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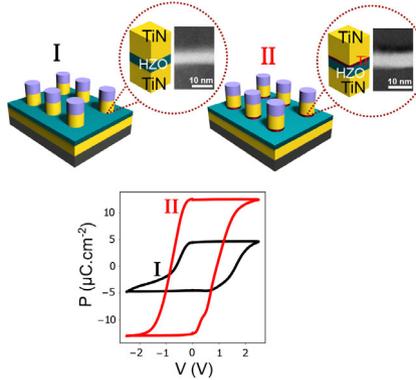
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Ferroelectricity Improvement in Ultra-Thin $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ Capacitors by the Insertion of a Ti Interfacial Layer



Interface engineering of ferroelectric hafnium zirconium oxide (HZO)-based devices is crucial to improve their electrical performances and their scalability. Here, the insertion of an ultra-thin titanium layer at the electrode/HZO interface drastically increases the remnant polarization of 6 nm thick HZO-based capacitors. The thickness of the interfacial layer proved to be a parameter of interest to account for the phenomena occurring at the electrode/HZO/electrode interfaces.

1 Ferroelectricity Improvement in Ultra-Thin $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ 2 Capacitors by the Insertion of a Ti Interfacial Layer

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6 The effect at the nanoscale of a Ti interfacial layer on the performances of TiN/
7 $\text{HfZrO}_2/\text{TiN}$ capacitors is reported. Ferroelectric hafnium zirconium oxide,
8 HZO, is synthesized by magnetron sputtering of a $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ ceramic target.
9 Titanium nitride top and bottom electrodes are grown by reactive magnetron
10 sputtering. The insertion of an ultra-thin Ti layer at the top electrode/HZO
11 interface impacts the crystalline phase and the electrical properties of the
12 ferroelectric HZO. Following post-deposition annealing, the Ti layer is
13 oxidized and becomes titanium oxide. Compositional and structural
14 characterization is performed using glancing incidence X-Ray diffraction
15 and electron energy-loss spectroscopy. The TiO_x layer is clearly distin-
16 guishable at the top electrode/HZO interface. Electrical characterization is
17 conducted by positive-up-negative-down (PUND) technique. The remnant
18 polarization reaches a maximum value of $25 \mu\text{C cm}^{-2}$ for 6 nm thick HZO.
19 The results are discussed in the framework of structural, compositional, and
20 physical properties of the electrode/HZO interfaces and their effect on the
21 electrical performances of thin HZO-based junctions, which could subse-
22 quently be considered for the demonstration of synaptic learning mechanisms
23 for neuromorphic applications.
24

1. Introduction 1

2 The discovery of ferroelectricity in hafnium 2
oxide (HfO_2) by Böschke et al.,^[1,2] in 2011, 3
paved the road for the development of a 4
wide range of concepts and devices based 5
on ferroelectric HfO_2 . Since then, HfO_2 6
has been demonstrated to be a very 7
promising material for the realization 8
of ferroelectric field-effect transistors 9
(FeFET), ferroelectric random access 10
memory (FRAM), negative capacitance 11
field-effect transistors (NCFET), and 12
ferroelectric tunnel junctions (FTJs) for 13
neuromorphic devices.^[3] Different chemi- 14
cal substitutions and processing conditions 15
have been explored to stabilize ferroelectric 16
polymorphs, based on HfO_2 , in polycrystal- 17
line thin films. Among different strategies, 18
which exploit compounds from the solid 19
solution of the physically and chemically 20
compatible zirconium oxide (ZrO_2) and 21
 HfO_2 , the Hf:Zr 1:1 substitution compo- 22
und is of particular interest,^[4,5] due to 23
its high polarization value. For instance, 24
25 $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (HZO) has shown robust ferroelectricity and
26 low-temperature preparation, which is a crucial aspect for its
27 integration into the semiconductor-based industry. The low crys-
28 tallization temperature of the ferroelectric phase guarantees the
29 compatibility of HZO with the complementary metal–oxide–
30 semiconductor process. Among HfO_2/HZO -based nonvolatile
31 memory devices, FTJs offer the possibility to increase the device
32 scalability for their integration into dense memory arrays.^[6]
33 HZO-based FTJs have also been considered promising for the
34 implementation of synaptic devices for neuromorphic comput-
35 ing.^[7] A FTJ is a trilayer stack where a thin ferroelectric material,
36 which serves as a tunnel barrier,^[8] is sandwiched between two
37 electrodes. In the literature, several examples of FTJs based
38 on electrode–ferroelectric–electrode structure for memory
39 applications have been reported.^[7,9] In the present work, we com-
40 pare the structural and electrical characteristics of an electrode-
41 ferroelectric-electrode stack with those of an electrode–ferroelec-
42 tric–metal–electrode structure. In the former, a thin layer of
43 HZO is sandwiched between a titanium nitride (TiN) bottom
44 (BE) and top electrode (TE), while in the latter, an ultra-thin layer
45 of titanium (Ti) is inserted at the TE/HZO interface. This type of
46 structure has previously been reported. Max et al.^[10] developed a

