Synaptic behaviour in ferroelectric epitaxial rhombohedral Hf$_{0.5}$Zr$_{0.5}$O$_2$ thin films

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Keywords: hafnia, ferroelectric, rhombohedral, epitaxial, switching mechanism, synaptic devices

Abstract

The discovery of ferroelectricity in HfO$_2$-based thin films brings tremendous opportunities for emerging ferroelectric memories as well as for synaptic devices. The origin of ferroelectricity in this material is widely attributed to the presence of a polar orthorhombic phase. However, a new ferroelectric rhombohedral phase displaying large polarization with no need of pre-cycling, has more recently been reported in epitaxial Hf$_{0.5}$Zr$_{0.5}$O$_2$ (HZO). In this work, the switching mechanism of the rhombohedral phase of HZO films is characterized by a two-stage process. In addition, the synaptic behaviour of this phase is presented, comparing it with previous reports on orthorhombic or non-epitaxial films. Unexpected similarities have been found between these structurally distinct systems. Even though the epitaxial films present a larger coercive field, the ratio between the activation field for intrinsic polarization switching and the coercive field ($F_a/E_c$) has been found to be close to 2, in agreement with that reported for other hafnia samples. This is about 5 times smaller than in most other ferroelectrics, confirming this characteristic as a unique feature of hafnia-based ferroelectrics.

1. Introduction

With the aim to achieve energy-efficient data processing, researchers are looking into non-von-Neumann architectures inspired by the human brain, gathered under the name of neuromorphic, cognitive or brain-inspired computing [1–3]. In order to attain significant energy savings, co-localization of memory and processing needs to take place at the smallest scales, requesting circuit elements that can perform both tasks. Memristive devices, whose resistance can be stored and switched among multiple states, determined by the history of the applied voltage, are ideally suited for this task [4–6]. Non-volatile memristive devices, with fast switching speeds bridge the existing memory gap and can be used for in-memory computing [7, 8]. They can also act as synaptic weights in a hardware version of artificial neural networks for deep learning acceleration or in spiking neural networks, in which information is of analog nature, encoded in the time between the excitation pulses, thus emulating biological neurons [9–14].

The implementation of synaptic plasticity in memristive devices is achieved by applying appropriate trains of electrical pulses that change the conductance of the devices through a diversity of physical mechanisms [8], such as ionic drift, ionic diffusion, redox reactions, phase transitions, spintronic effects, and ferroelectric polarization/domain switching, to name the most prominent ones. In this work, ferroelectric memristors based on the novel hafnia-based ferroelectric (Hf$_{0.5}$Zr$_{0.5}$O$_2$, hereafter HZO) are studied.

The discovery of ferroelectricity in the HfO$_2$-based ultrathin layer represented a breakthrough in the field [15]. Due to its CMOS-compatibility and presence of nanoscale ferroelectricity with large remanent polarization values of tens of $\mu$C cm$^{-2}$ (unattainable in other ferroelectrics upon miniaturization), HZO is boosting the...
Thin-films of HZO with thickness of 9 nm were grown on LSMO-buffered (001)-SrTiO3 substrates by pulsed laser deposition [25]. A KrF excimer laser with a wavelength of 248 nm was used to ablate home-made LSMO and HZO targets. An LSMO bottom electrode layer was deposited under a laser frequency of 1 Hz with a fluence of 1 J cm−2; the growth temperature was 775 °C and the oxygen atmosphere was 0.15 mbar. Afterwards, HZO thin film layer was deposited with a laser fluence of 1.1 J cm−2 and at a frequency of 2 Hz. The oxygen pressure and the growth temperature were 0.1 mbar and 800 °C, respectively. A third layer of LSMO was deposited as the top electrode under the same growth conditions as the first LSMO layer. After deposition, the films were cooled down to room temperature at the rate of 5 °C min−1 under 300 mbar oxygen atmosphere. X-ray diffraction (XRD) was used for structural characterization. As shown in figure 1(a), while the first LSMO layer expectedly follows the (001) orientation of the substrate, the HZO layer has oriented with the [111] direction out of the surface plane [25–30] driven by the low surface energy of these facets [34] in combination with domain matching epitaxy [35]. The capping top electrode of LSMO is also epitaxial and grows in the (110)-orientation. The polarization (P)–voltage (V) hysteresis loop of an LSMO/HZO (9 nm)/LSMO stack is shown in figure 1(b), with the coercive field (Ec) being around 2.8 MV cm−1.

