric behavior with increasing thickness is observed (see Fig. 5a and supplementary Fig. S3). This suggests a reduction of ferroelastic switching for thicker interfaces and therefore a reduction in tensile in-plane stress of the HSO film [38]. That stress relaxation is linked to the out-of-plane orientation and increased ferroelectric behavior has been reported previously [23, 39]. Moreover, previous results provide strong evidence by X-ray diffraction, that lower stress levels are present for thicker interfaces [39]. The increase in interface thickness is most likely the driving factor for increased ferroelectric behavior with increasing annealing temperature as well, besides the changes in crystallographic texture [37, 38]. As the here reported samples are annealed at 1050 °C, this has to be taken into account as well.

Consequently, the shift and broadening of the Si-doping optimum is most likely a direct result of the interface driven reduction of tensile in-plane stress. This should in principle improve device variability, as local doping concentration fluctuations should have a much smaller effect than in MFM stacks, and offers a wider tuning range of the relative permittivity of the HSO film for band engineering, which might help to improve devices in terms of retention and endurance.

However, the increase of interface thickness comes with a downside in terms of retention [38]. Previous reports have shown, that this results in high retention losses mainly attributed to the increased depolarization field [38, 40]. The latter is a direct result of the increased interface layer thickness. This trend can be clearly observed for the different interface thicknesses over time (see Fig. 5b).

As retention is an important figure of merit for the final device application as well, the impact of Si-doping is investigated (see Fig. 5c). Here, most samples show identical behavior. Nevertheless, a slight increase in retention loss is observed for the highly Si-doped film. This is most likely a result of the

Figure 5: Comparison of HSO MFIS samples with different interface thickness. Polarization hystereses of the pristine device (a) indicate a trend to AFE-like behavior for thinner interfaces. However, larger retention loss (b) is observed for thicker interfaces. MFIS samples with different Hf:Si cycling ratios show no significant dependence on the Si-concentration in terms of retention loss (c). Figure reproduced with permission from: (b) Ref. [38]

increased presence of ferroelastic switching in this sample. Consequently, more in-plane domains are stable and the depolarization field can support 90°-domain wall movement, as it would decrease the out-of-plane field generated by the polarization. Furthermore, the retention behavior could be affected by other effects, like charge trapping or defect pinning.

Previously, it has been already suggested that interface layers with higher relative permittivity could help to overcome the trade-off between retention and less AFE-like behavior [38]. An interface layer with high relative permittivity will improve the endurance of the FeFET as well, as demonstrated by theory and experiment previously [40, 41]. Here, two samples are compared with chemically grown SiO₂ and SiON interface (see Fig. 6), respectively. It can be observed that the SiON sample behaves less AFE-like, as shown for the pristine and cycled hysteresis loop in Fig. 6a and b, respectively. Moreover, no difference in the 2P_S values is observed, indicating no significant difference in the orthorhombic phase fraction and crystallographic texture. However, when comparing the retention of the two samples (see Fig. 6c), no significant difference is observed, even though the interface layer is thicker in case of the SiON interface, as it has seen a nitridation and oxidation anneal in addition. This confirms the previously suggested pathway for improving the ferroelectric properties without deterioration in terms of retention. Moreover, developing interfaces with even higher permittivity could improve the retention of HSO-based FeFETs.

While ferroelectric behavior can be easily modeled [42], modeling the AFE-like response is more complex, as it greatly depends on the physical origin. Since ferroelastic switching is strongly coupled with the electrical and mechanical stress fields in the film, analogue to the coercive electrical field, a coercive mechanical stress will be present as well. Here we propose a simple model, which represents the aforementioned AFE-like behavior based on ferroelastic switching. The induction of AFE-like behavior due to stress is modeled, here, based on a strongly simplified model of the ferroelectric response.

For 180°-domain switching, the simplified model is given in Eq. 1, with the coercive field E_C [42].

$$P_{FE} = P_S * \tanh \left[\frac{E \pm E_C}{2E_C} * \log \left(\frac{P_S + P_R}{P_S - P_R} \right) \right] \quad (1)$$

On the other hand, 90°-domain switching results in a two-step process to revert the polarization axis, namely out-of-plane to in-plane and in-plane to out-of-plane switching (see Eq. 2). Therefore, two effective fields should be considered for the switching processes.

$$P_{AFE} = 0.5 * \left\{ P_{FE} + P_S * \tanh \left[\frac{F \mp E_C}{2E_C} * \log \left(\frac{P_S + P_R}{P_S - P_R} \right) \right] \right\} \quad (2)$$

The fields E and F are defined by the external electric field E_{ext} and the additional contribution f(σ) of the stress (σ) induced stabilization of in-plane domains (see Eqs. 3 and 4). Since a switching process to in-plane orientation might be affected differently by the external electric field compared to a transition to out-of-plane polarization orientation, a coupling factor c is introduced in addition.

$$E = E_{ext} \mp f(\sigma) \quad (3)$$

$$F = c * E_{ext} \pm f(\sigma) \quad (4)$$

By introducing the stress coupling into the two field, the switching processes will take place at different applied voltages and the hysteresis will be pinched/AFE-like. The resulting behavior therefore resembles a first-order transition, as expected for ferroelastic switching [43]. Moreover, for a tensile stress of zero, the equation converges to the ferroelectric one. Since the model resembles a first-order transition, it can be also easily adapted for other mechanisms.