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1 TiN/HZO/Al₂O₃/TiN stack, where Al₂O₃ serves as a tunnel
2 barrier and the HZO film provides the ferroelectric switching.
3 Shekhawat et al.^[11] reduced the voltage of read and write oper-
4 ations of HZO-based FTJs by integrating a 1 nm-thick Al₂O₃
5 interfacial layer. Qi et al.^[12] demonstrated that the incorporation
6 of a TiO₂ layer at the bottom and top interface of a TiN/HZO/
7 TiN stack increases the amount of orthorhombic phase in as-
8 deposited HZO. Gaddam et al.^[13] showed that dielectric-
9 ferroelectric-dielectric capacitors based on HZO exhibit good
10 ferroelectric properties even at low annealing temperatures.
11 Finally, Ryu et al. proposed an Al₂O₃/HZO-based structure,
12 which shows a synaptic behavior, where the Al₂O₃ layer enables
13 a sizeable tunnel electroresistance ratio.^[14] The synthesis of
14 HZO films less than 8 nm thick that exhibit robust ferroelectric-
15 ity is a challenging task.^[15] In this work, we significantly
16 improve the ferroelectric properties of a few nm thick HZO
17 films, by inserting an ultra-thin metallic interfacial layer. We
18 demonstrate outstanding remnant polarization and high endurance
19 in 6 nm thick non-epitaxial HZO. The obtained results
20 show that by means of interface engineering it is possible to
21 scale the thickness of HZO down to a few nm, without
22 compromising its ferroelectricity. This would be of great inter-
23 est for FTJ applications. The heterostructure fabrication was
24 entirely performed by radio-frequency magnetron sputtering
25 ing.^[16] Subsequently, we investigated the effect of a Ti interfacial
26 layer of different thicknesses on the crystalline phase,
27 electronic structure, and electrical performances of 6 nm thick
28 HZO-based capacitors. We propose an optimized stack with
29 enhanced ferroelectric properties.

2. Experimental Section

2.1. Synthesis

The growth of the stack was performed on n⁺Si(100) substrates.
Prior to deposition, the substrates were cleaned with acetone and
ethanol, and freed from the native oxide layer by a buffer oxide
etching procedure. The depositions of the hafnium zirconium
oxide (HZO) layer, TiN bottom and top electrodes, and Ti/Pt
top electrical contacts were realized by magnetron sputtering
at room temperature, using an AC-450 sputtering machine by
Alliance Concept. The 50 nm thick TiN electrodes were grown
by radio-frequency reactive magnetron sputtering of a Ti target
at a pressure of 5 × 10⁻³ mbar, using a mixture of Ar and N₂. The
6 nm thick HZO layer was grown by magnetron sputtering of a
Hf_{0.5}Zr_{0.5}O₂ ceramic target at a pressure of 5 × 10⁻² mbar.^[16-18]
Afterward, UV photolithography (20 mW cm⁻² at a wavelength of
405 nm) was performed to obtain the electrical contacts, made by
a few nm thick Ti adhesive layer and 50 nm of Pt. The photoresist
used for the lithography process was a positive photoresist and
the exposure time was 5 s. Once synthesized, the stack was sub-
jected to rapid thermal annealing at a temperature of 450 °C, for
30 s, in an N₂ atmosphere. **Figure 1** shows the structure of the
synthesized samples. Figure 1a,b reports the structure of the
specimen without (1a) and with (1b) the insertion of the Ti layer,
together with the scanning transmission electron microscope
(STEM) high-angle annular dark-field (HAADF) image of the
TE/HZO/BE cross-section. Figure 1c shows the optical image
of the surface of the sample with the pattern of capacitors.

