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Investigation of Negative Feedback in Resistive Switching of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ Thin Films

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Abstract

This thesis investigates the characteristics and dynamics of resistive switching in $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ -based ReRAM (resistive random-access memory) cells, with a particular focus on the emergence of chaotic behavior driven by negative feedback mechanisms. In this context, MIM (metal-insulator-metal) structures have been fabricated and characterized. Energy dissipative effects in the switching process are described, leading to a negative feedback. Here, the relationship between applied voltage and resistance change in ReRAM devices is characterized.

A Feigenbaum diagram is introduced, revealing period-doubling bifurcations typical of deterministic chaos, and demonstrating that chaotic behavior in ReRAM cells can emerge when certain parameters of the resistive switch are met. The analysis of Lyapunov exponents further investigates the system's sensitivity to parameter variations.

The thesis also explores the impact of oxygen vacancy distributions and densities within the switching cycle on device behavior. The redistribution of vacancies during RESET and SET operations is identified as an important factor that may drive the onset of chaotic behavior in ReRAM devices.

Furthermore, the potential applications of chaotic ReRAM behavior are looked into, including its use in random number generation and modeling complex biological systems, such as neurodegenerative pathologies. The findings suggest that by optimizing the sensitivity of ReRAM cells to external stimuli – such as the distribution of oxygen vacancies – chaotic dynamics could be harnessed for practical applications.

Zusammenfassung

In dieser Arbeit werden die Eigenschaften und die Dynamik des resistiven Schaltens in $\text{Hf}_{0,5}\text{Zr}_{0,5}\text{O}_2$ -basierten ReRAM (resistive random-access memory)-Zellen untersucht, wobei der Schwerpunkt auf dem Auftreten von chaotischem Verhalten liegt, das durch negative Rückkopplungsmechanismen angetrieben wird. In diesem Zusammenhang wurden MIM-Strukturen (Metall-Isolator-Metall) hergestellt und charakterisiert. Es werden energiedissipative Effekte im Schaltprozess beschrieben, die zu einer negativen Rückkopplung führen. Hier wird die Beziehung zwischen angelegter Spannung und Widerstandsänderung in ReRAM-Bauelementen charakterisiert.

Es wird ein Feigenbaum-Diagramm eingeführt, das die für deterministisches Chaos typischen periodenverdoppelnden Bifurkationen aufzeigt und demonstriert, dass chaotisches Verhalten in ReRAM-Zellen auftreten kann, wenn bestimmte Parameter von dem resistiven Schalter aufgezeigt werden. Durch die Analyse der Lyapunov-Exponenten wird die Empfindlichkeit des Systems gegenüber Parameteränderungen weiter untersucht. Diese Ergebnisse unterstreichen die Rolle einer präzisen Kontrolle der Schaltparameter, um chaotisches Verhalten zu erreichen. In dieser Arbeit werden auch die Auswirkungen der Verteilung und Dichte von Sauerstoffvakanzten innerhalb des Schaltzyklus auf das Verhalten des Bauelements untersucht. Die Umverteilung von Vakanzten während der RESET- und SET-Vorgänge wird als wichtiger Faktor identifiziert, der das Auftreten von chaotischem Verhalten in ReRAM-Bauelementen fördern kann.

Darüber hinaus werden die potenziellen Anwendungen des chaotischen ReRAM-Verhaltens untersucht, einschließlich der Verwendung bei der Erzeugung von Zufallszahlen und der Modellierung komplexer biologischer Systeme, wie z. B. neurodegenerativer Erkrankungen. Die Ergebnisse deuten darauf hin, dass die chaotische Dynamik für praktische Anwendungen nutzbar gemacht werden könnte, indem die Empfindlichkeit der ReRAM-Zellen für externe Stimuli – wie die Verteilung von Sauerstoffvakanzten – optimiert wird.

Résumé

Cette thèse étudie les caractéristiques et la dynamique de la commutation résistive dans les cellules ReRAM (mémoire résistive à accès aléatoire) à base de $\text{Hf}_{0,5}\text{Zr}_{0,5}\text{O}_2$, en mettant l'accent sur l'émergence d'un comportement chaotique induit par des mécanismes de rétroaction négative. Dans ce contexte, des structures MIM (métal-isolant-métal) ont été fabriquées et caractérisées. Les effets dissipatifs de l'énergie dans le processus de commutation sont décrits, conduisant à une rétroaction négative. La relation entre la tension appliquée et le changement de résistance dans les dispositifs ReRAM est caractérisée.

Un diagramme de Feigenbaum est introduit, révélant des bifurcations période-doublément typiques du chaos déterministe, et démontrant qu'un comportement chaotique dans les cellules ReRAM peut émerger lorsque certains paramètres du commutateur résistif sont respectés. L'analyse des exposants de Lyapunov permet d'étudier plus en détail la sensibilité du système aux variations des paramètres. Ces résultats soulignent le rôle critique d'un contrôle précis des paramètres de commutation dans l'obtention d'un comportement chaotique.

La thèse explore également l'impact de la distribution et de la densité des vides d'oxygène dans le cycle de commutation sur le comportement du dispositif. La redistribution des vides pendant les opérations RESET et SET est identifiée comme un facteur important qui peut conduire à l'apparition d'un comportement chaotique dans les dispositifs ReRAM.

En outre, les applications potentielles du comportement chaotique des ReRAM sont examinées, notamment leur utilisation dans la génération de nombres aléatoires et la modélisation de systèmes biologiques complexes, tels que les pathologies neurodégénératives. Les résultats suggèrent qu'en optimisant la sensibilité des cellules ReRAM à des stimuli externes – tels que la distribution des vides d'oxygène – la dynamique chaotique pourrait être exploitée pour des applications pratiques.

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Acronyms

1T1R one-transistor-one-resistor. viii, 8

AFM atomic force microscopy. viii, 2, 29, 30, 37–39, 75

ALD atomic layer deposition. 12, 63

ALU arithmetic logic unit. 2

ANN artificial neural network. viii, 1–3, 8, 9, 54, 56, 60, 61

DC direct current. 25, 73

DRAM dynamic random-access memory. 6, 7, 59, 60

FTJ ferroelectric tunnel junction. 3, 4, 12–14, 26, 33, 39, 42, 47, 49, 54, 58, 64, 72, 74, 80

GIXRD grazing incidence X-ray diffraction. 28, 37, 40, 42, 75

HRS high-resistive state. 4, 5, 13–16, 32, 33, 35, 44–46, 58, 77–79

LLM large language models. 1

LRS low-resistive state. 4, 5, 13–15, 32, 33, 35, 44–46, 58, 77–79

MIM metal-insulator-metal. 2, 4, 12–15, 23, 24, 31, 37, 39, 42, 43, 54, 57, 64, 71, 75, 76

MOSFET metal-oxide-semiconductor field-effect transistor. 6, 7, 60

PRNG pseudo-random number generation. 55

PVD physical vapor deposition. 24, 73

ReRAM resistive random-access memory. vii, viii, 2–5, 8–16, 23, 24, 31–35, 37, 41, 43, 45–54, 56–66, 71, 72, 76, 78–80, 84, 85

RF radio frequency. 24–26, 37, 54, 73, 76

RNG random number generation. 54–56

SMU source/measurement unit. 31, 43, 76

SNN spiking neural network. 9, 61

SPM scanning probe microscopy. 29

SRAM static random-access memory. 6, 7, 59, 60

STDP spike-timing-dependent plasticity. viii, 4, 5, 9–11, 31, 34–37, 43, 46, 47, 50, 51, 54, 56, 58, 59, 61–63, 75, 79, 80, 82, 97

TRNG true random number generation. 55

XRD X-ray diffraction. 27, 28

XRR X-ray reflectivity. viii, 27, 28, 37, 40, 41

1. Introduction

In 1965, Gordon Moore deduced an empirical law predicting that the density of transistors in integrated circuits would double every 18 months [1]. Industries' efforts to abide to "Moore's Law" lead to drastic cutback in manufacturing cost, which significantly increased accessibility to microelectronics devices. However, this evolution also lead to an increased demand in data storage and computational efficacy. One current and very pronounced example for this trend is the recent availability of artificial neural network (ANN) algorithms – specifically large language models (LLM) like ChatGPT – to a broader population. Sevilla et al. reported a doubling of required training time every 5 to 6 months for regular-scale models between 2010 and 2022 and a doubling every 9 to 10 months for large-scale models between 2015 and 2022 [2]. Figure 1.1 shows the evolution of training time for different regular-scale and large-scale models as a function of their publication date. For both cases it is apparent that "Moore's Law" – especially when considering physical limitations of nano-scale processes that must lead to a slow-down – cannot keep up with this evolution.

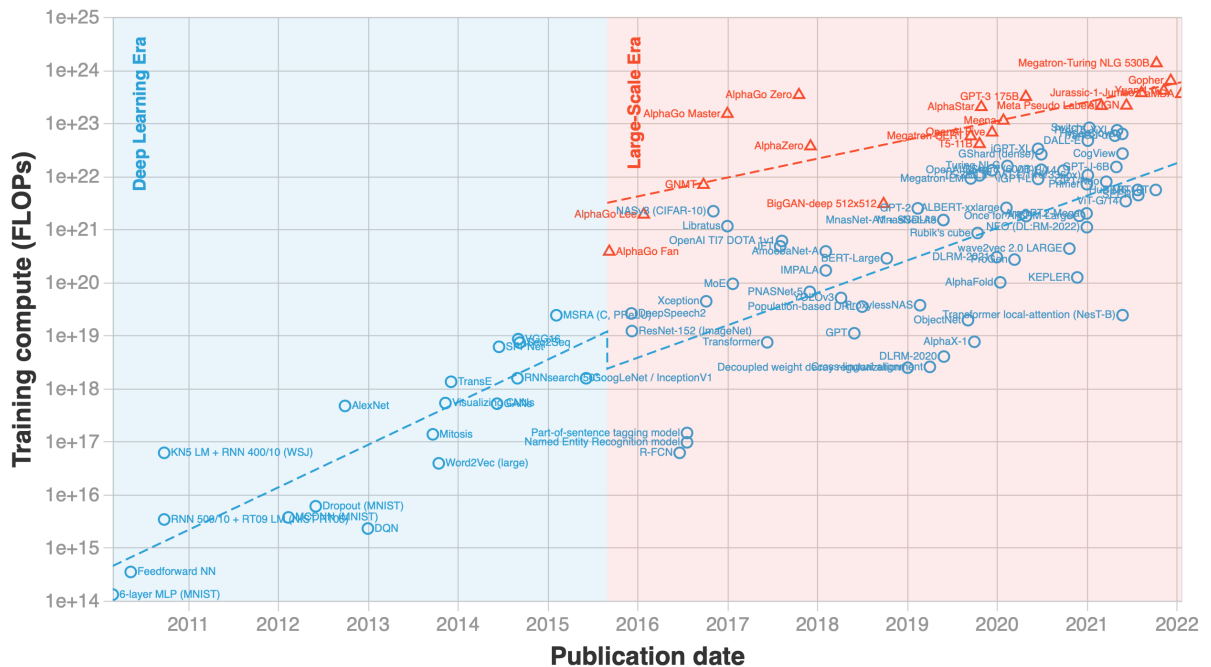


Figure 1.1. Evolution of artificial neural network (ANN) model training time between 2015 and 2022; adapted from [2].

Therefore, a paradigm-change is crucial to enable the continuation of the evolution of machine learning algorithms. Currently, ANNs are simulated inefficiently using binary von-Neumann-architecture, resulting in an overhead, as information repeatedly needs to be transferred between the arithmetic logic unit (ALU) and the external memory unit resulting in increased energy dissipation.

Therefore, the investigation of bio-inspired synapse-like neuromorphic systems is motivating increasing interest. In these systems both the information storage and the computations take place in the same physical location, alleviating the aforementioned energy dissipation. A strong contender for neuromorphic memory cells is the resistive random-access memory (ReRAM) whose resistive state is determined by the history of previously applied voltages [3]. When employed as a cross-bar structure, ReRAMs can directly mirror the structure of software-based ANNs. The resistive states of the individual cells represent the parameters of the neural network in this application [4].

Precise control over the cell's switching dynamics facilitates their integration in hardware-based ANNs and has thus been the center of attention in previous works in our group. Here, period-doubling bifurcations were observed during their switching [5]. These are known to serve as a pathway to chaotic behavior. ReRAM cells could, thus, exhibit chaotic switching characteristics given the right conditions for cascading period-doublings to occur. A negative feedback in the respective switching is required to allow for deterministic chaos to emerge. Chaotic switching in ReRAM cells has implications for their use as memory devices but also offers an opportunity for applications that specifically make use of this behavior.

1.1. Objectives

The primary objective of this thesis is to investigate the underlying negative feedback mechanisms within resistively switching devices, specifically focusing on their role as a precursor to chaotic behavior. This study has utilized a TiN/Hf_{0.5}Zr_{0.5}O₂/Au metal-insulator-metal (MIM) structure, fabricated via RF-magnetron sputtering, to explore these mechanisms. Detailed characterization of the device layers have been conducted through atomic force microscopy (AFM) and X-ray diffraction techniques to understand the structural properties and assess surface morphology. Electrical measurements have been performed on the devices to capture the resistive switching characteristics and establish evidence of a negative feedback mechanism. This negative feedback mechanism is proposed as a necessary condition for chaos, which could offer insights into the non-linear dynamics of resistively switching devices. Possible mechanisms responsible for inducing this feedback are explored in detail, with attention to material-specific phenomena such as oxygen ion movement and vacancy formation. Furthermore, a mathematical analysis is presented to demonstrate how this feedback could drive the device towards chaotic behavior under certain operational conditions. This analysis aims at laying the ground-work for future studies on the applications of chaos in resistive switching, with implications for neuromorphic computing and secure communication systems.

1.2. Thesis Outline

This thesis is divided into five chapters as follows:

1. This introduction to the thesis.
2. The "fundamentals" chapter introduces the core concepts of resistive switches with their application in both conventional and neuromorphic memory applications. Then two devices exhibiting resistive switching are introduced. First the ferroelectric tunnel junction (FTJ) and then the resistive random-access memory (ReRAM), based on oxygen vacancy conductive filaments. Finally, this chapter establishes a foundation on chaos theory, especially on how non-linear systems can produce deterministic chaos.
3. The "materials and methods" chapter presents the choice of materials that were used to fabricate the ReRAM devices as well as a discussion about the thin film fabrication and characterization techniques.
4. In the "results and discussion" chapter the device fabrication is presented in greater detail. Furthermore, the results of the conducted measurements are shown. The chapter concludes with a discussion of possible negative-feedback mechanisms that cause the emergence of chaotic behavior in the ReRAM switching behavior, as well as a discussion of device characteristics that enable the transition to chaotic switching.
5. Finally, this thesis summarizes its findings and provides an outlook. The outlook delivers a perspective on how chaotic resistive switches could be used to securely produce random numbers as well as on how a hardware-based artificial neural network (ANN) with chaotically behaving elements can be used to draw analogies to neurologic pathologies in human brains.