Photolithography was used to pattern the top electrodes. Ion milling etching was utilized to form different pad sizes, as indicated by the grey colour in figure 2(a). All electric characterizations were performed using a Keithley 4200A-SCS parameter analyzer and a 4225-PMU pulse measurement unit. The polarization change was measured using the electrical input signal shown in figure 2(b), which is a modification of the positive-up–negative-down method [36], following the protocol from reference [17]. In this way, the first positive voltage pulse (P) is able to switch the ferroelectric polarization in one direction. However, the measured current also includes other contributions such as dielectric charging and leakage. The application of a second positive pulse (U) allows to remove these non-switching contributions, such that the purely ferroelectric polarization, can be obtained as \( P_1 = \int (I_p - I_0)dt/A \), being \( I_p \) and \( I_0 \) the output currents measured after the P and U pulses, respectively, while \( A \) is the device area. Then, a third pulse is applied in the opposite direction (indicated by the blue rectangle in figure 1(b)). By changing the voltage amplitude (\( V_p \)) and time duration (\( t_u \)) of the pulse, the amount of switched polarization (\( \Delta P \)) can be tuned. In the end, the two negative voltage pulses (negative, N, and down, D) are used to calculate how much polarization was left to be switched (\( P_2 = \int (I_N - I_D)dt/A \), where \( I_N \) and \( I_D \) are the currents measured after pulses N and D, respectively). In principle, \( \Delta P \) induced by the intermediate rectangular pulse could also be calculated by time integration of the measured current, as done with \( P_1 \) and \( P_2 \). However, the present method avoids the inaccuracies that arise due to the short and small amplitude of the pulse. By this method, both the switched polarization (\( \Delta P = P_1 - P_2 \)) and the remanent polarization (\( P_1 = P_2 \)) after different switching pulses can be obtained.
3. Results and discussion

3.1. Polarization synaptic weight

We have studied the effect of applying multiple pulses on the remnant polarization of r-phase LSMO/HZO (9 nm)/LSMO stacks in order to optimize the number of accessible polarization states. Therefore, instead of measuring the conductance change (which is due to partial polarization switching), such as reported in FTJs and FeFET [37, 38], we directly measure the physical origin of this change, that is the potentiation and depression of the polarization in the FC. In order to compare the responses with those of o-phase polycrystalline films [17], \( P_r \) was measured under three different schemes of switching pulses [17], as shown in figure 2(c): in mode 1, a train of identical pulses with an amplitude of 3.5 V and time width of 400 ns are applied; in mode 2 (amplitude modulation), the applied pulses have an increasing amplitude (range 0.5–3.5 V) with the same time width of 400 ns; in mode 3 (duration modulation), the applied pulses have the same amplitude of 3.5 V, with increasing widths (range 50–1600 ns). Correspondingly, different trends of \( P_r \) potentiation (red) and depression (blue) are achieved. The slightly smaller \( P_r \) values observed with respect to the loop in figure 1(b) are due to slight differences in the fabrication process and electric field history.

In order to optimize the accuracy and power efficiency of synaptic weights change in neural networks, some characteristics, such as symmetric conductance update, large number of states, large on/off ratio, small performance variations, low voltages and linearity, are preferred. As observed in figure 2, mode 2 and 3 pulse schemes could trigger more symmetric weight changes and give access to more polarization states than mode 1. However, area-efficient circuit design strongly prefers mode 1 with identical pulse trains. In addition, the time regime of applied pulses in mode 1 and mode 2 could be in the hundreds of nanosecond range, largely increasing the efficiency during the network training. Surprisingly, the potentiation/depression behaviour of the polarization in the epitaxial r-phase films is qualitatively very similar to that reported in polycrystalline o-phase layers [17]. Quantitatively, we find some differences when using the same voltage pulses as in reference [17]: we find that the polarization update in our work is more gradual, which is an improvement for...
neuromorphic circuits, allowing to access more intermediate states. This can be especially observed in mode 5. In addition, in mode 2 our data does not show saturation yet at the maximum voltage amplitude of 3.5 V for the 400 ns pulses used for this mode in reference [17].