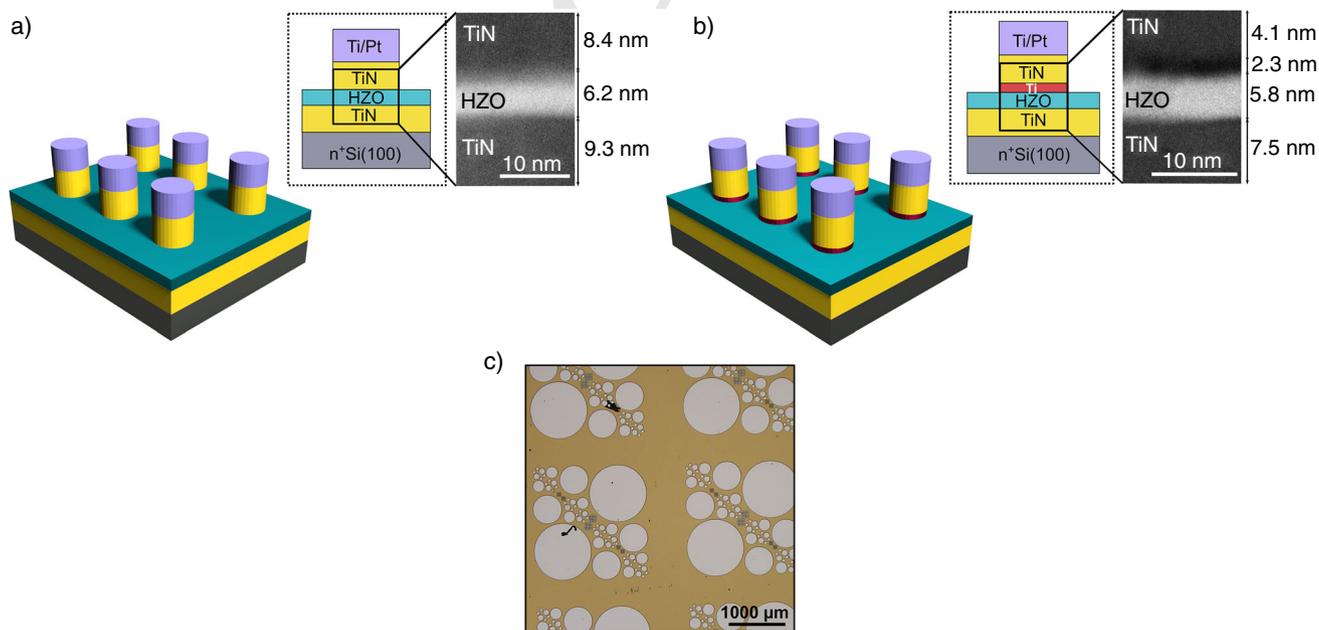


Figure 1. Schematic of the structure of the samples. a) n⁺Si/TiN/HZO/TiN/Ti/Pt, on the right is the scanning transmission electron microscope- high-angle annular dark field (STEM-HAADF) image of the TE/HZO/BE cross-section. b) n⁺Si/TiN/HZO/Ti/TiN/Ti/Pt, on the right is the STEM-HAADF image of the TE/HZO/BE cross-section. c) Optical image of the surface of the sample with the pattern of capacitors used for the electrical characterization.

Table 1. Film growth conditions.

		Sputtering Process			
Target-substrate distance		8 cm			
Base pressure		$<5 \times 10^{-7}$ mbar			
Ignition pressure		5×10^{-2} mbar			
Deposited elements	TiN	$\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$	Ti	Pt	
Substrate	$\text{n}^+\text{Si}(100)$	$\text{n}^+\text{Si}(100)/\text{TiN}$	$\text{n}^+\text{Si}(100)/\text{TiN}/\text{HZO}$	$\text{n}^+\text{Si}(100)/\text{TiN}/\text{HZO}/\text{TiN}$	
Target (purity)	Ti (99.995%)	$\text{ZrO}_2/\text{HfO}_2$ (50%/50%)	Ti(99.995%)	Pt (99.95%)	
Target RF power/voltage [w/v]	300 W	100 W	100 W	137 V	
Holder DC bias voltage [V]	60 V	None	None	None	
Gas [sccm]	Ar 50 sccm; N_2 3 sccm	Ar 50 sccm	Ar 50 sccm	Ar 50 sccm	
Working pressure [mbar]	5×10^{-3} mbar	5×10^{-2} mbar	5×10^{-2} mbar	5×10^{-3} mbar	
Deposition rate	≈ 5 nm min	≈ 4 nm min	≈ 3.5 nm min	≈ 17 nm min	
		UV Lithography Conditions			
Photoresist	Positive AZ5214				
Exposure time [s]	5 s				
Flood exposure time [s]	25 s				
Power per units area [mW cm^{-2}]	20 mW cm^{-2} at 405 nm				
		Rapid Thermal Annealing Conditions			
Temperature [°C]	450 °C				
Atmosphere (1 atm)	N_2				
Time [s]	30 s				

1 Growth, annealing, and capacitor fabrication conditions are
2 reported in **Table 1**.

3 2.2. Characterization

4 The thickness of the layers composing the stacks was evaluated
5 by X-Ray reflectometry (XRR) and their structural characteriza-
6 tion was performed by glancing incidence X-Ray diffraction
7 (GI-XRD) by means of a six-circle goniometer SmartLab
8 Rigaku diffractometer using a 9 kW copper rotating anode.
9 GI-XRD experiments were carried out using a parabolic multi-
10 layer mirror for parallel beam setting, Ni filter for Cu K alpha
11 radiation selection, 0.114° aperture parallel slit analyzer, and a
12 OD scintillating counter. The composition and the electronic
13 structure in the vicinity of the top interface (TE/HZO) were
14 investigated by electron energy-loss spectroscopy (EELS) in
15 STEM mode. The instrument used was a Jeol JEM-ARM200F
16 NeoARM transmission electron microscope, equipped with a
17 high-brightness cold-FEG, a CEOS ASCOR aberration-corrector
18 of the probe forming lenses, a Gatan imaging filter quantum, and
19 operated at 200 kV. The cross-section specimen for STEM
20 analysis was prepared by the Ga-focused ion beam (FIB) milling
21 technique. Core-loss STEM-EELS data were collected using the
22 spectrum-imaging technique implemented in the Gatan
23 microscopy suite, with a dispersion of 0.3 eV/channel.
24 Polarization versus voltage measurements were carried out at
25 room temperature on $20 \mu\text{m}$ -diameter capacitors, using a
26 Keithley 4200A-SCS semiconductor parameter analyzer. The

electrical characterization was performed using a manual probe 1
station, where samples were kept in a closed environment and 2
electrical contact was made with two tungsten-tip probes. The 3
voltage was applied by contacting the top electrode of each device 4
with one probe, while the other was kept on the common bottom 5
electrode. $P - V$ characteristics were obtained by positive-up- 6
negative-down (PUND) technique, which consists of a train of 7
five pulses. A negative reset pulse is applied to initialize the polar- 8
ization along one direction, subsequently two positive (P and 9
U) and two negative pulses (N and D) are applied. The PUND 10
pulses had a triangular shape, with an amplitude of 2.5 V and 11
a rising/falling time of $50 \mu\text{s}$. The endurance test was performed 12
by cycling the capacitors, usually until the breakdown. 13

3. Results and Discussion 14

3.1. Structural Characterization by GI-XRD and EELS 15

Four samples, labeled Samples 0, 1, 2, and 3 for simplicity, were 16
studied. For Sample 0, the HZO layer was sandwiched between 17
TiN bottom and top electrodes, while for Samples 1, 2, and 3 an 18
ultra-thin layer of Ti, of 1, 2, and 3 nm, respectively, was 19
deposited at the top interface by RF magnetron sputtering. 20
The GI-XRD patterns obtained for the four samples are shown 21
in **Figure 2**. Reference XRD patterns for TiN, HZO α -/ t -phase, 22
and HZO m -phase from ICDD00-038-1420, ICDD01-083-0808, 23
and ICDD00-034-0104, respectively, were considered to fit the 24
experimental pattern for each sample, and are overlaid in 25