2. Fundamentals

This chapter introduces fundamental concepts regarding resistive switches and their integration in memory applications. They promise for use as non-volatile, cost-efficient universal memory, as well as for neuromorphic computing due to their synapse-like spike-timing-dependent plasticity (STDP).

Building on that, their realization is outlined within the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ -material system as both oxygen vacancy filamentary switch, as well as ferroelectric tunnel junction (FTJ). A description of the emergence of period-doubling bifurcations in their switching properties requires the development of basics in chaos theory. Here chaotic characteristics in non-linear systems is investigated, with special emphasis on the Feigenbaum route to deterministic chaos.

2.1. Resistive Switches

Resistively switching structures show tunable resistances where the switching is induced by the application of an external electrical bias. The change in conductivity is usually driven by one of four mechanisms [3]:

1. Electrochemical reactions (e.g. redox and ion migration)
2. Phase changes (e.g. amorphous-crystalline transition)
3. Tunneling magnetoresistance (e.g. spin-dependent tunneling probability)
4. Ferroelectricity (e.g. lattice-polarization modulated tunneling barrier)

Discussions in this thesis will be limited to resistivity changes due to modulation of the tunneling barrier caused by ferroelectric polarization reversal and redox-reaction in subsection 2.2.1 and subsection 2.2.2.

Resistive random-access memory (ReRAM) consists of a simple metal-insulator-metal (MIM) structure and can show binary, multi-level and analog switching. In binary mode, the cells' resistance is switched between the high-resistive state (HRS) and the low-resistive state (LRS), signifying their use as classical memory cells. In multi-bit switching, resistance is switched between $2^n \mid n > 1$ levels to encode n bits per state [6]. Lastly, in the analogous mode, resistance values are achieved continuously. This mode is used in neuromorphic computing applications. ReRAM-cells have attracted interest due to their scalability, non-volatility, high endurance, and non-destructive read-out [4].

Figure 2.1 shows an idealized quasi-static switching curve for a bipolar ReRAM element. When the cell is in HRS, an external, positive, gradually increasing bias is applied until a threshold voltage V_{SET} is reached and the current shoots up abruptly due to a reduction of the cell's resistance, which is shown in the inset in Figure 2.1. This switching from HRS to LRS is also referred to as the SET-operation. When the positive bias is reduced again, the cell does not switch again and remains in LRS until a negative V_{RESET} is reached. At this voltage the resistance increases again, resulting in a decreased current. This switching from LRS to HRS is also called RESET and the cell remains in that state even after V_{RESET} has been surpassed again when the voltage is increased. When the bias reaches zero, the pinched hysteresis-loop is completed. While reading out the state of the cell, one has to consider that the absolute of V_{SET} and V_{RESET} cannot be surpassed respectively to ensure that the cell's state is not altered again, enabling non-destructive readout. Instead, a lower readout voltage is applied and the resistive state can be determined according to the current flowing through the ReRAM. This procedure is implied in Figure 2.1, as well as its inset, with a vertical red line.

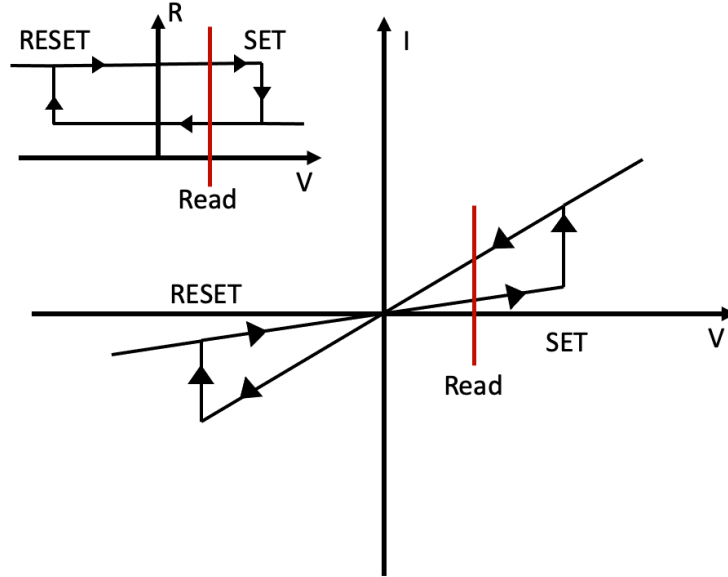


Figure 2.1. Quasi-static switching of resistive random-access memory (ReRAM).

In the following subsections the properties and applications of resistive switches are explored further. First, the potential of these cells as candidates for universal memory is inquired into. Here the cell is operated in binary mode. Afterwards, their neuromorphic properties are investigated with special emphasis on the spike-timing-dependent plasticity (STDP).

2.1.1. Universal Memory

In today's data-driven approach to technological advancements (cloud-computing, artificial intelligence), industries' and consumer's hunger for ever more information storage capabilities, both in large scale server farms and in embedded systems, increases. The nowadays dominant solid-state memories – storing binary information – can be divided into three categories [7]:

1. static random-access memory (SRAM) – based on latching circuitry
2. dynamic random-access memory (DRAM) – based on electric charge on capacitor
3. Flash – based on electrons tunneling on and off a transistor's floating gate

As all three technologies have demerits, many applications require a combination of all of them to provide good performance at reasonable cost, which leads to the disadvantage of increased implementation and fabrication complexity. SRAM provides fast read and write speeds and requires little power for memory retention. On the downside it requires a large cell size of typically six transistors – providing the flip-flop architecture – and is therefore not well suited for embedded applications requiring a lot of memory within a small footprint. Therefore it is primarily used for cache memory in processors where quick data-access is crucial over larger amounts of memory. Although it requires minimal power for memory retention, it remains a volatile memory, meaning that information is lost once power is no longer supplied to the cell. An exemplary circuit of a SRAM cell consisting of six transistors is shown in Figure 2.2a revealing the large footprint this technology requires. Here, the bit is stored on four transistors which form two coupled inverters. Two additional transistors are required for read and write operations. The word line enables access to cell by controlling the two access transistors where the state of the cell is either read out or written via the bit lines.

DRAM, in contrast, provides a smaller cell size as it only consists of one transistor along with one storage capacitor and is therefore suited for applications that require high memory density. A circuit diagram of a single DRAM-cell is provided in Figure 2.2b. Here, the bit is stored as the charge-state of a single capacitor which is shielded from the common bit line via a transistor. Access to the cell is granted via the word line connected to the transistor's gate. As this technology tends to leakage out of the capacitor, a rewrite of the cells is required every tens of milliseconds. The resulting increase in power consumption makes it undesirable for portable devices and devices with limited battery life.

Opposing to SRAM and DRAM, Flash offers a non-volatile memory solution, meaning that the information in a Flash cell is maintained even when power supply is no longer provided. The time that the cells can store their information without rewriting – their endurance – is at least 10 years. Hereby, a bit is saved as the charge-state of a floating-gate MOSFET's gate. Figure 2.2c shows an exemplary schematic where a MOSFET's gate is connected to the word line via a tunnel junction. By applying a bias – higher than a threshold voltage required for tunneling – to the word line, charge carriers can tunnel through the junction to change the charge-state

of the transistor's gate and therefore manipulating the conductivity of the MOSFET's channel. The state of the memory cell can then be read out via the bit line. Flash provides a small footprint and fast access times but only slow write times [7]. Moreover, repeated switching cycles lead to degradation of the dielectric in the tunnel junction, reducing the memory cell's longevity [8].

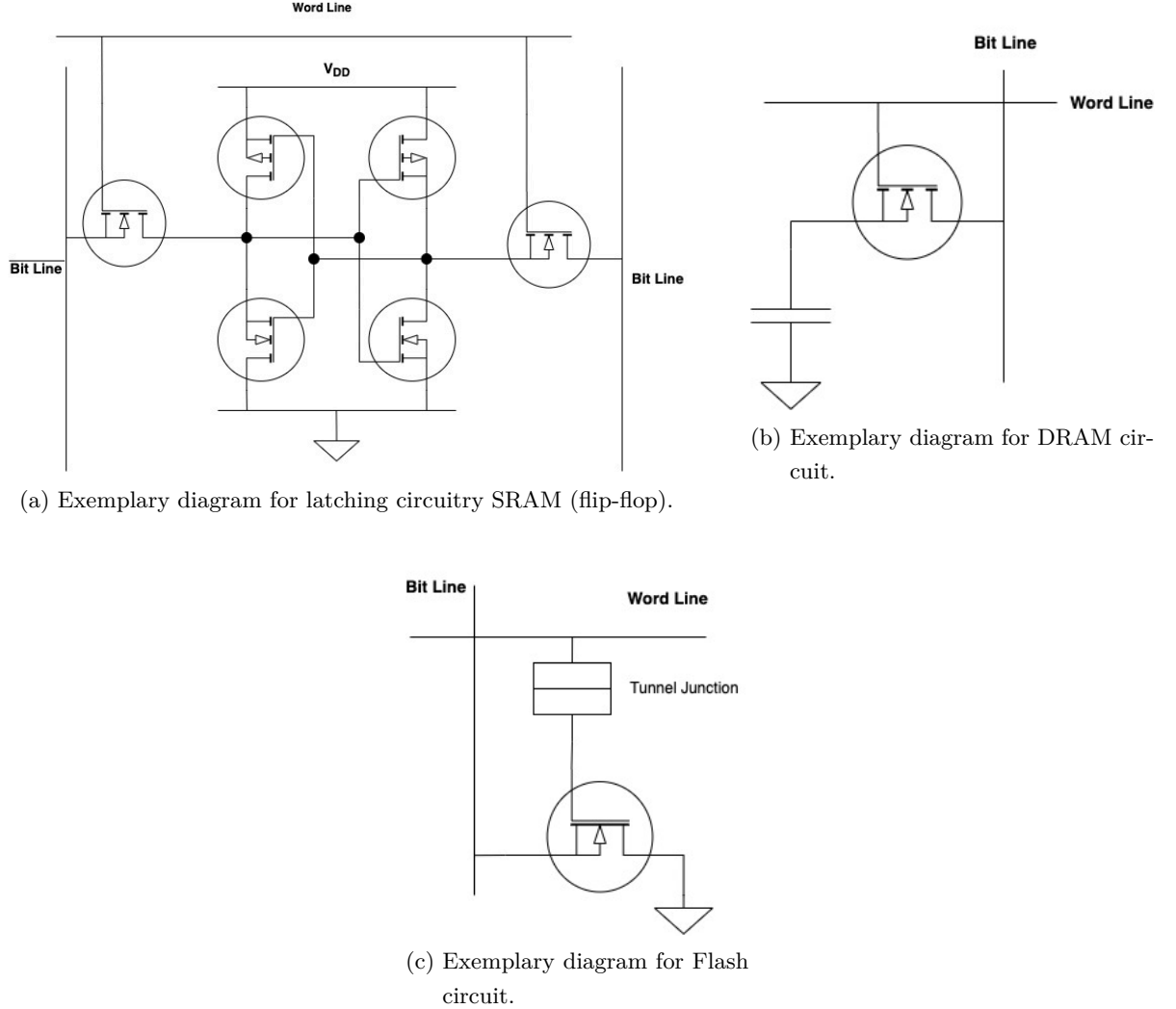


Figure 2.2. Examples for solid-state memory.

As has been shown, all of the aforementioned memory technologies have advantages but also drawbacks. Therefore, a combination of all three is usually embedded in the same device [7]. SRAM provides fast read and write speeds at the cost of high integration complexity and a large footprint. DRAM enables high memory density enabled by the small cell size but has a higher power consumption. Lastly, while Flash memory is non-volatile, it supports only a limited number of read and write cycles. In efforts to combine the advantages of high integration density, non-volatility, and fast read/write speeds while mitigating these limitations,

the concept of universal memory emerges.

ReRAM is considered a strong candidate for universal memory as it promises high scalability due to its simple structure, low operation voltages, and highly enduring and fast switching [9, 10, 11]. Figure 2.3 presents one possible ReRAM-cell in the one-transistor-one-resistor (1T1R) configuration, where a bias to the word line makes the transistor channel conductive and therefore increases the voltage drop over the resistive element with simultaneously biased bit line. This voltage drop can be used to change the conductive state of the resistor or conduct a read-out operation [12]. When no bias is applied to the resistive element, it remains in the state as-is when disregarding thermally-activated processes such as diffusion or spontaneous domain switching. Therefore, this memory-technology is considered non-volatile since data retention times of over ten years are achievable [6].

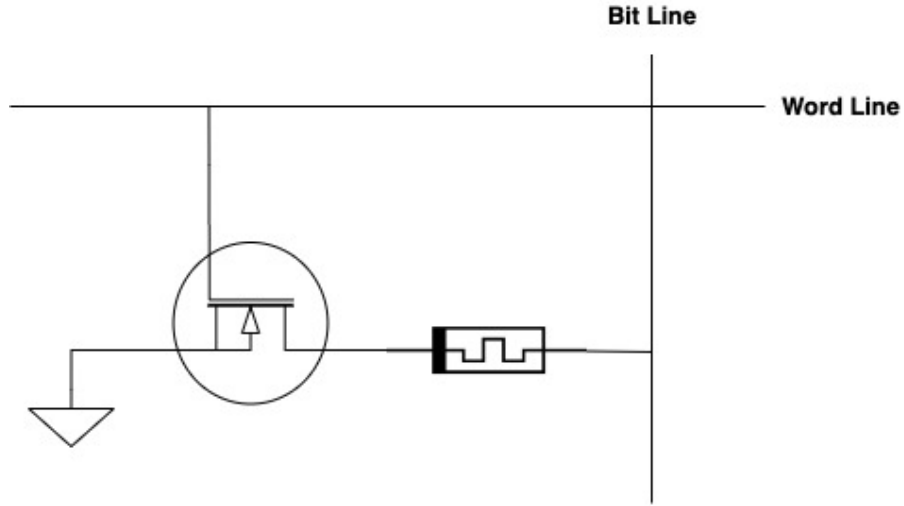


Figure 2.3. ReRAM in 1T1R configuration.