The simulated stress-dependent polarization hystereses are given in Fig. 7a. Here, the pinching with increased in-plane tensile stress can be observed and for low stress levels (f(σ) = 0.6)

Figure 6: Impact of interface permittivity on the electrical behavior of HSO MFIS stacks. Polarization hystereses of samples with SiO₂ and SiON interface in the (a) pristine and (b) cycled (1000 cycles) condition indicate less AFE-like behavior for SiON interface. No significant differences in retention are observed (c).

Figure 7: Modeled polarization (a) and displacement current (b) response for ferroelastic switching with a coupling factor $c = 0.7$ in for different values of the stress-dependent function $f(\sigma)$. Results are in agreement with the experimental results. A schematic phase diagram for the domain and phase composition of HSO in dependence of mechanical stress is given in (c). AFE-like and ferroelectric (FE) behavior resembles in-plane and out-of-plane orientation of the polarization axis at zero field, respectively.

a bulge around the central coercive field can be observed, like in the experimental case for the MFM sample with a cycling ratio of 14:1. The simulated hystereses of a first-order transition are therefore in very good agreement with the observed behavior. Consequently, the model can be used to easily model the different degrees of AFE-like behavior in HfO_2 based films and further investigations on the stress dependence $f(\sigma)$ could enable the tracking of stress evolution in HfO_2 films over electric field cycling.

In consequence, the shift in the $2P_R$ and $2P_S$ trends for MFIS compared to MFM samples is most likely a result of the stress reduction due to a slightly thicker interface layer. Since this affects directly the phase evolution in HSO samples, increasing the stable region for ferroelectric behavior in MFIS samples, it appears reasonable that the phase diagram of HSO is defined directly by the induced mechanical stress. Therefore, a simplified phase diagram (see Fig. 7c) can be sketched that is based on a function containing all influences on the mechanical stress, like annealing temperature, interface layer thickness and Si-doping concentrations. Since these factors are interweaved, process parameters have to be chosen carefully for achieving the desired stress level. Moreover, combined with results from other groups, which reported on a generalized doping dependence for different dopants [44], the here proposed phase diagram can be adapted for other doping elements. In addition, very high doping levels can result in super-cooled tetragonal phase [20, 21], which can be converted to orthorhombic phase by electric field cycling and should result in P_S increase. Depending on the present stress level, the orthorhombic phase will then either behave AFE-like or ferroelectric.

Conclusion

In conclusion, it was shown that the doping window for MFIS samples to achieve ferroelectric behavior is wider compared to MFM samples. The origin for this has been found to be the stress

relaxation resulting from the interface layer. While the thickness of the latter has a strong influence on the retention behavior, no significant impact for different Si-concentrations in the HSO layer was observed. Moreover, the impact of interface nitridation was discussed, enabling improved ferroelectric properties without retention loss. In addition a simplified model for the ferroelastic switching process was developed, which is in agreement with the observed electrical behavior. Finally, a general phase diagram for HSO based on the mechanical stress was deduced.

Experimental

The HSO MFIS samples are prepared on highly doped Si-substrates by depositing 10 nm HSO via atomic layer deposition (ALD) on a SiO_2 interface layer. HfCl_4 and SiCl_4 were used as precursor with varying cycling ratios ranging from 27:1 to 10:1. The 10 nm TiN capping layer was formed by physical vapor deposition (PVD). A crystallization anneal was performed at 1050 °C using rapid thermal processing (RTP). For the MFM samples, an ALD TiN bottom electrode with a thickness of 10 nm is used instead of the chemically grown SiO_2 layer. The MFM annealing temperature is 800 °C.

For comparing different interface compositions, samples were prepared as stated above on a highly doped Si-substrate with a $\text{Si}_{0.75}\text{Ge}_{0.25}$ epitaxial layer. Besides the reference sample with chemically grown SiO_2 , a SiON interface is formed by rapid thermal nitridation and subsequent rapid thermal oxidation.

X-ray photoelectron spectroscopy (XPS) was performed using an aluminum K_α source in the binding energy range of 10–540 eV. Only relevant regions of interest were measured (O 1s, C 1s, Cl 2p, Si 2p, Hf 4f) with a total integration time of 10 minutes per survey site. Grazing incident X-ray diffraction (GIXRD) patterns were collected in a 2θ range of 15° to 45° with a step size of 0.1° and a X-ray grazing angle of 0.5°.

For electrical characterization, capacitor structures were formed by depositing Ti/Pt electrodes with a shadow mask and

subsequent wet-etch to remove excess TiN. An Aixacct TF 3000 Analyser is used for dynamic hysteresis and retention measurements, as well as electric field-cycling. All measurements as well as the cycling were performed with an amplitude of 5 V or 3 V for MFIS and MFM, respectively. Dynamic hysteresis measurements and cycling were performed at a frequency of 1 kHz.

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Data availability

Data will be made available under reasonable request.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary Information

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