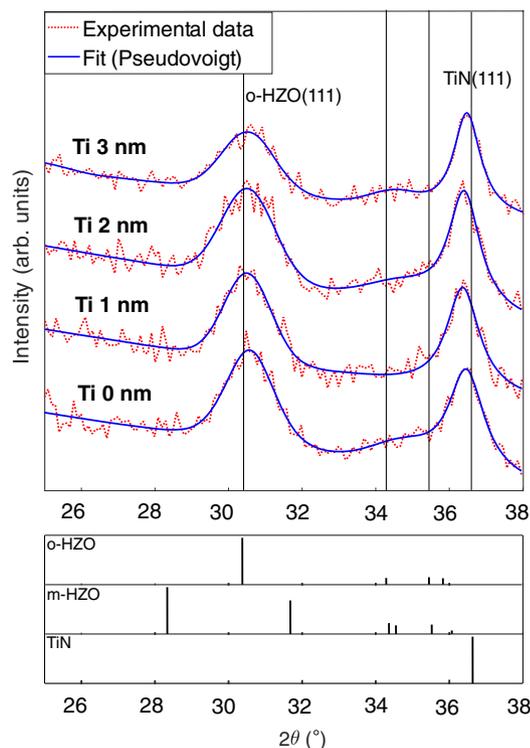


Figure 2. Glancing incidence X-Ray diffraction (GI-XRD) patterns that show the intensity versus scattering angle of the four considered samples. Starting from the bottom: Sample 0— n^+ Si/TiN/HZO/TiN/Ti/Pt, Ti 0 nm, Sample 1— n^+ Si/TiN/HZO/Ti/TiN/Ti/Pt, Ti 1 nm, Sample 2— n^+ Si/TiN/HZO/Ti/TiN/Ti/Pt, Ti 2 nm, Sample 3— n^+ Si/TiN/HZO/Ti/TiN/Ti/Pt, Ti 3 nm. Below, the expected peak positions for orthorhombic HZO, monoclinic HZO, and TiN. For the fit, only the position of Cu K alpha 1 has been considered.

Figure 2. The dotted red line represents the experimental data 1
and the straight blue line shows the fitted curve. The fitting func- 2
tion is a pseudo-Voigt that accounts for the Cu K alpha 1 and K 3
alpha 2 radiations. The position of the *o*-/*t*- peak at $\approx 30.5^\circ$, which 4
corresponds to (111) planes, coincides with the expected value.^[19] 5
No *m*-phase components at $\approx 28.4^\circ$ (*m*-HZO (11-1)), and at 6
 $\approx 31.6^\circ$ (*m*-HZO(111)) were detected. The intensity of *o*-/*t*-peak, 7
which is similar for the four cases, is not correlated to the pres- 8
ence of the Ti layer nor to its thickness. This analysis validates the 9
existence of the ferroelectric *o*-HZO phase for the analyzed sam- 10
ples. The diffraction peak of the *o*-HZO(111) family of planes, at 11
 $\approx 30.5^\circ$, was considered for the evaluation of the average crystal- 12
line size of the HZO layer by means of the Scherrer equation.^[20] 13
Overall, crystalline sizes around 5 nm were found for all samples. 14
Details of the calculation are shown in the Supplemental 15
Material. The crystalline size is not correlated to the thickness 16
of the Ti interfacial layer. 17

The structure and composition of the TiN/HZO top interface 18
in Sample 0 and the Ti/HZO top interface in Sample 2 were 19
investigated at the nanoscale by STEM-EELS on pristine capaci- 20
tors of $10\ \mu\text{m}$ diameter, as shown in Figure 3 and 4, respectively. 21
The spatial distribution of N (N-K edge at $\approx 400\ \text{eV}$), Ti (Ti- $L_{2,3}$ 22
edges at $\approx 455\ \text{eV}$), and O (O-K edge at $\approx 530\ \text{eV}$) across the TE/ 23
HZO interfaces are shown in Figure 3a and 4a. For the TiN/ 24
HZO top interface of Sample 0, a TiN(O) layer is evidenced from 25
the simultaneous presence of the N-K, Ti- $L_{2,3}$, and O-K edges, 26
resulting from the oxidation of the TiN layer. This oxidation is 27
localized over $\approx 2\ \text{nm}$, as indicated by the O-K edge fine struc- 28
tures, which decreases consistently from HZO to TiN, and is 29
accompanied by a shift of the O-K edge onset to lower energy, 30
as shown in Figure 3d. The TiN oxidation phenomenon is 31
also described in previous work by our group^[17] in a structure 32
synthesized in the same experimental conditions as the ones con- 33
sidered in this work. The N-K edge fine structures in the TiN 34
layer are similar to the ones reported in the literature,^[21] with 35