Figure 2. (a) Sketch of the electrical measurement configuration; (b) programmed electrical input to obtain a polarization change ($\Delta P$); (c) remnant polarization ($P_r$) after different pulse schemes (modes 1–3), as described in the insets and in the text, following reference [17].

Figure 3. Remnant polarization versus delay times for different $t_w$. Inset: schematic drawing of the measurement waveform.

5 https://ferroelectric-memory.com/.
Subsequently, the stability of the polarization states is investigated in figure 3. The curves of remnant polarization versus delay times are plotted for different time duration (see inset of figure 3), spanning 9 orders of magnitude, from 50 ns to 10 s. Each delay time was measured for at least 3 cycles. A negligible variation in the polarization states was observed at different delay times.

3.2. Spike-timing-dependent-plasticity

Based on the polarization modulation, learning in the r-phase capacitors can be emulated by implementing spike-timing-dependent-plasticity (STDP) [39]. STDP is one of the essential learning rules in unsupervised brain-like computing, by which the synaptic weight increases if the pre-synaptic neuron fires just before the post-synaptic neuron, and the synaptic weight decreases if the pre-synaptic neuron fires just after the post-synaptic neuron. To emulate this, two programmed voltage pulses are applied on the top and bottom electrodes, as shown in figure 4(a). Notice that the maximum voltage amplitude (2 V) of both pulses is below $V_c$ and, thus, it is not sufficient to switch the polarization. However, the superimposed pulse amplitude (magenta line in figure 4(b)) can reach values over the coercive field, enabling switching of the polarization and change of the synaptic weight. The relative time difference between the pre-synaptic spike and the post-synaptic spike results in a different total voltage pulse profile applied to the device, causing the different polarization weight updates. An example is shown in figure 4(b): with a time offset $\Delta t = 280$ ns between the pre- (black line) and the post- (blue line) synaptic spikes, the resultant pulse (magenta line) is applied on the synapse (the r-phase LSMO/HZO/LSMO stack), with the resultant pulse shape changing as a function of $\Delta t$ (a video is available in the SI).

As shown in the measured STDP curve (figure 4(c)), the device polarization varies sharply in the range from $-400$ ns to $400$ ns while it does not change with larger $\Delta t$. This is similar to the memory effect observed for two temporary close events in biological neural networks. In figure 4(c), an asymmetric anti-Hebbian STDP learning curve is achieved. It is expected that by changing the pulse shape, other types of STDP learning curves can also be obtained [39].

3.3. Switching mechanism

3.3.1. Two-stage nucleation-limited switching (2S-NLS)

Understanding the polarization switching kinetics in ferroelectric materials is essential to attain ultimate control of their synaptic plasticity. In bulk and single crystal ferroelectrics, the switching kinetics is governed by the statistics of domain wall propagation, according to the Kolmogorov–Avrami–Ishibashi (KAI) model [40, 41]. However, in thin films of polycrystalline layers, the dynamics are shown to be limited by the statistics of nucleation, following a nucleation limited switching (NLS) model, which assumes the film consists of many areas with independent switching dynamics. The switching time of one of the regions is equal to the time needed for nucleation of a switching event in that region; while the time to propagate that domain to the entire region is negligible in comparison with the nucleation time [42]. o-phase doped-hafnia films have been reported to also obey the latter model [43–45].

Following this model, thus, indicates that domain wall motion is not decisive for the switching dynamics and that other processes with a broad distribution of relaxation times are determining the switching. Since thin films usually are not perfect single crystals, and they contain structural and chemical defects, such as dislocations and oxygen vacancies, the switching kinetics can be described in terms of the distribution function of the nucleation probabilities at those defects [42]. The NLS model uses a broad Lorentzian distribution of the logarithm of switching times and can be expressed in a simplified form as [46]:

$$\Delta P(t) = 2P_r \omega \frac{A}{\pi} \left[ \arctan \left( \frac{\log t - \log t_m}{\omega} \right) + \frac{\pi}{2} \right]$$

where $A$ is a normalization constant, $\omega$ is the half width at half maximum of the Lorentzian distribution, and $t_m$ is the average characteristic switching time of the nuclei.