2.1.2. Neuromorphic Computing

Neuromorphic computing aims at using analogue electrical components to mimic – at least some of – the behaviors and functionalities found in biological neural networks such as mammalian brains [13]. The endeavour to use brain-like structures to imitate their remarkable computational capabilities has led to the development of software-based artificial neural networks (ANNs) as a platform for a variety of tasks, including pattern recognition, but also the generation of text and visual and auditive content. In these software-based systems – operating on the von-Neumann-architecture – data needs to be repeatedly transferred to and from an external memory to the logic unit as both of them are strictly separated in this architecture. This is true for both the learning procedure as well as the operation of the neural network and concerns both the data that is being processed and the parameters of the ANN. The data-transfer requires an overhead in power consumption and furthermore constitutes a bottleneck for the system’s throughput [14]. In the recently proposed neuromorphic, hardware-based approach

data – in the form of the neural network’s weights – are stored, manipulated, and used for computations in the same physical location reducing the aforementioned overhead and introducing inherent parallelization [15]. Resistive random-access memory (ReRAM) is a promising candidate for this way of in-memory computing, as neural network weights can be represented as their resistances. Here, the cells’ resistances are not set to discrete values, but are continuously tunable by adjusting the strength external stimulus. Thus, the strength of a connection in the neural network depends on how often or strongly it was stimulated during a learning process. Furthermore, they can be configured in crossbar-arrays connecting the individual neurons to each other [13] and representing the ANN structure in hardware. Here, the input of the ANN is represented by the applied voltages. The current, constituting the output of a layer, is then directly given by Ohm’s law and Kirchhoff’s current law [4]. By connecting to the two terminals of the ReRAM element, the timing between pulses applied to the respective connections can additionally be learned due to their spike-timing-dependent plasticity (STDP) enabling the use as a spiking neural network (SNN) [15].

2.1.3. Spike-Timing-Dependent Plasticity

In neural networks, a synapse is the directional connection between two neurons. The neurons can therefore be referred to as pre-synaptic and post-synaptic neurons. These neurons ”fire”, meaning they apply their respective pre- and post-synaptic action potential to the synapse. The time-dependent shape of the action-potentials varies in mammalian brains depending on their respective function [16] and it is the sum of both the pre- and post-synaptic action potentials that are coinciding at the synapse. Depending on the time difference Δt between the arrival of the pre-synaptic and the post-synaptic action potential, the conductivity of the synapse can increase – resulting in a stronger connection of the two neurons –, decrease – leading to a weaker connection of the neurons, or not influence the connection due to the resulting voltage not surpassing a threshold. As this synaptic plasticity is strongly dependent on the delay between the two action-potentials, it is referred to as spike-timing-dependent plasticity (STDP). Figure 2.4 shows the influence of different time-delays of the action potentials on the resulting potential over the synapse. Here, piece-wise functions with two exponential branches have been used for the individual spikes in reference to [4]:

$$V_{spike}(t) = \begin{cases} A \cdot \exp\left(\frac{-t}{B}\right), & t > 0 \\ -A \cdot \exp\left(\frac{t}{B}\right), & t \leq 0. \end{cases} \quad (2.1)$$

The resulting voltage pulse, depending on the time delay Δt is then constructed:

$$V_{res} = V_{spike}\left(t + \frac{\Delta t}{2}\right) + V_{spike}\left(-t + \frac{\Delta t}{2}\right) \quad (2.2)$$

In Figure 2.4a, the pre-synaptic spike arrives briefly before the post-synaptic spike resulting

in an accumulated potential that surpasses an arbitrarily chosen threshold. This leads to a decrease of the synapse's resistance and therefore a strengthening of the neurons' connection. In analogy to the ReRAM-memory cells, this could be considered a SET-operation. On the other hand, in Figure 2.4b, there is a delay in the arrival of the pre-synaptic spike, thus it arrives after the post-synaptic spike. The resulting pulse is therefore negative which weakens the connection of the neurons. In ReRAM this would be analogous to the RESET-operation. Finally, in Figure 2.4c, the pre-synaptic action potential arrives long before the post-synaptic spike. The resulting sum does not exceed the threshold and thus does not change the conductivity of the neurons' connection.

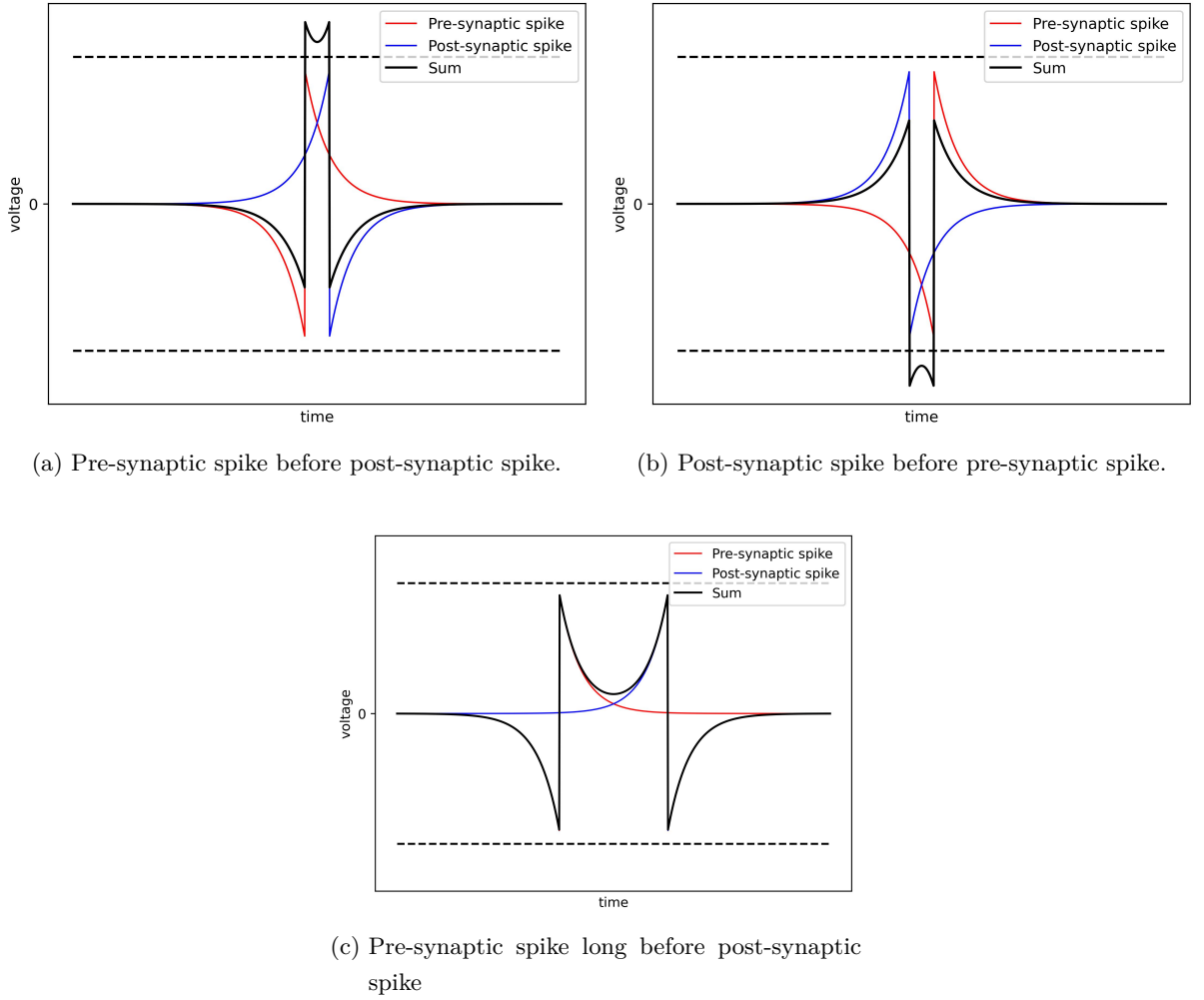


Figure 2.4. Spike-timing-dependent plasticity (STDP) with different delays.

It can be constituted, that starting from a long negative delay – meaning that the pre-synaptic spike arrives long before the post-synaptic spike – the synapse's response increases monotonously at first with decreasing time delay – as the pulses height increases – while the pulses width decreases. As the potential is now applied of an increasingly shorter duration, the effect on the synapse decreases. At $\Delta t = 0$ the two spikes cancel each other out completely

and the sign of the STDP-pulse and therefore also the response of the synapse, flips from a SET to a RESET. When the, now positive, delay is increased further, the synapses response increases again, as the width of the pulse increases. At last, the pulses height decreases, until it does not exceed the threshold anymore, thus reducing the synaptic response again. This transition is depicted in Figure 2.5, where the integral of the parts in which the STDP-pulse exceeds the threshold is shown as a function of the respective time-delay. Similar curves have been measured in ReRAM-memory cells by Mittermeier *et al* [4] and are presented in Appendix A, but also in biological synapses, such as rat hippocampal neurons [17] where the influence of the spike-timing delay onto the synapses' conductivity is presented directly, thus suggesting, that only pulses that exceed the threshold alter the synaptic configuration. It is therefore feasible to approximate the superposition of the pre- and post-synaptic spike with a rectangular function in investigations of the STDP-behavior of ReRAM-structures later on in this thesis in subsubsection 3.3.4.3.

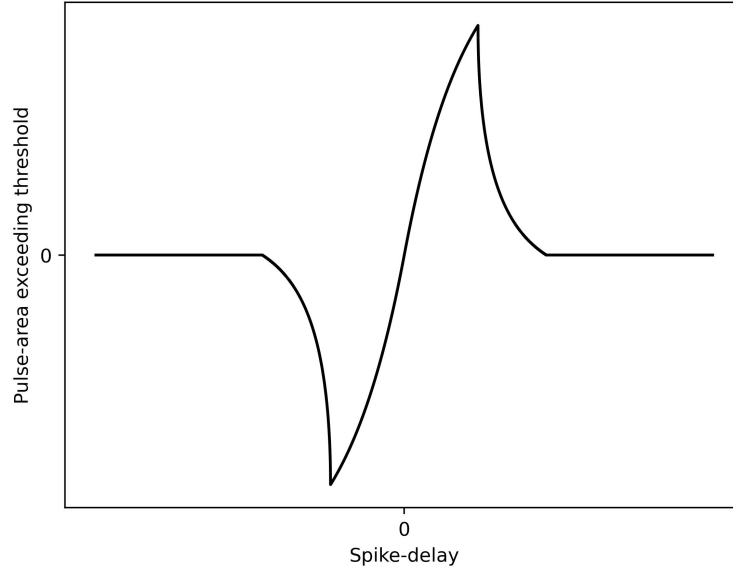


Figure 2.5. Area exceeding threshold as function of spike-timing delay.

2.2. Switching in $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$

Hafnium Oxide (HfO_2) has been introduced as a high- k gate-dielectric for the 45 nm technology node in 2007 [18], as its amorphous phase provides a combination of a high dielectric permittivity of ~ 25 and a band-gap of ~ 5.7 eV. The material has, thus, been established in the semiconductor-industry for many years. HfO_2 crystallizes in a monoclinic phase at room temperature, undergoes a phase transition to a tetragonal lattice at ~ 2000 K and finally another transition to a cubic phase at ~ 2870 K [19]. In 2011, orthorhombic, silicon oxide-doped, HfO_2 was reported, which exhibited ferroelectric and antiferroelectric behavior [20]. Since then a multitude of different dopants have been investigated to stabilize the orthorhombic phase.

Zirconium is a promising candidate as it has similar chemical properties as Hf, and the maximum ferroelectric polarization in $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ (HZO) is achieved close to $x = 0.5$. This means that HZO can easily be deposited by atomic layer deposition (ALD) – a process favored by the industry – by alternating the respective precursors. Furthermore, ferroelectric properties in HZO thin films are achieved at relatively low deposition temperatures, which makes their fabrication compliant with existant processes [21].

Ferroelectricity denotes the property of a crystal undergoing reversible polarization when an electric field is applied to it. Furthermore, when the external field is removed, the remanent polarization stays non-zero [5]. These two distinguishable states can be utilized to store binary information. Pulvari [22] proposed a barium titanate based permanent memory utilizing the remanent polarization of the perovskite in 1951. Another way to store information using ferroelectricity was proposed by Esaki *et. al.* [23] in the form of a ferroelectric tunnel junction (FTJ) where the modulation of the tunneling barrier, caused by the screening charges, induced by the polarization state of the dielectric, is utilized for resistive switching. These HZO FTJs will be discussed in subsection 2.2.1 Ferroelectric HfO_2 is an interesting candidate for ferroelectric memories due to its CMOS-compability. Furthermore, it does not show a dead layer effect which is inherent to perovskite ferroelectrics [24] facilitating its use in tunnel junctions.

Additionally, the formation and retraction of a conductive oxygen deficient filament can be used to exhibit resistive switching properties in hafnium-based oxides. Here, oxygen is removed from a filament in the crystal lattice and electronic conduction takes place via the oxygen vacancies [25]. A single device can show both conduction via tunneling and using an oxygen deficient filament. Here, the magnitude of the applied voltage determines which of the two switching mechanisms takes place, since the oxygen vacancies for building a filament are typically generated at higher voltages than required for ferroelectric polarization reversal. Oxygen vacancy based filamentary switches will be discussed in greater detail in subsection 2.2.2.

2.2.1. Ferroelectric Tunnel Junctions

A ferroelectric tunnel junction (FTJ) is a resistive random-access memory (ReRAM) where an ultra-thin, insulating ferroelectric is placed in between two metallic electrodes. The insulator must be thin enough to enable quantum-mechanical tunneling between the two electrodes. In 2009, Garcia *et al* established that ferroelectric polarisation reversal was responsible for the FTJ's resistive switching [26]. Thus, the direction of the remanent polarization, which can be altered by an external electric field across the metal-insulator-metal (MIM)-stack, can be directed either towards the bottom- or the top-electrode.

The remanent polarization in the ferroelectric layer of a ferroelectric tunnel junction (FTJ) modulates the tunneling barrier due to the interaction between the polarization-induced bound charges and the dissimilar electrode materials. When the polarization points towards one electrode, it induces bound charges at the interfaces: positive charges at the electrode towards which the polarization points and negative charges at the opposite electrode. If the polariza-

tion points towards the electrode with a higher work function, the positive charges reduce the potential barrier at that interface, facilitating electron tunneling and leading to a low resistance state. Conversely, when the polarization points towards the electrode with a lower work function, the potential barrier at the interface with the electrode with the higher work function is increased due to the negative charges, hindering electron tunneling and resulting in a high resistance state. The screening charges that are attracted to the electrode-ferroelectric interface also cause an expansion or shrinkage of the effective tunneling barrier, which constitutes another effect influencing the tunneling probability.

The modulation of the tunneling barrier, which depends on the direction of the polarization relative to the asymmetric electrode materials, is the underlying mechanism driving the resistance change in FTJs [27]. The influence of the polarization reversal of the ferroelectric layer in an FTJ is depicted in Figure 2.6. Thus, it can be constituted that FTJs require asymmetric electrodes. However, different electrode materials are not required, as interfacial effects – particularly during the deposition of the films – can already induce the compulsory symmetry breaking [28].