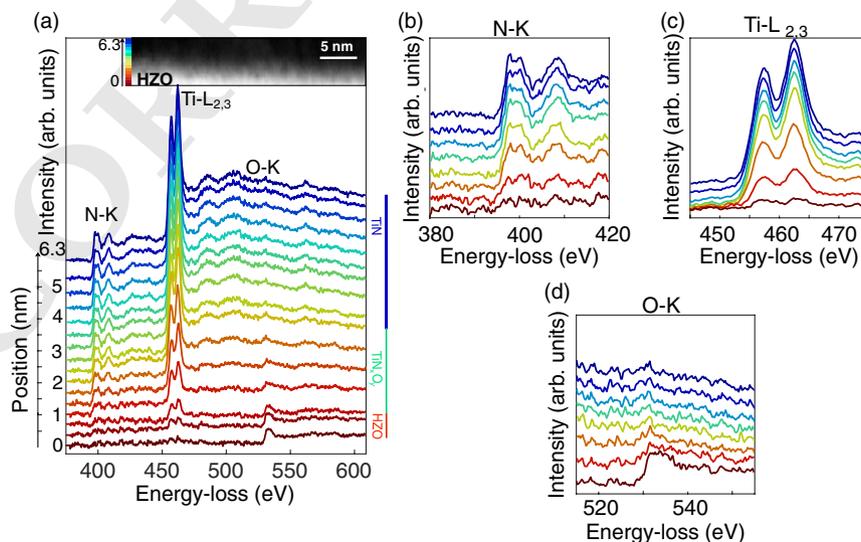


Figure 3. STEM- electron energy-loss spectroscopy (EELS) analysis of Sample 0. a) EELS spectra acquired across the TE/HZO interface. Each spectrum is the average of 81 spectra projected horizontally along the interface, and is shifted vertically for clarity. The HAADF image acquired simultaneously is shown in the inset. A spectrum image dataset of 16×81 pixels was acquired with a step size of $3.9\ \text{\AA}$, over an area of $\approx 6.3 \times 32\ \text{nm}^2$. b), c), d) Display over a narrower energy range of the N-K, Ti- $L_{2,3}$, and O-K edges, respectively.

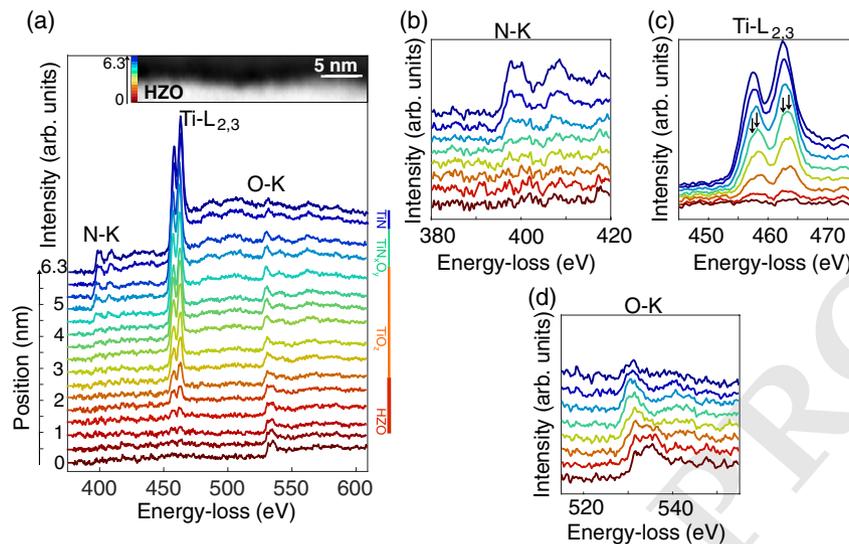


Figure 4. STEM-EELS analysis of Sample 2. a) EELS spectra acquired across the TE/HZO interface. Each spectrum is the average of 81 spectra projected horizontally along the interface, and is shifted vertically for clarity. The HAADF image acquired simultaneously is shown in the inset. A spectrum image dataset of 16×81 pixels was acquired with a step size of 3.9 \AA , over an area of $\approx 6.3 \times 32 \text{ nm}^2$. b), c), d) Display over a narrower energy range of the N–K, Ti–L_{2,3}, and O–K edges, respectively.

1 some fine structure variations and an overall decrease of the N–K
2 edge intensity in the TiN(O) layer, potentially resulting from
3 oxidation^[22] (Figure 3b). In addition, the constant energy and
4 shape of the Ti–L_{2,3} fine structures across the interface, shown
5 in Figure 3c, suggest a low oxidation. For the Ti/HZO top
6 interface of Sample 2, a TiO₂ layer is evidenced over a couple
7 of nanometers, from the simultaneous presence of the O–K
8 and Ti–L_{2,3} edges and the absence of the N–K edge, as shown
9 in Figure 4a,b, thus indicating the oxidation of the Ti layer.
10 Specifically, the Ti–L_{2,3} fine structures split (Figure 4c), as
11 expected in TiO₂, where the L₃ and L₂ peaks split under the influ-
12 ence of the crystal field.^[23] The L₃ and L₂ peaks also shift to
13 higher energy compared to TiN. The O–K edge fine structures
14 change across the HZO/TiO₂ interface, and the edge onset shifts
15 to lower energy in the TiN(O) layer, as shown in Figure 4d. The
16 TiN layer deposited on top of Ti is thus partially oxidized over a
17 very narrow range, as exemplified from the simultaneous
18 presence of N–K, Ti–L_{2,3}, and O–K edges. The N–K edge fine
19 structures at the Ti/TiN interface are different from TiN, as a
20 result of oxidation and subsequent chemical bonding between
21 Ti *d* and O *p* states. Finally, the O–K near edge structures of
22 HZO are different in both samples. In Sample 2 (Figure 4d),
23 two distinct peaks are visible within 10 eV above the edge onset,
24 as expected in HZO polymorphs,^[24,25] contrary to Sample 0
25 (Figure 3d). The near-edge structures reflect the local electronic
26 structure around O atoms, which are covalently bonded to Hf and
27 Zr atoms. Several parameters could be the cause of these spectral
28 variations, such as local changes of the crystal field,^[26] the pres-
29 ence of oxygen vacancies,^[27–30] or local inhomogeneities in Hf
30 versus Zr content^[31] integrated over in the spectra displayed
31 in Figure 3 and 4. The origin of these differences at the O–K edge
32 in both HZO layers is still under investigation. The EELS analysis
33 demonstrates that the Ti layer is fully oxidized (Sample 2),
34 whereas in the absence of Ti, the TiN layer is only partially