Figure 5(a) plots the normalized polarization change $\Delta P$ versus the width ($t_m$) of the applied switching pulses for different pulse amplitudes ($V_p$), for the r-phase epitaxial LSMO/HZO/LSMO stacks. Also in this case, $\Delta P$ does not follow a KAI model (see details in figure S1). Although the curves fit significantly better to the NLS model (see fitting parameters in figure S2), it can be noticed that the switching curves in figure 5(a) show a small kink about halfway of the total polarization switching, particularly for the larger $V_p$ values, as observed more clearly in figure 5(b). This indicates that the overall switching takes place in two stages with $\Delta P = \Delta P_1 + \Delta P_2$. Indeed, the two-stage nucleation-limited switching (2S-NLS) model shows a significantly better fit (curves and fitting parameters shown in figure S3) than the one-stage switching (standard NLS). This type of ‘wavy’ switching curves have been observed in some ferroelectrics following both KAI and NLS models, and were interpreted as originating from samples that contain different zones of distinct polarization.
switching [47, 48]. In our case the number of distinct stages is two. Fitting with the KAI model using a two-stage switching mode (see details in figure S4) also gives rise to a significantly improved fit. The fit seems worse than the 2S-NSL model for the high voltage data but slightly better for the low voltage (partial switching data). However, one must be cautious because the dimensionality of domain walls obtained with the 2S-KAI model is $n < 1$. Even though, $n < 1$ has been ascribed to needle-like domains in the past [49], the physical meaning of these values is often doubted [33, 50].

3.3.2. Two switching times
As shown in figure 5(c), two different characteristic average switching times, $t_{m1}$ and $t_{m2}$, are extracted from the switching curves in figure 5(a) with the 2S-NLS fitting model, each associated to one stage of the switching. The difference between $t_{m1}$ and $t_{m2}$ is 1–2 orders of magnitude. However, we notice that both show the same dependence with $V_P$ with a step-like decrease at a voltage of about 3 V, which is larger than the $V_c$ of the films (see figure 1(b)). As shown in figure 5(d), above this voltage, $t_m$ vs the electric field ($E$) follows Merz’s law: $t_m \sim \exp(F_a/E)$, with $F_a$ being the activation electric field, which has been shown to be proportional to $E_c$ in different ferroelectrics [51]. The $F_a$ values obtained from the fit of the two different $t_m$ curves to Merz’s law are 4.1 MV cm$^{-1}$ and 4.6 MV cm$^{-1}$, respectively, larger than the values reported in polycrystalline hafnia films ($F_a = 1.5$ MV cm$^{-1}$ with $E_c = 0.9$ MV cm$^{-1}$ [52] or $F_a = 2.4$ MV cm$^{-1}$ with $E_c = 1.1$ MV cm$^{-1}$ [53]).
Figure 5. (a) Normalized $\Delta P$ as a function of pulse duration ($t_p$) under different pulse amplitude ($V_p$); (b) 2S-NLS fitting of the switching curve in (a) for $V_p = 4, 4.2, 4.6, 5$ V; (c) the extracted $t_m$ from 2S-NLS model; (d) Merz’s law fitting of $t_m$ vs electric field [range with $V_p$ above 3 V indicated in (c)], with extracted activation electric field ($F_a$) shown inset.

Considering that in our case $E_c = 2.8$ MV cm$^{-1}$, the obtained $F_a$ values are consistent with the $F_a/E_c$ ratio observed in polycrystalline o-phase hafnia, as observed in figure S5. These $F_a/E_c$ ratios are 5–6 times smaller than those in standard ferroelectrics, which is related to a reduction of the dipole–dipole interactions, making collective switching of dipoles in hafnia-based materials less advantageous than in other ferroelectrics. In addition, it is believed that the larger $E_c$ in our case arises from the clamping of the epitaxial layer [25]. A larger $E_c$ is detrimental in terms of power consumption in the case of FTJs but it is advantageous in the case of FeFET devices, as it increases the memory window. Again, despite the clear differences in crystallinity, orientation and magnitude of the polarization and switching fields, which give rise to very different activation fields, hafnia-based devices display a surprisingly universal switching and synaptic behaviour.

3.4. Discussion

3.4.1. Possible origin of the 2S-NLS switching

The NLS model containing two different switching stages could be explained by different mechanisms:

(a) Multi-step polarization switching. The polarization of r-phase ferroelectrics is along the [111] direction, perpendicular to the surface. Both molecular dynamics simulations and scanning probe experiments in rhombohedral ferroelectric PZT thin films have shown that, for this symmetry, a two-step switching is favoured [54]. In addition, the presence of defects in the thin films could lower the switching energy barrier and favour the non-180° domain switching [55]. Although our films are under the very large compressive in-plane strain [25] and, therefore, the energy required to switch to the in-plane polarization axis is expected to be very large, this possibility cannot be discarded and it requires further investigation.