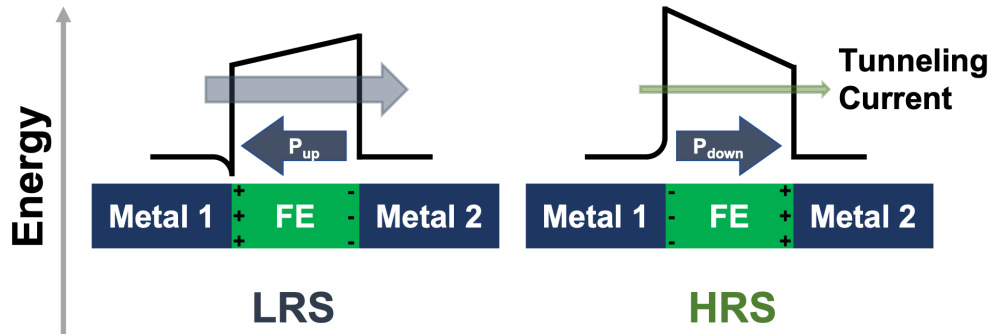


Figure 2.6. Band diagram of the MIM structure with the influence of different polarization directions represented. Adapted from [5].

FTJs have been thoroughly investigated in previous work in our group. Hereby, the fabrication of the MIM-structures [29], theoretical modeling of their switching behavior [30] and the influence of oxygen vacancies [5] have been in the center of attention.

During the latter, an interesting behavior in their switching dynamics has been observed. As described in section 2.1, ReRAM can be utilized – besides its neuromorphic capabilities – as classical, binary memory. This requires a reliable switching between two physical states when the externally applied stimulation (in this case a voltage-pulse) remains the same as a function of time. However in Gonzalez’ thesis [5], a deviation from this desired behavior was observed. During the switching between high-resistive state (HRS) and low-resistive state (LRS) (in an endurance-measurement; more information in subsection 3.3.4.2) the acquisition of additional states, constituted by a splitting of HRS and LRS respectively, emerged. The splitting

of the states is depicted in Figure 2.7. This behavior is referred to as a period-doubling bifurcation and is inherent to many non-linear systems in nature and similar behavior in the form of intermittency-bifurcations has been reported in the polarization-reversal in ferroelectrics before [31]. These forms of bifurcations are known to be routes towards deterministic chaos [32] and will be investigated in greater detail in section 2.3. Thus, chaotic switching in ReRAM are a prospect of this observation.

The existence of a negative feedback in the system is required to produce period-doubling bifurcations [32] and the investigation of their occurrence in ReRAM-elements will constitute the main contribution of this thesis. However, the negative feedback implies energy dissipative effects in the cells switching behaviour. The investigation of other ReRAM-elements such as oxygen-vacancy switches is therefore promising, as other dissipative effects such as thermally activated processes play a role here.

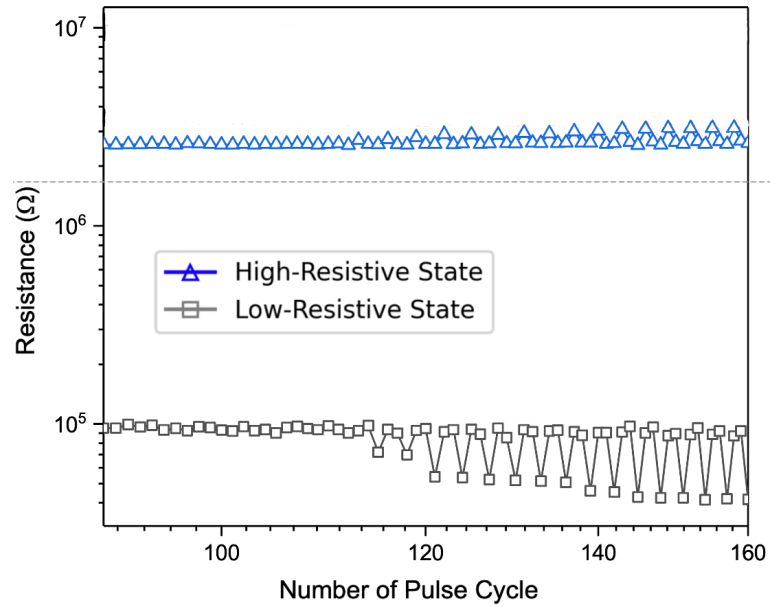


Figure 2.7. Emerging period-doubling bifurcations in FTJ endurance measurement for both the HRS and the LRS. The occurrence of two succeeding values with the same resistance can be attributed to a measurement artifact. Adapted from [5].

2.2.2. Oxygen Vacancy Switching

Oxygen-vacancy switches consist of metal-insulator-metal (MIM) structures, similarly to the ferroelectric tunnel junction (FTJ). However, here the thickness of the insulating layer can be up to tens of nanometers thick as the conduction mechanism through the dielectric does not depend on quantum-mechanical tunneling. A controlled, soft dielectric breakdown creates a conductive path, or filament, to connect the two electrodes [33]. A change of the chemical composition of a part of the insulating layer – more precisely reduction for the SET operation and oxidation for the RESET operation – is responsible for the switching of the resistive state.

The resulting formation of a conductive filament with sub-stoichiometric phase is caused by an externally applied bias which causes the migration of oxygen ions [34].

An exemplary schematic for the operation of bipolar resistive random-access memory (ReRAM) based on oxygen vacancy filamentary switching is depicted in Figure 2.8. In the device's pristine state (a), some oxygen vacancies are randomly distributed within the dielectric. (b) shows the result of an electroformation step. Applying a positive bias to an electrode causes the migration of oxygen to that electrode due to its high electronegativity and the creation of additional vacancies. This results in a filament, consisting of oxygen vacancies to gradually grow, connecting both electrodes. When the filament is completed, a conductive path is created and the cell switches from the high-resistive state (HRS) to the low-resistive state (LRS). When the biasing of the cell is reversed in (c), the direction of the migration of the oxygen vacancies is also reversed until the filament breaks and the resistance of the MIM-stack rises again. It should be noted, that the filament does not retract completely, but only a gap of a few nanometers emerges. In a functional memory cell, this effect is reversible many times and the closing and breaking of the filament are associated with the SET and RESET operations [35].

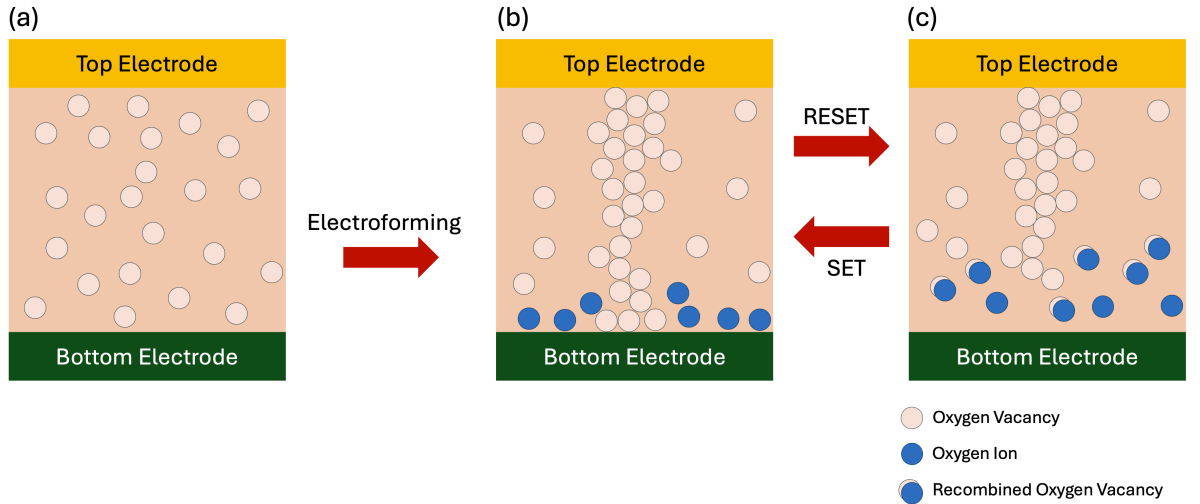


Figure 2.8. Schematic for Oxygen Vacancy Switching based ReRAM.

As the performance of these devices is strongly dependent on oxygen vacancy density and distribution, whereas these parameters are strongly dependent on the conditions under which the structure was fabricated, a lot of work has been done to improve the control of oxygen vacancy concentration during fabrication, aiming to achieve more consistent and reliable resistive switching behavior. This involves optimizing deposition techniques, annealing processes, and doping strategies to fine-tune the oxygen vacancy distribution within the active layers of the device. Exemplary, Gonzalez [5] investigated the influence of oxygen partial-pressure and annealing methods on vacancy density and the resulting switching behavior, while De Stefano *et al* [34] inserted a metallic Hf layer between the dielectric and the top electrode to promote

vacancy formation. Cagli *et al* [36] reported a reduced forming and switching voltage when using an electrode material with high oxygen affinity such as titanium. Here, an interfacial layer which is a vacancy-rich region is introduced and assists in switching. Ryu *et al* [37] suggest that doping with ZrO_2 improves the switching characteristics such as larger on/off ratio, as well as lower operating voltages and currents.

In regard to the period-doubling bifurcations mentioned in the previous section, ReRAM based on oxygen vacancy switching, offer energy dissipative effects that could be responsible for the required negative feedback. Exemplary, unipolar switching behavior could lead to a decrease in on/off ratio with increasing temperature. In unipolar ReRAM-cells, thermal energy, introduced by Joule-heating dissolves the conductive filament. Thus, an increased voltage and therefore an increased current introduces a mechanism that decreases the cells response with increasing voltage [35]. Figure 2.9 (adapted from Nardi *et al* [38]) shows a typical quasi-static switching curve of an unipolar ReRAM element. After an initial forming step the cell is transformed into HRS when a threshold current is surpassed and enough heat for lateral ion migration is produced. Afterwards, the SET operation is performed at a higher voltage, resulting in ion drift and closing of the conductive filament, while including a current compliance to ensure that a threshold current is not surpassed. The process is reversible. This cause of negative feedback in ReRAM switching characteristic will be discussed, among others, in greater detail in subsection 4.3.1.

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Figure 2.9. Quasi-static switching curve for unipolar switching ReRAM. Adapted from [38].

2.3. Deterministic Chaos

The concept of chaos is often associated with disorder and unpredictability. However, in the context of deterministic chaos, it refers to a specific type of behavior of dynamical systems that is deterministic, but extremely sensitive to initial conditions. Differently from traditional randomness, deterministic chaos is still governed by well-defined equations that describe a

system's evolution, yet it produces outcomes that only appear random and unpredictable. This phenomenon, where systems, that are described by deterministic laws, exhibit behavior that is so sensitive to initial conditions that long-term predictions become impossible due to noise and limited sensitivity of measuring devices. Despite the systems being deterministic in nature – meaning that their future states are completely determined by their initial conditions – slight variations in those conditions will eventually lead to drastically different outcomes. This phenomenon is famously also called the "butterfly effect", coined by Edward Lorenz, who demonstrated that tiny changes in the starting conditions of non-linear weather models could lead to rapidly diverging forecasts [39].

The study of deterministic chaos emerged in the 20th century, but its conceptual roots are based on earlier work. Henri Poincaré contributed significantly to the understanding of instabilities of systems, particularly in his study of the three-body problem. He discovered that even simple systems could exhibit highly complex, chaotic behavior. His work laid the groundwork for modern chaos theory [40]. It wasn't until the 1960s, and the arrival of computer-based approaches, that deterministic chaos began to gain widespread attention. Edward Lorenz's work on atmospheric models led to the identification of chaotic behavior in deterministic systems, giving rise to what is now known as the Lorenz attractor [41]. An attractor is the representation of a dynamic system in phase space to which the system evolves asymptotically given enough time, regardless of the systems initial conditions. An example for a simple attractor would be the single point attractor for a damped system that eventually comes to rest, meaning it just occupies one trivial point in phase space. As described before, the long-term evolutions of chaotic systems depend strongly on the initial conditions. Therefore, simple attractors do not satisfy this condition which leads to the concept of strange attractors, whereas the Lorenz attractor is an example for a strange attractor. Like simple attractors, the strange attractors draw in trajectories of the dynamic system with the peculiarity that the distance between two neighboring points in phase space diverge exponentially with time [32], resulting in the aforementioned unpredictability of the system due to its sensitivity towards initial conditions. These attractors, furthermore, have a fractal nature, meaning that they form a complex structure that has a fractional dimension, which is greater than its topological dimension but less than the dimension of the space it inhabits [42]. This fractal nature allows the attractor to contain an infinite amount of detail in a finite area. The model, used by Lorenz to describe weather phenomena in which he discovered deterministic chaos is given in Equation 2.3 [41] and has been used to calculate the curve depicted in Figure 2.10 with $\sigma = 10$, $\beta = \frac{8}{3}$ and $\rho = 28$.

$$\begin{aligned}\dot{X} &= \sigma X + \sigma Y \\ \dot{Y} &= -XZ + \rho X - Y \\ \dot{Z} &= XY - \beta Z.\end{aligned}\tag{2.3}$$

This discovery revolutionized the understanding of dynamic systems, revealing that chaos could be present in a wide variety of physical systems, from fluid dynamics [43] to electrical circuits

[44], and even biological processes [45].

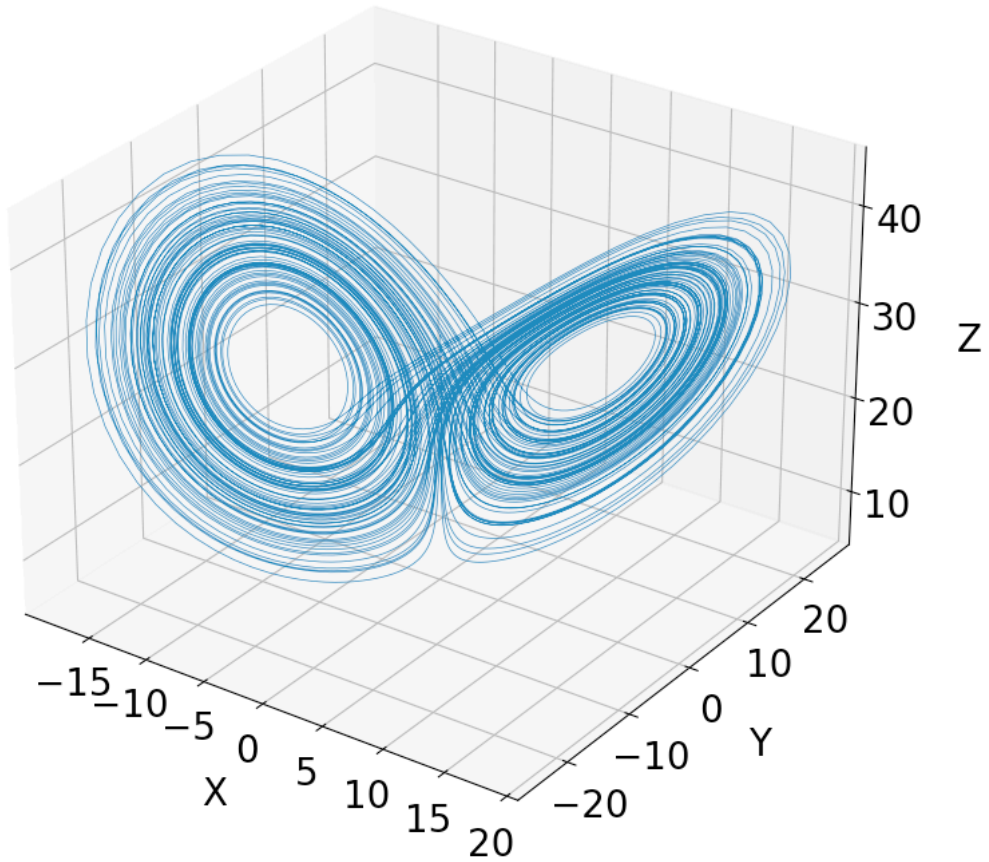


Figure 2.10. Lorenz Attractor

2.3.1. Fundamentals of Chaos Theory

As seen in the previous section, chaotic behavior can be found in many non-linear systems. However, non-linearity is a required but not satisfying condition for deterministic chaos in dynamic systems. Thus, the Lyapunov-exponents and the Kolmogorov-Sinai entropy will be introduced here as important metrics to describe chaos in dynamic systems.