oxidized. The oxygen redistribution induced by the Ti layer is
1 meant to produce oxygen vacancies inside the HZO film by
2 pulling oxygen atoms toward the top interface. The oxidation
3 phenomenon of the Ti layer explains the contrast difference at
4 the TE/HZO interface in the cross-sectional HAADF images
5 in Figure 1a,b. In Sample 2, the TE/HZO interface appears dark
6 from the presence of the TiO₂ interfacial layer. 7

3.2. Electrical Characterization by PUND

Polarization (*P*) versus applied voltage (*V*) measurements were
9 performed on the four samples at room temperature (300 K).
10 **Figure 5** shows the *P* – *V* curves after 10⁴ cycles of Samples 11

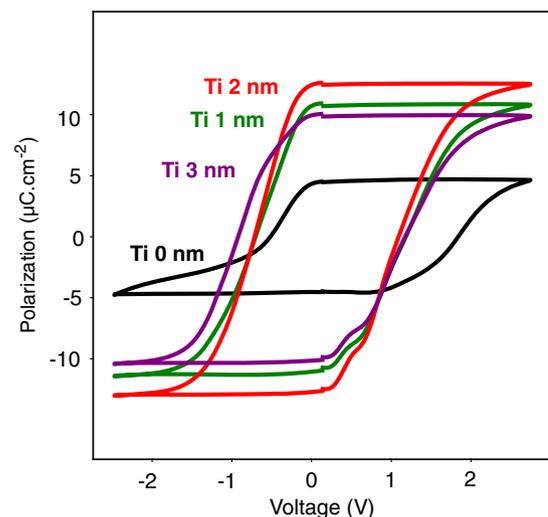


Figure 5. Electrical characterization for Samples 0, 1, 2, and 3: *P*–*V* curves taken on woken up capacitors after 10⁴ cycles.

Table 2. Values of remnant polarization in $\mu\text{C cm}^{-2}$ for samples 0, 1, 2, and 3 for the pristine state, after 10^4 cycles, and before breakdown.

	Pristine	After 10^4 cycles	Before breakdown
Sample 0 (Ti 0 nm)	0	10	9
Sample 1 (Ti 1 nm)	9	23	25
Sample 2 (Ti 2 nm)	10	25	30
Sample 3 (Ti 3 nm)	11	20	22

0, 1, 2, and 3. For an applied voltage of ± 2.5 V, the value of the remnant polarization, $2P_r$, ranges between $10 \mu\text{C cm}^{-2}$ for Sample 0 and $25 \mu\text{C cm}^{-2}$ for Sample 2. Samples 1 and 3 show a $2P_r$ of 23, and $20 \mu\text{C cm}^{-2}$, respectively. The $P - V$ curves indicate that the presence of the Ti layer increases the ferroelectric imprint, introducing a systematic left shift of the hysteresis loops of Samples 1, 2, and 3. In these cases, the Ti layer modifies the work function of the top electrode. This creates an asymmetry between the electrodes, which is responsible for a built-in field. This phenomenon has been already described in the literature for other ferroelectric-based stacks with different electrodes.^[32] The obtained results show that the presence of the Ti layer clearly increases the value of $2P_r$. The highest $2P_r$ is obtained for Sample 2 and the lowest for Sample 0. This could be attributed to two factors: I) The chemical properties of the Ti/HZO interface, which are different from the ones of the interface TiN/HZO, promotes the formation of α -phase grains. The thermal expansion coefficient (TEC) of Ti and TiN have close values, 0.9410^{-5} and $0.810^{-5} \text{ K}^{-1}$, respectively.^[33,34] Because Ti and TiN TECs are similar, we propose that the main cause of ferroelectricity enhancement in HZO, in samples with Ti, could arise from the different chemical reconstructions of the top interface. II) The increased number of oxygen vacancies in HZO, which is induced by the Ti layer,^[35] takes part in the stabilization of the orthorhombic phase in the HZO film.^[36,37] For a thicker interfacial layer, the polarization inverts its rising, dropping to $20 \mu\text{C cm}^{-2}$ for Sample 3. This behavior can be explained by the increasing depolarizing field produced at the interface by

the TiO_2 dielectric layer, which is responsible for the lower remnant polarization in Sample 3.^[38,39] This tendency is also confirmed in the literature, Si et al.,^[40] Qu et al.,^[41] and Shekhawat et al.^[11] have reported a suppression of the ferroelectricity when the thickness of the dielectric layer is increased. Furthermore, Samples 1, 2, and 3 show a positive $2P_r$ in the pristine state, contrary to the null value of Sample 0. This result is explained by the hypothesis that the interfacial properties of Ti/HZO promote the formation of α -phase crystallites. The endurance curves in Figure 7 show that $2P_r$ increases for Samples 1, 2, and 3 until breakdown occurs, while Sample 0 enters in a fatigue state after $\approx 10^6$ cycles, where $2P_r$ decreases to $\approx 9 \mu\text{C cm}^{-2}$. The increase of the remnant polarization is associated to the well-known wake-up effect, which is partly due to the redistribution of the defects, typically oxygen vacancies, during the cycling process.^[42,43] Table 2 gives the value of the remnant polarization of Samples 0, 1, 2, and 3 in the pristine state, after 10^4 cycles, and before breakdown. Figure 6 shows its trends as a function of the Ti thickness.