(b) A two-step switching, mediated by a non-polar intermediate tetragonal phase, has been earlier reported in Hf$_{0.4}$Zr$_{0.6}$O$_2$ films [56]. However, this was correlated with double hysteresis loop and wake-up behaviour that we do not observe in the present capacitors.

(c) According to Merz’s law and from the observed fixed $F_a/E_c$ ratio, two activation fields and two mean switching times are expected if imprint is present in the films. As shown in figure S6, the imprint field is small, of about 0.1 MV cm$^{-1}$ at room temperature (corresponding to 0.1 V), but it linearly increases with decreasing temperature to reach a value of 1.7 MV cm$^{-1}$ at 10 K. At room temperature, the two coercive fields are already similar but not identical ($E_c^+ = 2.7$ MV cm$^{-1}$ and $E_c^- = -2.9$ MV cm$^{-1}$), which will give rise to a two-stage switching. This behaviour has been associated with the presence of positively charged
oxygen vacancies compensating the polarization, as migration is more efficient at higher temperatures and practically frozen at low temperatures [29]. Therefore, the observed asymmetry originates from the different capacity to supply oxygen vacancies of the two electrodes. Despite using the same material as top and bottom electrodes, the orientations and interfaces are different (see in figure 1(a), with (001)-oriented bottom LSMO and (110)-oriented top LSMO electrodes). That the imprint field effect gives rise to two different switching times has been recently reported in epitaxial HZO on GdScO$_3$ substrates [33]. We notice that in the two-stage switching, the kink usually happens about halfway through the polarization switching curve, which is also consistent with this scenario.

Figure 5(c) shows the switching speed of the r-phase epitaxial film is in the $\mu$s range for voltages above $V_c$. The relatively larger switching times (at similar driving electric field and device area) compared to the polycrystalline films [53, 57–59] (these are usually reported in the few hundreds of ns or even below, by minimizing device area and series resistance effects, see figure S7), can then be associated to the larger activation fields due to the larger $E_a$ [29, 31].

In previous works on r-phase epitaxial layers [29, 31], ion migration (oxygen diffusion) between the electrodes, across the HZO layer, has been proven to play a key role during the electric field-driven switching process. Interestingly, in figure S8, the Arrhenius plot of $E_a$ shows an activation energy ($E_a < 0.2$ eV) that is significantly lower than that of the polycrystalline o-phase films ($\sim 2$ eV). $E_a$ for diffusion of positively charged oxygen vacancies is measured to be 0.52 eV in thin HfO$_2$ films [60]; DFT calculations show it to be 0.85 eV in reference [61], or 0.39 eV/0.54 eV in reference [62]. $E_a$ values as small as 0.12 eV, in agreement with our observations, have been reported for the oxygen vacancy migration in some perovskite oxides such as PZT films [63] and the cobaltates [64]. This could reflect the fact that the supply of charges at the perovskite electrode interface is the key process determining the switching field and thus, the switching times.

The fact that we observe similar neuromorphic and switching behaviour in r-phase epitaxial films, compared to polycrystalline films and o-phase epitaxial films [17, 33], with and without perovskite electrodes, with differences that can be associated just to a larger $E_a$, adds a piece to the puzzle of the origin of ferroelectricity in hafnia-based materials.

4. Conclusion

We have characterized the synaptic behaviour of epitaxial r-phase HZO, which shows symmetric update, multi-states, small cycle-to-cycle variability and memory stability. We compare this behaviour with that of other reported hafnia-based devices (polycrystalline and/or o-phase) and we find surprising similarities, despite the difference in structure, polar orientation and crystallinity. We investigate the synaptic plasticity of these devices by measuring the changes in polarization, rather than resistance, therefore obtaining a direct view of the origin of switching. We observe two mean switching times, as recently reported in epitaxial (reportedly o-phase) HZOs [33], and we find them to originate from a 2S-NLS process, where each stage is responsible for about half of the total polarization switching. The two processes show characteristic switching times in the micro-second and tenths of micro-second regimes, respectively, which are 2 orders of magnitude slower than those reported for other polycrystalline hafnia-based MIM devices (for similar driven field and device area). The switching behaviour follows Merz’s law for $V > V_c$ with two activation fields and with a $F_a/E_a$ ration in agreement with that reported for other hafnia samples.