2.3.1.1. Lyapunov-Exponents

Lyapunov-exponents are critical to the understanding of chaos because they quantify how sensitive a system is to its initial conditions. They measure the average, exponential rate of divergence (or convergence) of nearby trajectories in phase space. If two trajectories in phase space that start very close to each other are considered, then the distance between them grows exponentially in chaotic systems. The Lyapunov exponent λ is defined as the rate of this

divergence according to [32]:

$$\varepsilon e^{t\lambda(x_0)} = |f(t, x_0 + \varepsilon) - f(t, x_0)|, \quad (2.4)$$

where ε is the distance between the initial positions in phase space, t is the system-time, and f is the model describing the system. For $\varepsilon \rightarrow 0$ and $t \rightarrow \infty$ this leads to the formal definition of the Lyapunov-exponent:

$$\begin{aligned} \lambda(x_0) &= \lim_{t \rightarrow \infty} \lim_{\varepsilon \rightarrow 0} \frac{1}{t} \ln \left| \frac{f(t, x_0 + \varepsilon) - f(t, x_0)}{\varepsilon} \right| \\ &= \lim_{t \rightarrow \infty} \frac{1}{t} \ln \left| \frac{\partial f(t, x)}{\partial x} \right|_{x=x_0}. \end{aligned} \quad (2.5)$$

The Lyapunov-exponent provides a direct measure of how quickly small errors or uncertainties in the initial state of a system grow over time. If $\lambda > 0$, nearby trajectories diverge exponentially, indicating chaotic behavior. If $\lambda < 0$, trajectories converge, leading to orbits or fixed points in dissipative systems and therefore to predictable behavior (e.g. damped oscillation) [46]. If close trajectories in phase space remain at the same average distance then $\lambda = 0$ (e.g. undamped oscillation). This behavior is again predictable and thus not chaotic. It can therefore be concluded that the Lyapunov-exponent provides a measure for how "quickly" a system will appear chaotic by indicating how fast close trajectories will diverge.

2.3.1.2. Kolmogorov-Sinai Entropy

In analogy to entropy in statistical mechanics, Shannon introduced the concept to information theory [47]. Where entropy is a metric for disorder in physical systems, in information theory it measures the lack of information one has about the system and is then defined as:

$$S = -C \sum_i p_i \log p_i, \quad (2.6)$$

where S is the Shannon-entropy, p_i are the probabilities of a set of events and C is a positive constant which is set to $C = 1$ for further considerations without loss of generality. The Shannon-entropy S is a measure for the information of the system that is required to localize it in the state i [32]. If a trajectory $\vec{x}(t)$ in a d -dimensional phase space, which is split into elements i_i of size l^d , is considered, then the probabilities of the trajectory $\vec{x}(t)$ passing through element i_0 at $t = 0$, through element i_1 at $t = \tau$, and so on until it passes through element i_n at $t = n\tau$, are given by p_i . The Shannon entropy is then given by:

$$S_n = - \sum_i^n p_i \log p_i. \quad (2.7)$$

Thus, the entropy of the system is given by Equation 2.7 and is proportional to the information that is required to find the system on a trajectory i_i . Therefore, $S_{n+1} - S_n$ is equal to the

information required to find the trajectory in the element i_{n+1} if it was previously in the elements i_i , which results in the change of information when transitioning from element i_n to i_{n+1} .

The Kolmogorov-Sinai entropy is the average rate at which information about the system is lost:

$$K = \lim_{\tau \rightarrow 0} \lim_{l \rightarrow 0} \lim_{N \rightarrow 0} \frac{1}{N\tau} \sum_{n=0}^{N-1} (S_{n+1} - S_n). \quad (2.8)$$

The Kolmogorov-Sinai entropy is a suitable metric for chaotic behavior in dynamic systems, like the Lyapunov-exponents. For $K = 0$ no information is lost along the trajectory which leads to close points in phase space also remaining close. For stochastic, truly random systems, K becomes infinite and for chaotic systems K becomes a positive constant and measures how quickly information is lost. It is therefore not surprising that the Kolmogorov-Sinai entropy can be connected to the Lyapunov-exponents of a system [32].

2.3.2. Feigenbaum Scenario

Now that useful metrics for chaotic behavior in non-linear systems have been established, a special emphasis will be put on deterministic chaos in non-linear, recursive maps. A recursive map,

$$x_{n+1} = f(x_n) \quad (2.9)$$

in non-linear, when $f(x)$ has at least one non-linear term. For the following considerations, a simple system of order two will be used:

$$x_{n+1} = rx_n(1 - x_n). \quad (2.10)$$

This map is called the logistic-map and has first been used, in a time-continuous version, by Pierre Verhulst in 1845, to model population dynamic in a confined space [48]. The discrete version in Equation 2.10 can be used to model the evolution from e.g. year-to-year. Here, r constitutes a growth factor that models the reproduction rate of the modeled species, which is multiplied with the current population to model reproducibility. For $r < 1$ the reproduction rate is negative and the species goes extinct while for $r > 1$ non-zero populations are possible. The term $1 - x_n$ introduces a negative feedback, which is critical for chaotic behavior, as will be shown later. In the context of population modeling, this term represents factors such as limited resources, diseases, and other constraints that lead to a reduction in the population size from one generation to another.

The investigation of the evolution of this simple difference-equation yields surprising results. When r , as the only variable in Equation 2.10, is varied, first the population goes extinct as discussed before for $r < 1$. For $1 < r < 3$ the population settles down on one point,

meaning that these fixed points are mapped onto themselves. Once $r = 3.0$, the population starts to oscillate, as two stable points emerge that are mapped onto each other respectively ($x_1 = f(x_2) \wedge x_2 = f(x_1) \implies x = f^2(x)$). This splitting from one stable value, to two is referred to as a period-doubling bifurcation, as the number of times the sequence has to be iterated to reach the original value doubles. Another period-doubling bifurcation happens at $r \approx 3.44949$, another one at $r \approx 3.54409$, and so on. It should be noted that the space between succeeding period-doubling decreases quickly which leads to a sequence of cascading period-doublings that occur in less and less space. With every bifurcation, the period of the sequence doubles, from 1 to 2 to 4 to 8 and so on. However, for $r < 3.569945 \approx r_\infty$ the sequence remains periodic and thus distinctly non-chaotic. After this critical growth rate r_∞ has been surpassed, the sequence is no longer periodic which means $\nexists n \mid x = f^n(x) \forall x$ and becomes chaotic [49, 50]. The different populations that can be reached are depicted in Figure 2.11. This representation of the transition into chaos in difference equations is commonly referred to as a Feigenbaum diagram. Here the period-doubling bifurcations as well as how they lead to chaotic, non-periodic evolution of the species' population can be recognized.

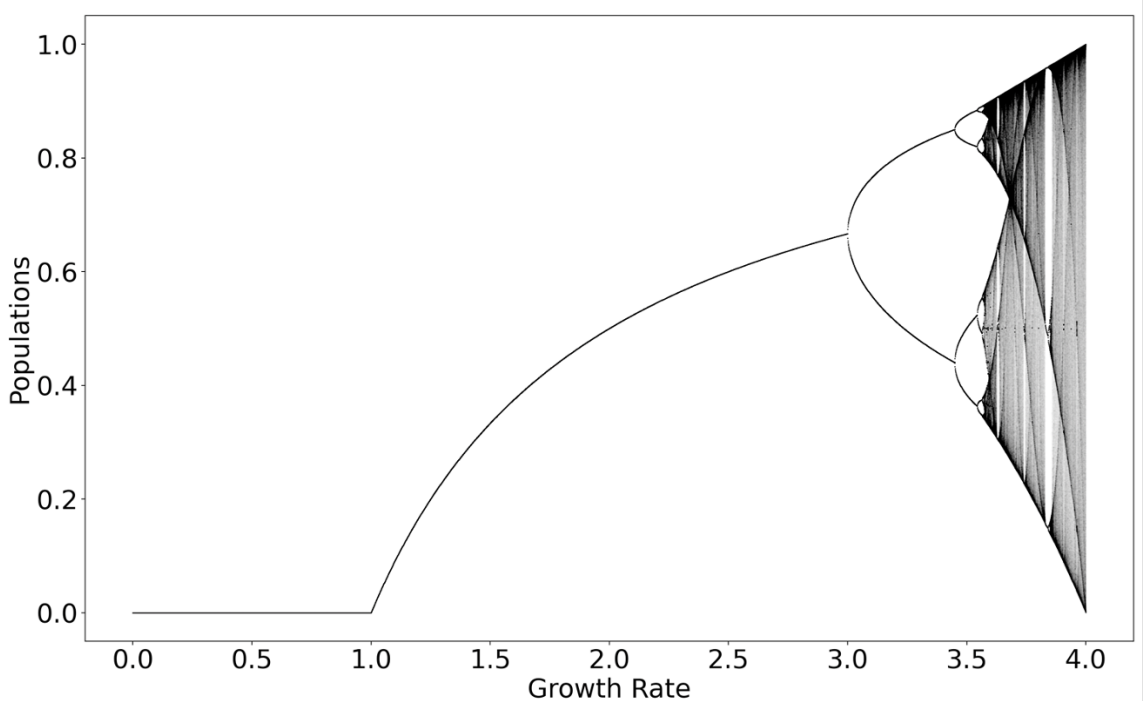


Figure 2.11. Feigenbaum diagram of the logistic map

To investigate the transition from stable behavior with a single fixed point to the emergence of multiple fixed points and eventually erratic, chaotic sequences, the Lyapunov-exponents as a function of the growth factor r are approximated according to Equation 2.5, with the sum terminated after 10,000 iterations. These values are depicted in Figure 2.12 for growth rates $r \in [2.5; 4]$. When compared to Figure 2.11, it is evident that the Lyapunov-exponents remain

negative while the logistic map follows a periodic sequence, indicating non-chaotic behavior. At the bifurcation points, however, the Lyapunov-exponents λ become zero. This signifies a neutral dynamic where nearby trajectories neither converge nor diverge. However, these points mark the onset of new behavior of the system. The periodicity of the attractor then doubles and draws the sequence to an ordered behavior. As r increases further, the bifurcation points become more frequent until the Lyapunov-exponent becomes positive at $r = r_\infty$ which marks the onset of deterministic chaos in the sequence. For higher r , windows of periodic behavior can be found, which are again dissolved into chaos by means of cascading period-doubling bifurcations. The emergence of chaos via period-doubling bifurcations is often referred to as the Feigenbaum-route or the Feigenbaum-scenario [51].

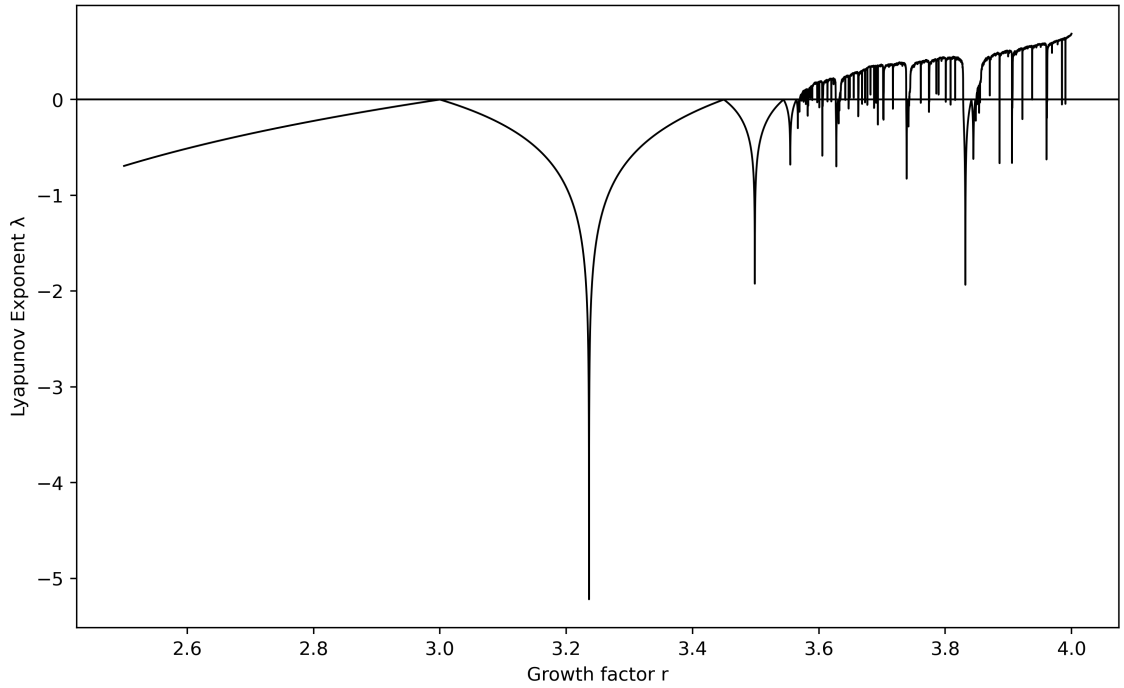


Figure 2.12. Lyapunov-exponents of the logistic map

The transition to deterministic chaos via period-doubling bifurcations can be observed in many non-linear maps as long as they show a negative feedback which constitutes itself by the presence of a local maximum in the iterated interval. Feigenbaum diagrams for maps using trigonometric functions, exponential functions and triangular maps are shown in Appendix B. must be negative for all x in the interval that is mapped [52].

3. Materials and Methods

This chapter details the materials for the fabricated resistive random-access memory (ReRAM) devices as well as the thin film deposition techniques to create the metal-insulator-metal (MIM) stacks. Furthermore, the characterization procedures are briefly introduced.