The endurance tests were performed on the four samples until breakdown. Figure 7 shows the change of remnant polarization P_+ and P_- according to the applied number of voltage cycles. At 2.5 V, the value of $|P_+|$ and $|P_-|$ starts at $\approx 5 \mu\text{C cm}^{-2}$ for Samples 1, 2, and 3, and at $\approx 0 \mu\text{C cm}^{-2}$ in the case of Sample 0, for which it starts rising after 5×10^2 cycles. In Sample 0, P_r reaches its maximum after 10^5 cycles. For Samples 1, 2, and 3, P_r rises until breakdown, which occurs after 10^6 , 5×10^5 , and 10^7 cycles, respectively. On average, the obtained results indicate that the endurance value of the here tested devices is comparable to what is reported in the literature.^[10,18]

From the analysis of the presented results, we formulated a hypothesis that could explain the obtained trends for P_r and endurance as a function of the thickness of the Ti layer. A 2 or 3 nm thick Ti interfacial layer, is enough to ensure the bulk-like chemistry of titanium and titanium oxide, favoring the α -phase formation through oxygen vacancy generation, and providing a higher remnant polarization. This is true in the case of the pristine state as well. The decrease of P_r of Sample 3 can be ascribed to the increased depolarizing field that is induced by a

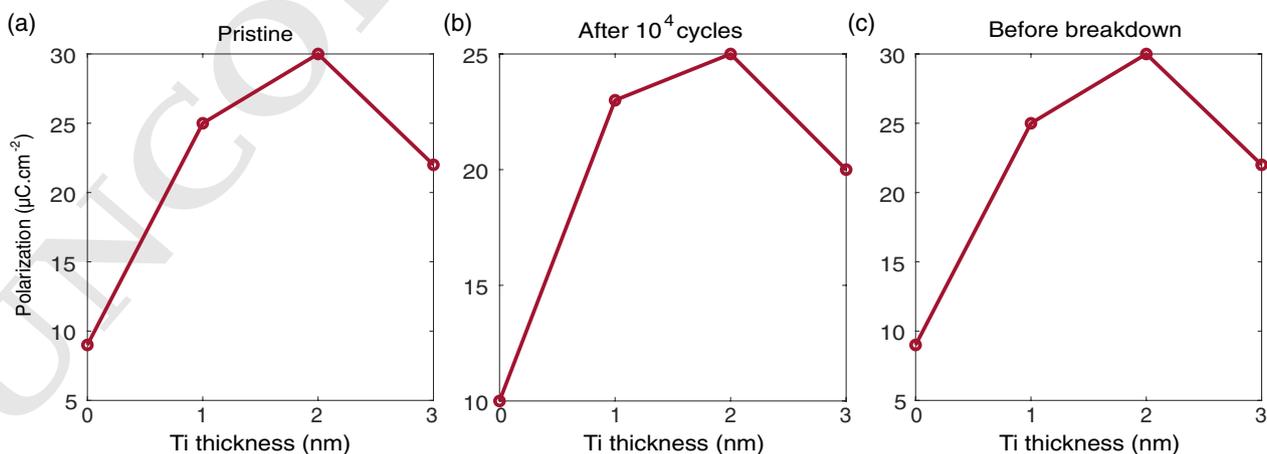


Figure 6. Remnant polarization versus Ti thickness for Samples 0, 1, 2, and 3, indicating the trend of $2P_r$ in: a) pristine state, b) after 10^4 cycles, c) before breakdown.

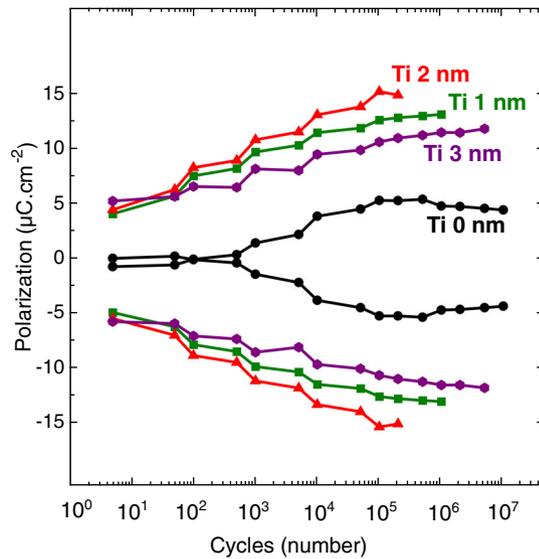


Figure 7. Electrical characterization of Samples 0, 1, 2, and 3: endurance tests.