Acknowledgments

We are grateful to Andrew Rappe, Pavan Nukala, Laura Begon-Lours for very useful discussions. Financial support by the Groningen Cognitive Systems and Materials Centre (CogniGron) and the Ubbo Emmius Foundation of the University of Groningen is gratefully acknowledged. Gaurav Vats acknowledges funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Grant Agreement No. 892669.

Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: https://doi.org/10.34894/2PP3TR.
References

[1] Mehonic A and Kenyon A J 2022 Brain-inspired computing needs a master plan Nature 604 255–60
[2] Jaeger H 2021 Towards a generalized theory comprising digital, neuromorphic and unconventional computing Neuromorph. Comput. Eng. 1 012002
[3] Chicca E, Stefanini F, Bartolozzi C and Indiveri G 2014 Neuromorphic electronic circuits for building autonomous cognitive systems Proc. IEEE 102 1367–88
[4] Waser R and Aono M 2007 Nanoionics-based resistive switching memories Nat. Mater. 6 833–40
[5] Sawa A 2008 Resistive switching in transition metal oxides Mater. Today 11 28–36
[6] Waser R, Dittmann R, Staikov C and Szt K 2009 Redox-based resistive switching memories—nanoionic mechanisms, prospects, and challenges Adv. Mater. 21 2632–63
[7] Schenk T, Pesic M, Sleszasic S, Schröder U and Mikolajik T 2020 Memory technology—a primer for material scientists Rep. Prog. Phys. 83 086501
[8] Ielmini D and Wong H S P 2018 In-memory computing with resistive switching devices Nat. Electron. 1 333–43
[9] Jo S H, Chang T, Ebbong I, Bhadviya B B, Mazumder P and Lu W 2010 Nanoscale memristor device as synapse in neuromorphic systems Nano Lett. 10 1297–301
[10] Mehonic A, Sebastian A, Rajendran B, Simeone O, Vasilaki E and Kenyon A J 2020 Memristors—from in-memory computing, deep learning acceleration, and spiking neural networks to the future of neuromorphic and bio-inspired computing Adv. Intell. Syst. 2 2000085
[11] Payvand M, Nair M V, Müller L K and Indiveri G 2019 A neuromorphic systems approach to in-memory computing with non-ideal memristive devices: from mitigation to exploitation Faraday Discuss. 213 487–510
[12] Sung C, Hwang H and Yoo I K 2018 Perspective: a review on memristive hardware for neuromorphic computation J. Appl. Phys. 124 151905
[13] Chua L, Shibite V and Kim H 2012 Hodgkin–Huxley axon is made of memristors J. Bifurcation Chaos 22 1230011
[14] Indiveri G, Linares-Barranco B, Legenstein R, Delgeorgis G and Prodromakis T 2013 Integration of nanoscale memristor synapses in neuromorphic computing architectures Nanotechnology 24 385010
[15] Bööscke T S, Müller J, Bräuhaus D, Schröder U and Böttger U 2011 Ferroelectricity in hafnium oxide thin films Appl. Phys. Lett. 99 102930
[16] Trentzas M et al 2016 A 28 nm HKMG super low powered embedded NVM technology based on ferroelectric FETs IEEE Int. Electron Devices Meeting (IEDM) p 11.5.1
[17] Jerry M et al 2017 Ferroelectric FET analog synapse for acceleration of deep neural network training IEEE Int. Electron Devices Meeting (IEDM) vol 6 pp 6.2.1–4
[18] Oh S, Kim T, Kwak M, Song J, Woo I, Jeon S, Yoo I K and Hwang H 2017 HiZrOx-based ferroelectric synapse device with 32 levels of conductance states for neuromorphic applications IEEE Electron Device Lett. 38 732–5
[19] Oh S, Hwang H and Yoo I K 2019 Ferroelectric materials for neuromorphic computing APL Mater. 7 091109
[20] Kang H et al 2021 Two- and three-terminal HfO2-based multilevel resistive memories for neuromorphic analog synaptic elements Neuromorph. Comput. Eng. 1 012002