In the first section the electrode materials for the TiN/Hf_{0.5}Zr_{0.5}O₂/Au structure are discussed. Titanium nitride and gold function as electrode materials; their thicknesses are not as critical as for the Hf_{0.5}Zr_{0.5}O₂ dielectric. However, especially for the TiN bottom electrode, a low surface roughness as well as small grain sizes are important to provide optimal conditions for the deposition of Hf_{0.5}Zr_{0.5}O₂ on top. Afterwards, the principle of the thin film fabrication technique sputtering – specifically RF-magnetron sputtering – will be discussed. This technique constitutes an industry standard as it allows for precise control of the thickness of the individual elements of the stack as well as good scalability. Finally, the means to characterize the fabricated stacks as well as the individual layers are presented. Here, techniques to analyze material composition, film-thickness, surface morphology as well as electrical characterization of the complete devices are described.

3.1. Materials

The devices that have been fabricated, in the frame of this thesis, consist of three-layer stacks: The titanium nitride bottom electrode, the active, switching layer consisting of Hf_{0.5}Zr_{0.5}O₂ and the gold top-electrode. The combination of these materials offers advantages, which are detailed in the following sections.

3.1.1. Titanium Nitride Bottom-Electrode

Titanium nitride constitutes a favorable material for a bottom electrode due to its low price, high temperature resistance, mechanical stability excellent electrical conductivity of 4,000 – 5,000 S cm⁻¹ [53], as well as relatively high work function of 4.5 eV [54]. Additionally, its compatibility with CMOS processes makes it particularly advantageous for integration into practical applications. The material's ability to suppress the diffusion of oxygen and its inert nature during switching events contribute to the stability and endurance of the device. It has been shown that titanium nitride electrodes stabilize the ferroelectric, orthorhombic phase in Hf_{0.5}Zr_{0.5}O₂ thin films due to the tensile strain induced into the HZO layer [55].

3.1.2. Gold Top-Electrode

Gold (Au) has been selected as the top electrode material in the TiN/Hf_{0.5}Zr_{0.5}O₂/Au metal-insulator-metal (MIM) stack as it possesses favorable properties for ReRAM applications, despite of its incompatibility with CMOS processes. It provides an inherent chemical inertness, which minimizes the risk of reactions at the electrode/insulator interface. Chemical stability is crucial in ReRAM, where the device undergoes repeated switching events that are driven by reduction and oxidation reactions. The switching could thus lead to electrode degradation, resulting in a negative effect towards device performance and lifetime. The resistance of gold to oxidation and other chemical changes ensures the stability of the interface with the Hf_{0.5}Zr_{0.5}O₂ layer, promoting consistent switching behavior over multiple cycles.

In addition to its stability, the high work function of gold (5.3 eV [56]) aligns well with the functional requirements of a ReRAM electrode. A higher work function electrode results in a higher Schottky barrier at the interface with Hf_{0.5}Zr_{0.5}O₂, enabling a limiting of charge injection into the dielectric. Although platinum (Pt) also has a high work function and is often considered for electrode applications [57], it was not chosen due to its high oxygen permeability. Platinum allows oxygen ions to quickly diffuse through the electrode, which can destabilize the device by altering the oxygen vacancy content in the switching layer. Gold's lower oxygen permeability ensures that the oxygen ions remain confined within the Hf_{0.5}Zr_{0.5}O₂ layer.

Gold, furthermore, provides a direct feedback for the quality of the deposited dielectric due to its tendency to form conductive, metallic filaments through porous materials. This ensures a dense, high quality dielectric as the stack would undergo an electric breakthrough otherwise.

3.2. Thin Film Deposition

Each of the aforementioned layers (titanium nitride, hafnium-zirconium-oxide and gold) are deposited via RF-magnetron sputtering. In this section, this deposition technique will be detailed. The stack is deposited on a silicon substrates with natural oxide, the influence of which can be neglected due to the polycrystallinity and the relatively high thickness of the TiN bottom electrodes.

3.2.1. Radio Frequency (RF)-Magnetron Sputtering

Radio frequency (RF)-magnetron sputtering is a deposition method from the family of physical vapor deposition (PVD) deposition techniques. In these PVD techniques, a vapor of ions and atoms of the target material is generated. This vapor can then spread throughout the chamber and condense on the substrate to create a thin-film.

In sputtering, a plasma is ignited close to the target resulting in a bombardment of its surface with ions from the plasma. The incident ions eject atoms from the target's surface due to momentum transfer leading to the deposition of target atoms on the substrate and the chamber walls. The principle is indicated schematically in Figure 3.1. One or multiple gases – in our case argon, nitrogen and/or oxygen – are pumped into a previously evacuated chamber (up

to 10^{-6} Torr) and a plasma is ignited, whereas the target is placed on one electrode and the substrate on the other. The plasma's ions are accelerated towards the target and "bump" into the surface, removing target atoms which then transfer onto the substrate where they form a thin film. Sputtering is widely employed in both academia and industry as it allows for both large- and small-scale applications. Furthermore, deposition parameters such as pressure, power and substrate temperature can be controlled precisely.

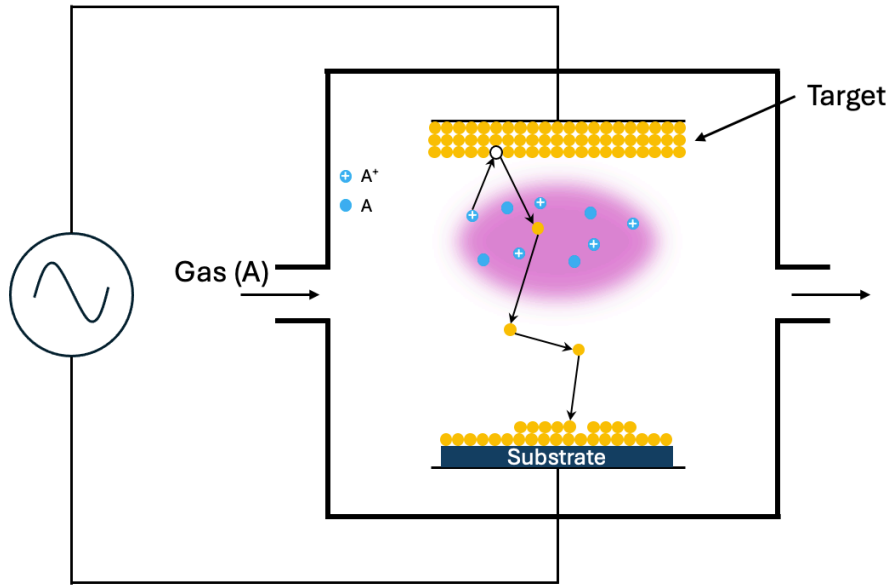


Figure 3.1. Schematic of the RF-Sputtering Process

Different to DC sputtering, RF-sputtering enables the deposition of insulating, semiconducting, and conductive materials can be achieved since no charge built-up on the target material occurs [58]. While frequencies above 1 MHz are sufficient to generate an almost continuous discharge, most systems operate with a frequency of 13.56 MHz as to not interfere with radio-communication protocols [59].

Placing magnets behind the target and thus immersing the target in a magnetic field may be used to increase the deposition speed. This process, referred to as "magnetron-sputtering", causes a confinement of primary and secondary electrons close to the target surface and therefore increases the probability of them colliding with gas atoms increasing the ionization-density of the plasma close to the target. The increased ionization efficiency results in an increased ion current density towards the target where more atoms will be "kicked out" as the average number of extracted atoms from the target per incident gas ion remains the same. The result is an increased sputtering yield compared to non-magnetron sputtering [60].

Additionally, a gas which is reactive with the target material present in the chamber during the deposition process. Hereby, the plasma can be generated from that gas or it can be present in addition to the gas from which the plasma is formed. This technique is called "reactive sputtering" and may be used to ensure stoichiometry of the target material (e.g. in the case of

oxide targets). This is often required for metal-oxides since oxygen is quicker pumped from the chamber as its metallic counterparts. Furthermore, this process can be employed to modify the thin film composition with respect to the target material. Thus, e.g. oxides or nitrides can be deposited while using a metallic target when the respective gases are present in the chamber.

3.2.2. Sputtering Tool SPT310-TT

A SPT310-TT RF-Magnetron sputtering tool from Plasmionique Inc. has been used for the fabrication of the devices investigated in this thesis. The unit is equipped with three magnetrons mounted at an angle above the substrate holder. This configuration allows for co-deposition, using two magnetrons at the same time. The tool is equipped with two mass flow controllers allowing the control of flow of two gases into the chamber simultaneously. The distance between substrate and targets is relatively high with approximately 11 cm. This high distance results in a low deposition rate, enabling precise control of the thickness of the deposited films.

The unit does provide a heating element to control the temperature of the substrate. However, during the time when devices that are detailed in this thesis were fabricated, the heating element suffered from technical difficulties, rendering the employment of desired temperatures of around 650 °C impossible. This limitation was particularly noticeable in the deposition of HZO layers with an orthorhombic phase, as high temperatures would be required here. Therefore, it was not possible to produce a ferroelectric tunnel junction (FTJ) within the scope of this work. Since the period-doubling bifurcations were first observed in these devices (see subsection 2.2.1 and [5]), a model for the negative feedback in their switching behavior will still be discussed in subsection 4.3.2.

3.3. Characterization Techniques

In the fabrication of these films a thorough investigation of their properties is critical, constituting a feedback for the optimization of the performance of the fabricated devices. The individual layers and the entire stacks have been analyzed with regard to their thickness, their surface morphology as well as their electrical properties such as the switching behavior.

3.3.1. X-Ray Reflectivity

X-rays are a form of electromagnetic radiation with wavelengths ranging from 0.01 to 10 nm, enabling them to penetrate deeply into various materials, including metals, semiconductors, and biological tissues. Here, they scatter elastically on the present electron density, allowing for interference patterns to emerge. Bragg's law can be used to describe these interference patterns:

$$n\lambda = 2d \cdot \sin \theta_n, \quad (3.1)$$

where λ is the wavelength of the incident X-rays, n is the order of the interference peak at the

angle θ_n and d is either the distance between to lattice planes (in the case of X-ray diffraction (XRD)) or the film thickness (in the case of X-ray reflectivity (XRR)).

XRR is a non-destructive technique, determining the thickness, density, and roughness of thin films. It utilizes the interference of X-rays reflected from the surface and interfaces of the film. In this setup, the detector is positioned symmetrically to the X-ray source with respect to the sample surface in a $\theta - 2\theta$ configuration, meaning that the angle enclosed by the detector and the surface is the same as that enclosed by the incident beam and the surface. For the measurement, θ is then increased gradually and the intensity of the reflected beam is measured. Starting from an incident angle of $\theta = 0$ the X-rays are reflected totally as the refractive index for X-rays in materials is slightly less than one. Only once $\theta > \theta_C$, the critical angle is surpassed does the beam enter the thin film and the measured intensity drops. Apart from absorption while the rays are traveling through the material, interference phenomena between the rays that are reflected on the surface and the rays that are reflected on the interface between the thin film and the substrate can be observed [61]. This is schematically depicted in Figure 3.2 and the interference pattern follows Bragg's law (Equation 3.1). As the refractive index is close to one for X-rays and as θ is small, an expression for these so called Kiessig interference fringes independent of the refractive index can be approximated:

$$\Delta\theta \approx \frac{\lambda}{2d}, \quad (3.2)$$

where $\Delta\theta$ constitutes the distance between two fringes.

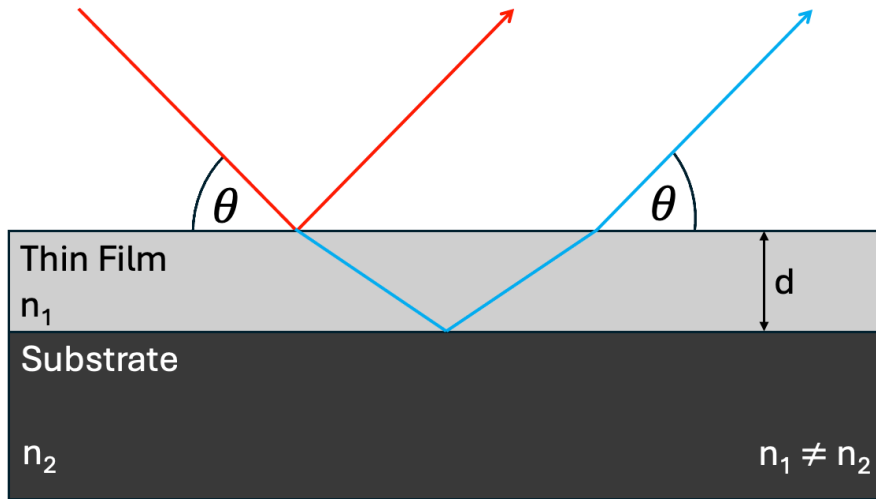


Figure 3.2. Schematic of procedure for the X-ray reflectivity (XRR) method.

Figure 3.3 shows an exemplary XRR measurement on an approximately 50 nm thick gold film. The critical angle θ_C as well as the distance between two neighboring fringes are displayed. Using these values, the film thickness can be calculated according to Equation 3.2.

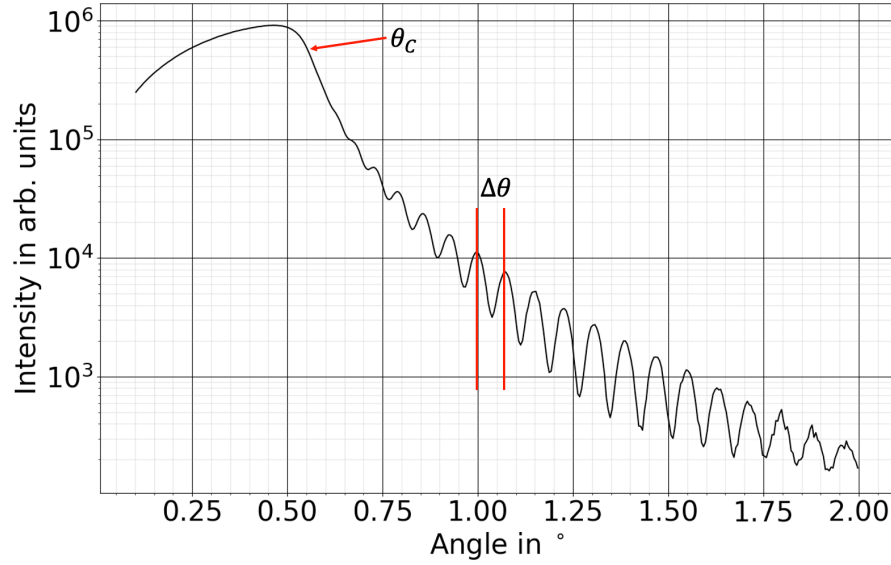


Figure 3.3. XRR pattern of an approximately 50 nm thick gold film. The critical angle θ_c as well as the distance between two fringes $\Delta\theta$ are indicated. Measurement courtesy of Katharina Kohlmann.