1 thick dielectric layer. We can suppose that a 3 nm thick Ti layer is
2 not as beneficial as a 2 nm thick one, as far as P_r is concerned.
3 Furthermore, in Sample 1, the Ti layer is too thin to provide the
4 same interface conditions as in Samples 2 and 3, and so to
5 increase P_r at the value of Sample 2. This could be due to the
6 fact that a 1 nm thick Ti layer is not enough to have the same
7 chemical properties as bulk Ti. As mentioned, Ti scavenges
8 oxygen from HZO, thus creating oxygen vacancies at the top
9 interface. Besides stabilizing the ferroelectric phase at low
10 HZO thickness, a high amount of oxygen vacancy is responsible
11 for an increased leakage current that could make the specimen
12 more fragile.^[44] About the endurance, the highest value corre-
13 sponds to Sample 0, which can be considered satisfying for a
14 6 nm thick HZO film. For Sample 1, we mentioned that the
15 1 nm thick Ti layer is not sufficient to increase P_r , as for
16 Sample 2. However, it might produce more oxygen vacancies that

can impact the endurance, which decreases with respect to 1
Sample 0. In Sample 3, a 3 nm thick Ti layer is sufficient to 2
efficiently scavenge oxygen from the HZO film, but since the 3
formed dielectric layer is thicker with respect to Samples 1 4
and 2, it might result in a more resistant sample than 5
Samples 1 and 2. Eventually, for Sample 2, the chemical proper- 6
ties of the Ti/HZO interface promote the α -phase formation, and 7
the Ti layer is thin enough to limit the effect of the depolarizing 8
field, compared to Sample 3. Nevertheless, these benefits could 9
be impacted by an enhanced fragility of the sample, where the 10
increased number of oxygen vacancies is responsible for a break- 11
down after a low number of cycles.^[44] The stacks containing the 12
Ti layer can be compared to other structures reported in the lit- 13
erature, as shown in **Table 3**. The studies presented in Table 3 14
highlight that the insertion of an ultra-thin interfacial layer at one 15
or both electrode/HZO interfaces is beneficial for the electrical 16
properties of HZO-based devices. For instance, an ultra-thin 17
interfacial layer improves the value of the remnant polarization 18
of HZO by favoring the α -phase nucleation at low annealing 19
temperatures, simplifying the integration of ferroelectric HZO 20
into the CMOS process. Furthermore, it is helpful to enhance 21 Q4
the tunnel electroresistance ratio for FTJ applications. Here, 22
we demonstrate that the Ti layer is fundamental to improve 23
the ferroelectricity of ultra-thin HZO films. We show an 24
enhanced value of the remnant polarization in the pristine state 25
for samples with Ti layer, which almost triples once the capaci- 26
tors are cycled. This result makes the insertion of the interfacial 27
layer a very promising approach to further scale down the thick- 28
ness of ferroelectric HZO for FTJ devices. However, 29
additional experiments are necessary to deeper investigate the 30
electrical properties of the presented devices and the role of 31
the interfacial layer. It would be of great interest to perform cur- 32
rent versus voltage (I - V) measurements to explore the dominant 33
conduction mechanisms inside the HZO film, capacitance 34
versus voltage measurements (C - V) to probe the impact of the 35
Ti interfacial layer, and the conductance method ($G_{P/\omega}$)^[45] to evalu- 36
ate the density of trap states at the dielectric/ferroelectric 37
interface.^[40,41] 38

Table 3. State of the art: thin-HZO-based structure with the addition of interfacial layers (ALD stands for atomic layer deposition, PE-ALD for plasma-enhanced ALD).

Reference	Structure	Fabrication method	HZO thickness [nm]	Interfacial layer thickness [nm]	$2P_r$ [μCcm^{-2}]	Endurance
Gaddam et al. ^[13]	TiN/TiO ₂ /HZO/HfO ₂ /TiN	PE-ALD	10	1	16	10 ⁸
Shekhawat et al. ^[11]	p-Ge/Al ₂ O ₃ /HZO/TiN/Pt	ALD	8.4	1	15	10 ⁵
				1.8	12	10 ⁵
				2.2	7	between 10 ⁵ and 10 ⁶
Qi et al. ^[12]	Si/TiN/TiO ₂ /HZO/TiO ₂ /TiN	PE-ALD	10	2	8 (as deposited and after wake-up)	
Ryu et al. ^[14]	p-Si/HZO/Al ₂ O ₃ /Ti/Au	ALD	12	3	21	10 ⁶
In this work	n ⁺ Si/TiN/HZO/Ti/TiN/Ti/Pt	RF MS	6	1	23	10 ⁶
				2	25	5 × 10 ⁵
				3	20	10 ⁷

1 4. Conclusion

2 The structural, compositional, and electrical characterizations of
3 HZO-based stacks were performed by X-Ray diffraction, electron
4 energy-loss spectroscopy, and PUND technique, respectively.
5 The impact of a Ti interfacial layer of different thicknesses
6 was investigated with the aim of optimizing the ferroelectric
7 properties of thin HZO films for future ferroelectric tunnel junction
8 applications. The results revealed that the Ti interfacial layer
9 plays an important role in the microstructure and the electrical
10 performances of HZO-based capacitors. The most promising
11 structure is the one where a 2 nm thick Ti layer was inserted
12 at the top electrode/HZO interface. This consideration is a
13 tradeoff between, on the one hand, the chemistry of the Ti/
14 HZO interface, and the induced oxygen redistribution that
15 stabilizes the o-phase in HZO and, on the other hand, the effect
16 of the depolarizing field that diminishes the value of the remnant
17 polarization. The improvement of the electrical performances of
18 HZO-based heterostructures by engineering the electrodes/
19 HZO interfaces is a promising approach that can lead to a further
20 scaling of these devices for nonvolatile memory applications.

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34 Conflict of Interest

35 The authors declare no conflict of interest.

36 Data Availability Statement

37 The data that support the findings of this study are available from the
38 corresponding author upon reasonable request.

39 Keywords

40 ferroelectricity, HZO, thin films

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