[21] Buragohain P et al 2022 Effect of film microstructure on domain nucleation and intrinsic switching in ferroelectric YHfO3 thin film capacitors Adv. Funct. Mater. 32 2108876
[22] Covi E, Malaosmanovic H, Max B, Sleszasic S and Mikolajik T 2022 Ferroelectric-based synapses and neurons for neuromorphic computing Neuromorph. Comput. Eng. 2 012002
[23] Bégon-Lours L et al 2022 Effect of cycling on ultra-thin HiZrOx, ferroelectric synaptic weights Neuromorph. Comput. Eng. 2 024001
[24] Tysmbal E Y and Kohlstedt H 2006 Tunneling across a ferroelectric Science 313 181–3
[25] Wei Y et al 2018 A rhombohedral ferroelectric phase in epitaxially strained Hf0.5Zr0.5O2 thin films Nat. Mater. 17 1095–100
[26] Nakula P, Wei Y, de Haas V, Guo Q, Antoja-Lleonart J and Noheda B 2020 Guidelines for the stabilization of a polar rhombohedral phase in epitaxial Hf0.5Zr0.5O2 thin films Ferroelectrics 569 148–63
[27] Bégon-Lours L et al 2020 Stabilization of phase-pure rhombohedral HfZrOx in pulsed laser deposited thin films Phys. Rev. Mater. 4 043401
[28] Nakula P et al 2021 In situ heating studies on temperature-induced phase transitions in epitaxial Hf0.5Zr0.5O2/La2/3Sr1/3MnO3 heterostructures Appl. Phys. Lett. 118 062901
[29] Nakula P et al 2021 Reversible oxygen migration and phase transitions in hafnia-based ferroelectric devices Science 372 630–5
[30] Silva J P B et al 2021 Wake-up free ferroelectric rhombohedral phase in epitaxially strained ZrO2 thin films ACS Appl. Mater. Interfaces 13 51383–92
[31] Wei Y et al 2019 Magneto-ionic control of spin polarization in multiferroic tunnel junctions NPJ Quantum Mater. 4 62
[32] Luy J, Fina I, Solanas R, Fontcuberta J and Sánchez F 2018 Robust ferroelectricity in epitaxial Hf1/2Zr1/2O2 thin films Appl. Phys. Lett. 113 082902
[33] Song T, Sánchez F and Fina I 2022 Impact of non-ferroelectric phases on switching dynamics in epitaxial ferroelectric Hf0.5Zr0.5O2 films APL Mater. 10 031108
[34] Mukhopadhyay Atashi B, Sanz Javier F and Musgrave Charles B 2005 First-principles calculations of structural and electronic properties of monoclinic hafnia surfaces Physical Review B 73 115330
[35] Estandia S et al 2021 Insights into the atomic structure of the interface of ferroelectric Hf0.5Zr0.5O2 grown epitaxially on La2/3Sr1/3MnO3 Phys. Rev. Mater. 5 074410
[36] Scott J F et al 2017 Ferroelectricity in the metal–organic ferroelectric tris-sarcosine calcium chloride Phys. Rev. B 95 094119
[37] Mulaosmanovic H et al 2017 Novel ferroelectric FET based synapse for neuromorphic systems Digest of Technical Papers—Symp. on VLSI Technology pp T176–7
[38] Chen L et al 2018 Ultra-low power Hf0.4Zr0.6O2 based ferroelectric tunnel junction synapses for hardware neural network applications Nanoscale 10 15826–33
[39] Serrano-Gotarredona T, Masquelier T, Prodromakis T, Indiveri G and Linares-Barranco B 2013 STDP and STDP variations with memristors for spiking neuromorphic learning systems Front. Neurosci. 7 1–15
[40] Orihara H, Hashimoto S and Ishibashi Y 1994 A theory of D–E hysteresis loop based on the Avrami model J. Phys. Soc. Japan 63 1031–5
[41] Hashimoto S, Orihara H and Ishibashi Y 1994 Study on D–E hysteresis loop of TGS based on the Avrami-type model J. Phys. Soc. Japan 63 1601–10
[42] Tagantsev A K, Stolichnov I and Setter N 2002 Non-Kolmogorov–Avrami switching study on D–E hysteresis loop of TGS based on the avrami-type model Phys. Rev. B 66 214109