For measurements conducted in the scope of this thesis an X'PERT PRO from PANalytical has been used. It provides a copper $K\alpha$ source ($\lambda_{CuK\alpha} \approx 1.5405925 \text{ \AA}$ [62]). A $1/32^\circ$ slit has been employed behind the source and a 0.18° slit has been put before the detector.

3.3.2. Grazing Incidence X-ray Diffraction

Grazing incidence X-ray diffraction (GIXRD) is an X-ray characterization technique, analyzing thin films, providing information of the near-surface structure of materials with minimal impact from underlying substrates. Unlike traditional X-ray diffraction, which probes through the first few thousand atomic layers of a sample, GIXRD uses a very low incidence angle to confine the X-ray to the volume close to the film's surface. A shallow angle of 1° was used for measurements throughout this thesis to enhance sensitivity to the film structure and alleviating the influence of the substrate. In GIXRD, X-rays are directed at the sample. The X-rays are scattered at the film's electron density, generating a diffraction pattern that characterizes the crystal structure. The scattered X-rays are detected over a range of 2θ angles, and the resulting pattern represents the film's crystal structure. This pattern is analyzed to provide information about the film's lattice structure as well as its lattice parameters. By comparing the peak positions and intensities to standard reference patterns, phases of the investigated film can be determined.

The same X'PERT PRO from PANalytical as in the XRR measurements has been used for GIXRD measurements throughout this thesis. Here, a $1/4^\circ$ slit has been employed behind the source, while the 0.18° parallel plate collimator has remained the same as in the XRR configuration.

3.3.3. Atomic Force Microscopy

Atomic force microscopy (AFM) is a metrology technique from the family of scanning probe microscopy (SPM) techniques, which are characterized by measuring a material's properties by means of scanning a probe over its surface and investigating the interaction of said probe with the surface. Properties that can be studied are topography, morphology, as well as some elastic surface properties. Measurements may be conducted in vacuum, gaseous atmospheres and even liquid environments. The probe – usually a tip with a small radius of curvature – is mounted on a flexible cantilever and brought to "contact" or close proximity to the sample's surface. The tip is attracted or repulsed by the sample's surface whereby the curvature of the cantilever is measured by means of deflection of an incident laser-beam onto the cantilever. The position of the beam on a four-quadrant photodiode is thus directly representative of the curvature of the cantilever and therefore the strength of interaction between tip and sample-surface. A control-loop is then responsible for keeping either the distance or the force between the tip and the sample surface constant by utilizing highly precise piezo-actors. Figure 3.4 details the operation of the AFM schematically as described before.

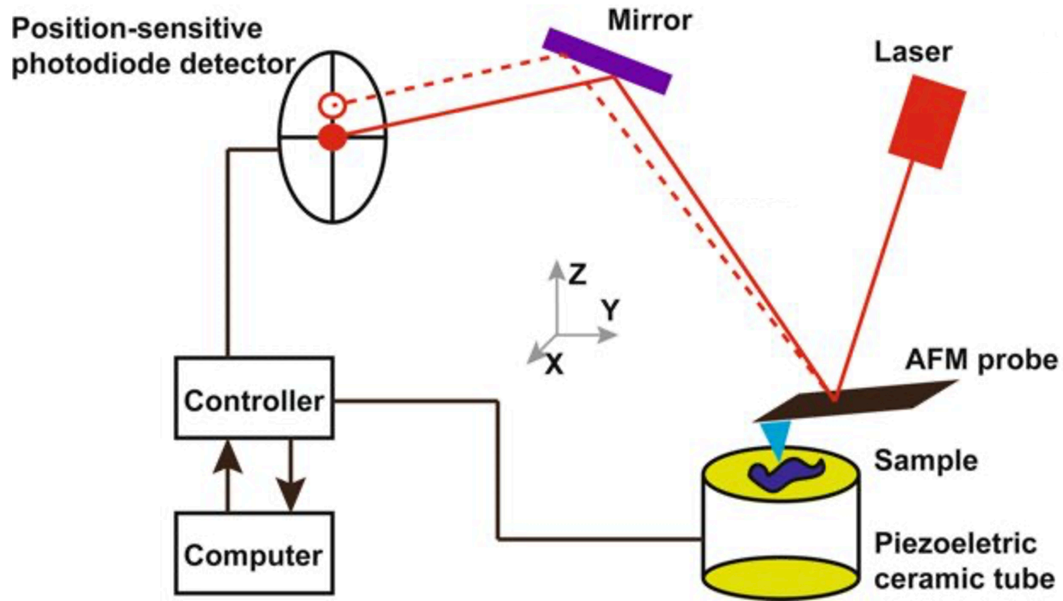


Figure 3.4. Schematic for AFM operation. Adapted from [63].

Here, three modes of operation are typically distinguished: contact mode, tapping (or semi-contact) mode, and true non-contact mode. These modes mainly differ based on the distance between the tip and the sample, but also on the relative motion between them during the scanning process. To detail differences between these operational modes, a glance at the interaction between tip and surface is required.

In 1931 a potential, modeling the inter-atomic interactions was formulated by Lennard-Jones which consist of an attractive term due to van-der-Waals interactions and a repulsive term

[64]. In its general form, this potential is given by

$$V_{LJ}(r) = \frac{A_n}{r^n} - \frac{B_m}{r^m}. \quad (3.3)$$

Phenomenological and quantum-mechanical considerations [65] resulted in $n = 12$, $m = 6$, $A_n = 4\varepsilon\sigma^{12}$ and $B_m = 4\varepsilon\sigma^6$ which gives rise to the widely spread Lennard-Jones 12-6 potential:

$$V_{LJ,12-6} = 4\varepsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right), \quad (3.4)$$

where ε is the depth of the potential well, r is the distance between the two considered particles and σ is the distance where their potential energy, with respect to each other, is zero. Figure 3.5 shows the attractive and repulsive contributions to the Lennard-Jones potential. In contact-mode AFM the tip interacts repulsively with the sample-surface while the tip is attracted to the surface in non-contact mode.

The cantilever is set into vibration in tapping and non-contact mode. Proximity to the surface changes the amplitude of the vibration which serves as the value which is controlled by the feedback loop. This enables the measurement of not only the surface topography but also of varying composition due to different contributions to the phase-response of the system. This phase-response depends on the Hamaker constant and thus the "stickiness" of the material below the tip.

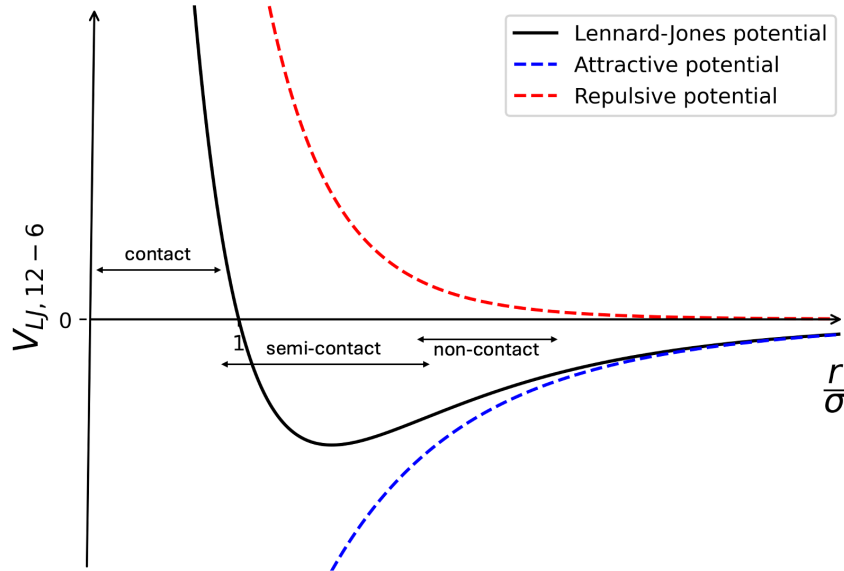


Figure 3.5. Representation of the Lennard-Jones 12-6 potential with regions for different AFM-operation modes indicated.

For this thesis, a SmartSPM1000 atomic force microscopy from AIST-NT has been used to investigate surface topography of synthesized thin-films. The AFM has been operated in tapping mode with a line scanning speed of 0.8 Hz using aluminum-coated silicon tips (HQ:NSC15/Al

BS) fabricated by MikroMash. They provide a tip radius of approximately 8 nm, a nominal spring constant of $20 - 80 \text{ N m}^{-1}$, a resonance frequency of $265 - 410 \text{ kHz}$ (the frequency of the individual probe is measured before it is utilised) and a length of approximately $125 \mu\text{m}$.

3.3.4. Electrical Characterisation

As the fabricated metal-insulator-metal (MIM) structures should serve as memory devices, a thorough electrical characterization is crucial. In this thesis, three different electrical characterization techniques have been employed. First, the quasi-static voltage sweep, where a slowly ramping voltage has been applied to the structure. This measurement technique is referred to as quasi-static as the voltage varies only slowly, compared to the switching speed of the resistive random-access memory (ReRAM) and is detailed in subsubsection 3.3.4.1.

In the endurance measurement, a train of switching voltage pulses with alternating signs has been applied to the memory cell. As this is closer to the waveforms that are applied in actual operation, this measurement type is well suited to investigate the longevity of the structure. This procedure is described in subsubsection 3.3.4.2.

Last, the cells' response to spike-timing has been measured. The cell's resistance changes depending on the height and width of the applied voltage pulse, as detailed in subsection 2.1.3. The spike-timing-dependent plasticity (STDP) of the cell has thus been investigated by applying a pulse-train to the cell with increasing pulse height. The influence of altering the pulse width has not been considered here. The STDP measurement is described in more detail in subsubsection 3.3.4.3.

For all electrical characterizations a Keysight B2901A source/measurement unit (SMU) has been used. Contact between the SMU and the MIM-stacks has been established by placing one tungsten needle on top of the gold top-electrode, which presented itself as difficult as the devices could easily be destroyed when the needle accidentally penetrates the stack. The second needle has been punched through the entire stack to reach the bottom-electrode. A schematic of this setup with the contacting of the MIM structure is shown in Figure 3.6.

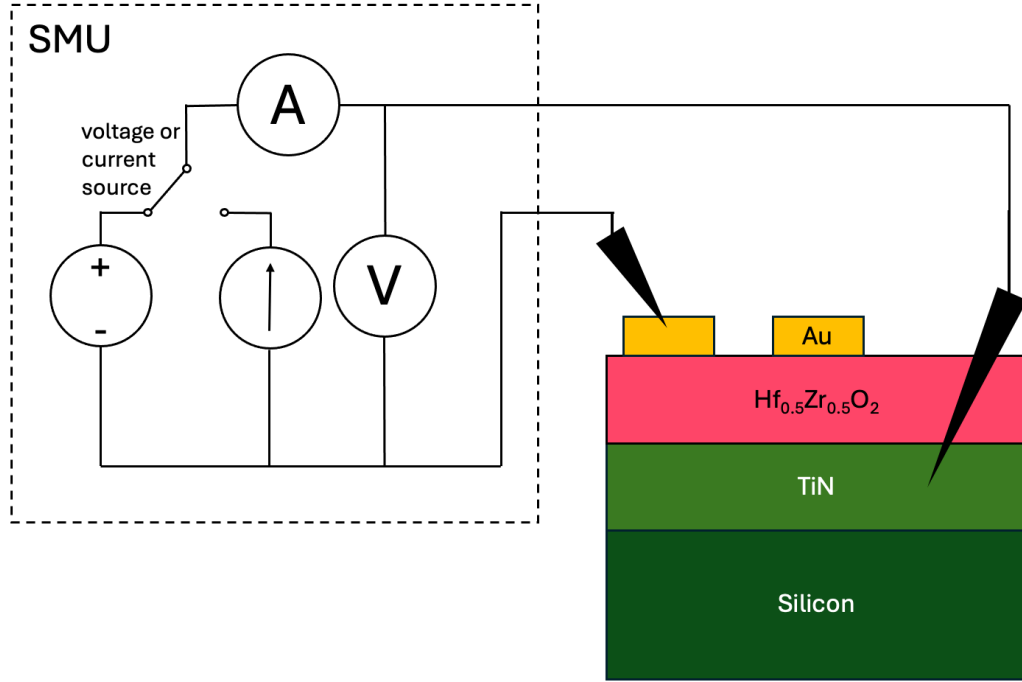


Figure 3.6. Schematic of setup for electrical characterization.

3.3.4.1. Quasi-Static Switching

In resistive switches, quasi-static switching refers to the gradual and reversible transition between high-resistance and low-resistance states (HRS and LRS, respectively) by applying a relatively slow, triangular voltage sweep across the memory cell. This measurement allows the observation of both the SET and RESET processes under near-static conditions.

Figure 3.7a shows the triangular voltage waveform applied to the ReRAM device during quasi-static switching. The voltage is swept, starting from 0 V a positive value (+V), then to a negative value (-V) and then back to 0 V, allowing the system to cycle through different resistance states. It should be stated that for measurements, conducted in this work, the negative voltage was swept to first, meaning that the sign of the waveform, shown in figure 3.7a was reversed. The dashed, red lines represent the portions of the voltage sweep where the cell is in HRS while the device is in LRS during the application of voltages depicted with the solid, green lines.

Figure 3.7b shows a typical corresponding current-voltage (I-V) characteristic of the ReRAM cell during the voltage sweep. The system starts in the HRS, and as the voltage is increased, the cell undergoes a transition at V_{SET} , where the resistance switches to the LRS. This manifests itself with a sudden increase of the current. The LRS is maintained until the voltage is swept in the negative direction, and the cell resets to the HRS when V_{RESET} is reached.

Quasi-static measurements are useful for characterizing the switching properties of ReRAM devices as insights into the gradual evolution of the conductive filaments that form or rupture

(in the oxygen-vacancy switch), or the growth of ferroelectric domains (in the ferroelectric tunnel junction (FTJ)) are provided. Thus, parameters such as V_{SET} , V_{RESET} , and the current levels associated with the LRS and HRS states can be approximated.

Figures removed due to copyrights issues

(a) Shape of voltage employed in quasi-static ReRAM measurements. (b) Typical I-V curve for ReRAM devices investigated in this thesis under quasi-static measurement.

Figure 3.7. Schematics for quasi-static measurements. Adapted from [66].

3.3.4.2. Endurance Measurement

When the ReRAM cell is used as memory device, quasi-static voltage sweeps cannot be used to switch their resistive states. They are too slow and impose an unnecessary electrical strain on the device which accelerates aging. Here, voltage pulses will rather be used. The cells' resilience when continuously subjected to voltage pulses are evaluated with the so-called endurance measurements.