[43] Mueller S, Summerfelt S R, Muller J, Schroeder U and Mikolajick T 2012 Ten-nanometer ferroelectric Si:HfO2 films for next-generation FRAM capacitors IEEE Electron Device Lett. 33 1300–2
[44] Muller J et al 2013 Ferroelectric hafnium oxide: a CMOS-compatible and highly scalable approach to future ferroelectric memories IEEE Int. Electron Devices Meeting pp 10.8.1–4
[45] Gong N et al 2018 Nucleation limited switching (NLS) model for HfO2-based metal–ferroelectric–metal (MFM) capacitors: switching kinetics and retention characteristics Appl. Phys. Lett. 112 262903
[46] Jo J Y et al 2007 Domain switching kinetics in disordered ferroelectric thin films Phys. Rev. Lett. 99 267602
[47] Huang W et al 2018 A high-speed and low-power multistate memory based on multi ferroelectric tunnel junctions Adv. Electron. Mater. 4 1700560
[48] Chanthbouala A et al 2012 A ferroelectric memristor Nat. Mater. 11 860–4
[49] Dimmler K, Parris M, Butler D, Eaton S, Pouligny B, Scott J F and Ishibashi Y 1987 Switching kinetics in KNO3 ferroelectric thin-film memories J. Appl. Phys. 61 5467–70
[50] Shu V, Rumyantsev E and Makarov S 1998 Kinetics of phase transformations in real finite systems: application to switching in ferroelectrics J. Appl. Phys. 84 445–51
[51] Lee H J et al 2020 Scale-free ferroelectricity induced by flat phonon bands in HfO2 Science 369 1343–7
[52] Zhou D et al 2015 Electric field and temperature scaling of polarization reversal in silicon doped hafnium oxide ferroelectric thin films Acta Mater. 99 240–6
[53] Alessandri C, Pandey P, Abusleme A and Seabaugh A 2018 Switching dynamics of ferroelectric Zr-doped HfO2 IEEE Electron Device Lett. 39 1780–3
[54] Xu R, Liu S, Grinberg I, Karthik J, Damodaran A R, Rappe A M and Martin L W 2015 Ferroelectric polarization reversal via successive ferroelastic transitions Nat. Mater. 14 79–86
[55] Daniels J E et al 2007 Neutron diffraction study of the polarization reversal mechanism in [111]-oriented Pb(Zn1/3Nb2/3)O3-x PbTiO3 J. Appl. Phys. 101 7
[56] Park M H, Kim H J, Lee Y H, Kim Y J, Moon T, Kim K D, Hyun S D and Hwang C S 2016 Two-step polarization switching mediated by a nonpolar intermediate phase in Hf0.4Zr0.6O2 thin films Nanoscale 8 13896–907
[57] Lyu X, Si M, Shrestha P R, Cheung K P and Ye P D 2019 First direct measurement of sub-nanosecond polarization switching in ferroelectric hafnium zirconium oxide Int. Electron Devices Meeting pp 342–5
[58] Si M et al 2019 Ultrafast measurements of polarization switching dynamics on ferroelectric and anti-ferroelectric hafnium zirconium oxide Appl. Phys. Lett. 115 072107
[59] Yoo H K et al 2018 Engineering of ferroelectric switching speed in Si doped HfO2 for high-speed IT-FERAM application Int. Electron Devices Meeting
[60] Zafar S, Jagannathan H, Edge L F and Gupta D 2011 Measurement of oxygen diffusion in nanometer scale HfO2 gate dielectric films Appl. Phys. Lett. 98 152903
[61] He R et al 2021 Charged oxygen vacancy induced ferroelectric structure transition in hafnium oxide (arXiv:2106.12159)
[62] Cheng Y et al 2021 Extrinsic ferroelectricity originated from oxygen vacancy drift in HfO2-based films (arXiv:2112.13431)
[63] Suchanek G, Koehler R, Padmini P, Sandner T, Frey J and Gerlach G 1999 Self-polarization control of radio-frequency-sputtered lead zirconate titanate films Surf. Coat. Technol. 116–119 1238–43
[64] Wu H and Li F 2019 Oxygen vacancy-assisted high ionic conductivity in perovskite LaCoO3−δ (δ = 1/3) thin film: a first-principles-based study Phys. Lett. A 383 210–4