Endurance measurements for ReRAM cells are used to assess the device's ability to sustain repeated switching between the high resistive state (HRS) and the low resistive state (LRS) over time. These measurements involve applying successive voltage pulses to the cell, alternating between positive and negative sign of the pulse, to perform the SET and RESET operations respectively. As illustrated in Figure 4.7, alternating voltage pulses are applied in endurance measurements. Positive pulses are applied for the SET operation (switching from HRS to LRS), and negative pulses for the RESET operation (switching from LRS to HRS). Between each switching cycle, a READ pulse is applied to assess the resistance state of the cell. The height of the READ pulse must be low enough to omit any significant changes in the cell's resistive state. The current is measured during each READ operation, but also at the end of the SET and RESET pulses respectively. To maintain a consistent distinction between LRS and HRS across multiple switching cycles is crucial, as any degradation in switching behavior would lead to a reduced reliability of the memory device.

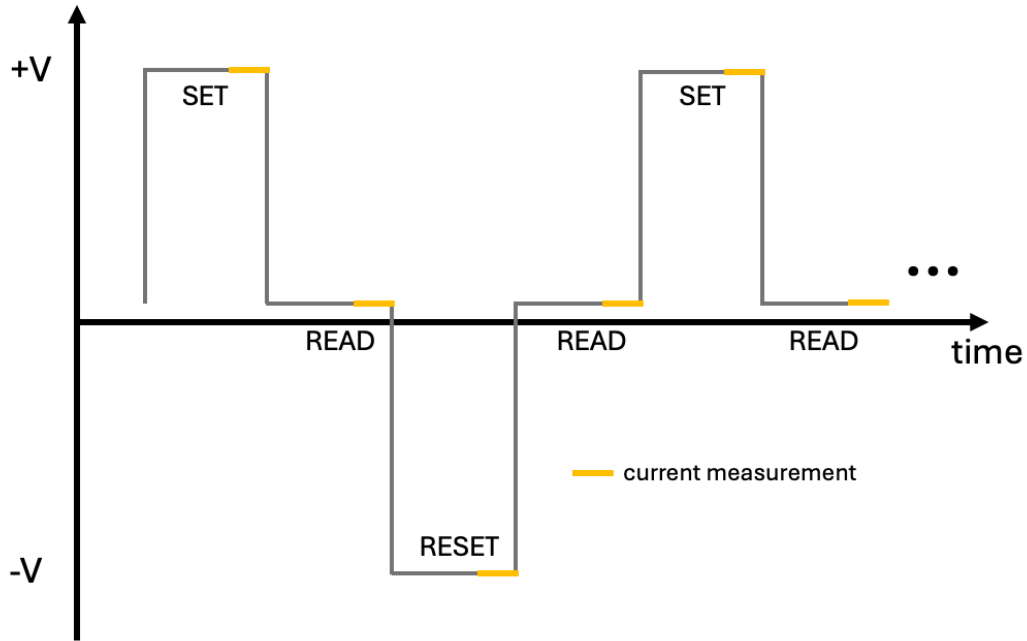


Figure 3.8. Voltage pulse-train used for endurance measurements.

3.3.4.3. Spike-Timing-Dependent Plasticity Measurement

Resistive random-access memory (ReRAM) cells are known for their ability to exhibit neuromorphic properties, mimicking the behavior of biological synapses. These cells respond to external stimuli, such as voltage pulses, in a way that depends on the energy delivered through the stimulus. In the case of a voltage pulse, the total energy is determined by the height (amplitude) and the width (duration) of the pulse. This dynamic response is similar to that of biological systems, where synaptic plasticity, such as spike-timing-dependent plasticity (STDP), relies on the timing of action potentials sent to synapses by two neighboring neurons.

In biological synapses, the superposition of pre- and post-synaptic spikes results in a complicated waveform, with the timing between them determining how the synapse strengthens or weakens. The timing of these spikes, referred to as "spike-timing", determines the evolution of the network and results in long-term potentiation or depression (learning and forgetting). In neuromorphic computing systems, ReRAM cells could replicate this characteristic by responding to supplied voltage pulses.

However, reproducing the complex spike-timing behavior of biological synapses with precise waveforms can be challenging in hardware implementations. Thus, rectangular pulses can be applied as a feasible simplification. These nominally rectangular pulses are easier to generate and control in an experimental setup and are effective in replicating the complex voltage forms in biological systems, as discussed in subsection 2.1.3.

To study how the resistive state of the ReRAM cell evolves with varying external stimuli, a pulse train consisting of rectangular voltage pulses is employed. In this case, the SET pulse

height is gradually increased in a linear fashion while the width of the pulses remains constant. The RESET pulse remains at a constant height. This approach isolates the effect of pulse amplitude on the resistive switching process. The ReRAM cell can be programmed into a low-resistive state (LRS) or a high-resistive state (HRS), depending on the characteristics of the applied voltage. After each pulse, the resistive state is measured to track how the cell's internal resistance changes as a function of the applied stimulus. The pulse train consists of a series of positive voltage pulses with incrementally increasing in amplitude. Following the application of these pulses, the device is RESET using a consistent negative voltage pulse to return the cell to a well-defined HRS state. In between the positive pulse and the RESET pulse, a low-amplitude READ voltage is applied to measure the cell's resistance without altering its state.

The response of the ReRAM cell to these voltage pulses is directly linked to its synaptic-like behavior. By applying voltage pulses of increasing amplitude and reading the resistive state after each pulse, it is possible to assess the cell's spike-timing-dependent plasticity (STDP). This measurement technique has been termed the "STDP measurement" as it enables direct observation of the memory cell's adaptive behavior, similar to synaptic plasticity in biological systems. This technique measures the difference in resistance between the HRS and LRS, expressed as the relative change in resistance $\frac{R_{HRS} - R_{LRS}}{R_{LRS}} = \frac{\Delta R}{R_0}$. As these resistances are obtained after each pulse, the applied voltage and the resulting change in resistive state can be correlated.

An example of the voltage waveform used for this STDP measurement is depicted in Figure 3.9. As shown, the waveform consists of a series of positive voltage pulses followed by RESET pulses, with intermittent READ operations to monitor the resistive state of the cell. The gradual increase in the height of the positive pulses, coupled with the consistent RESET operation, allows for an assessment of the cell's response on gradually increasing stimuli which serves as a representation of their STDP behavior.

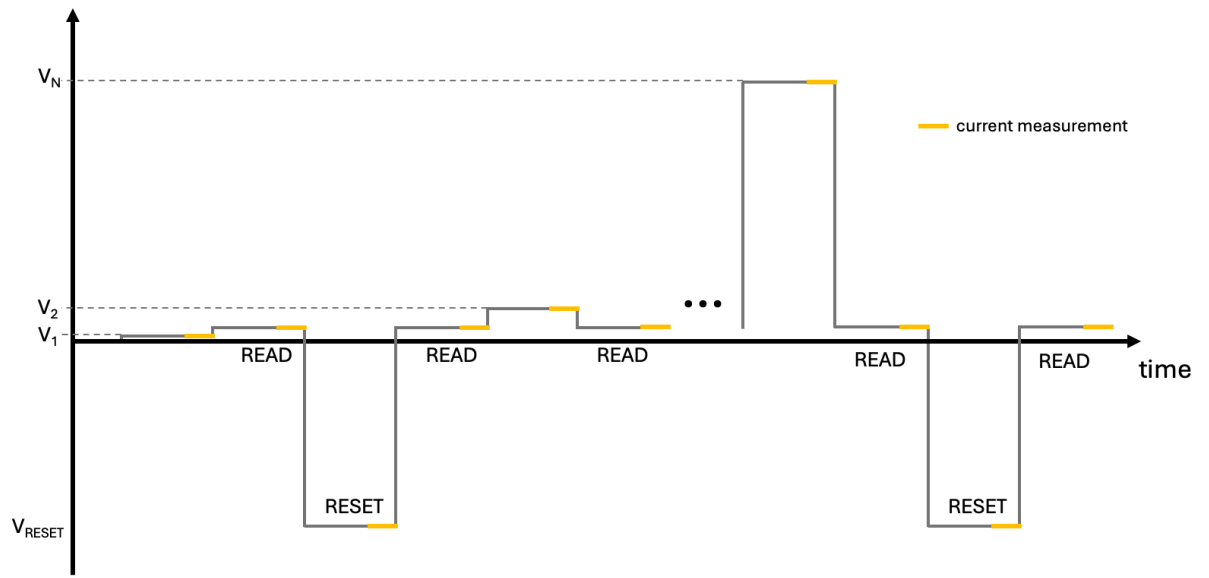


Figure 3.9. Voltage pulse-train used for STDP measurements.

4. Results & Discussion

The obtained results are presented, followed by a concluding discussion in the upcoming chapter. First, the fabrication and characterization of both the individual layers and the full TiN/Hf_{0.5}Zr_{0.5}O₂/Au metal-insulator-metal (MIM) structure will be detailed. All films have been deposited using RF-Magnetron sputtering, and their properties have been examined using atomic force microscopy (AFM), X-ray reflectivity (XRR), and grazing incidence X-ray diffraction (GIXRD), where applicable. Additionally, the electrical properties of the full stacks, including quasi-static behavior, endurance, and STDP measurements, are discussed. The latter, in particular, shows a negative feedback mechanism in the cell's switching behavior, where an increasing amount of energy – exceeding a threshold – which is supplied to the device does actually lead to a reduced response of the cell. The second half of this chapter will treat microscopic factors influencing the emergence of this feedback mechanism. Finally, these results are employed to mathematically investigate the potential onset of chaotic switching in ReRAM cells. Here, conditions which enable the transitions to chaotic behavior in resistive switches are analyzed.

4.1. TiN/Hf_{0.5}Zr_{0.5}O₂/Au Structure

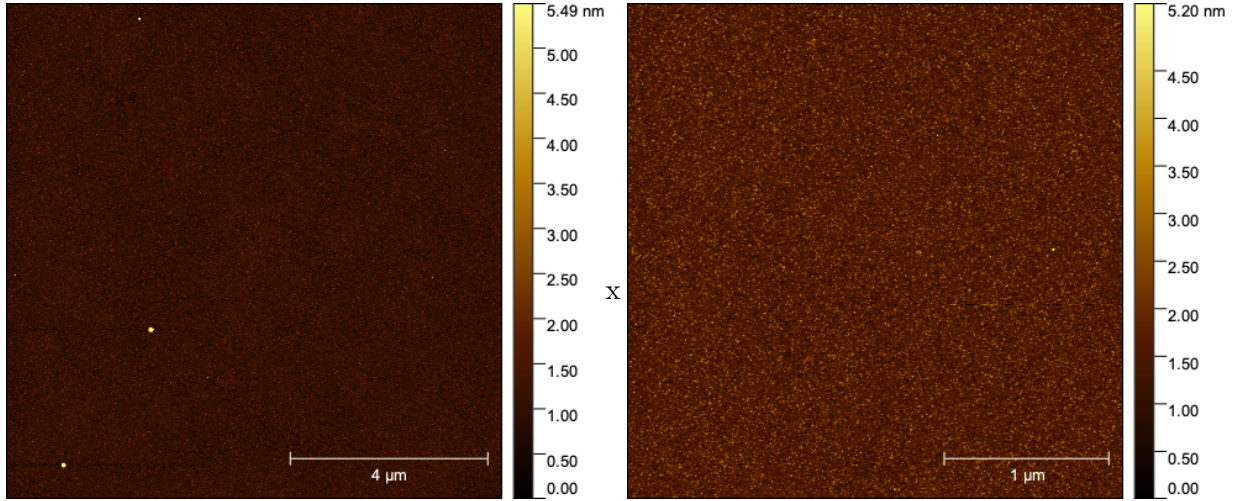
This section details the fabrication of the TiN/Hf_{0.5}Zr_{0.5}O₂/Au metal-insulator-metal (MIM) structure as well as their structural characterization. Here, one subsection is devoted to each individual layer of the stack. The aforementioned SPT310-TT RF-Magnetron sputtering tool from Plasmionique Inc. has been used to deposit each layer. Pieces of a silicon wafer (1 mm x 1 mm) with a native oxide layer have been used as substrates. Prior to deposition, the substrates have undergone a chemical cleaning process. They have been placed in a beaker and sequentially submerged in a series of polar and non-polar solvents, followed by sonication for five minutes in each solvent. The cleaning steps involved acetone, isopropanol, ethanol, and deionized water, in that order. Afterwards, the substrate has been dried under pressurized high-purity nitrogen flow.

The Hf_{0.5}Zr_{0.5}O₂ has been deposited directly onto the TiN without breaking vacuum to minimize external pollution. The deposition chamber has been vented afterwards to place shadow-masks onto the dielectric to fabricate multiple devices on one chip. The chamber has been evacuated to a base pressure of 10⁻⁵ Torr between each deposition.

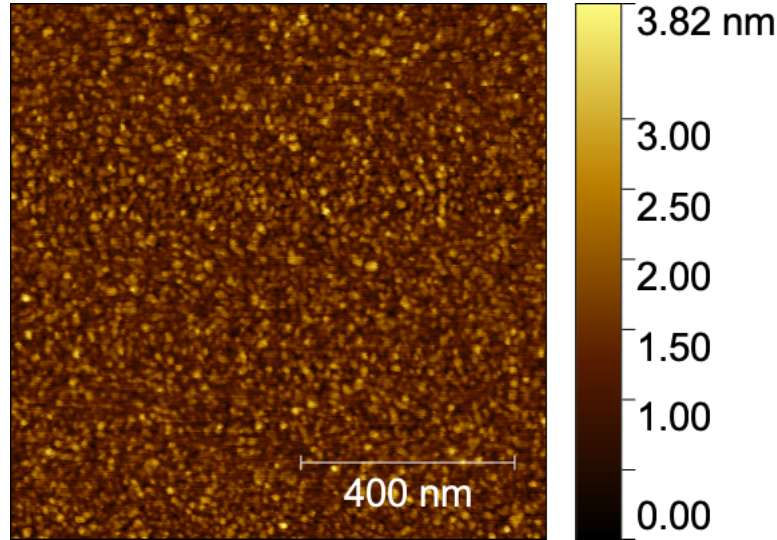
4.1.1. TiN Bottom Electrode

Titanium nitride has been reactively sputtered using a nitrogen plasma and a titanium target. The deposition pressure has been maintained at 6 mTorr by setting the N₂ gas flow to 7 sccm, with a power of 40 W on a 1" target. Prior to deposition, a 5 min pre-sputtering process has been performed by igniting the plasma with a shutter placed between the target and substrate to remove surface contaminants from the target. After this, the shutter has been opened, and the deposition process has begun for a duration of 1 h. During the deposition, the substrate has been heated to $\sim 270^\circ\text{C}$.

To evaluate the surface morphology – especially the surface roughness – tapping mode AFM has been used. Figure 4.1 shows the images with a scan range of $10\mu\text{m} \times 10\mu\text{m}$ (4.1a), $3\mu\text{m} \times 3\mu\text{m}$ (4.1b) and $1\mu\text{m} \times 1\mu\text{m}$ (4.1a) respectively. The RMS roughnesses are given in the captions of the figures and are consistently very low. Figure 4.1c has been used to measure the average grain size, which has been determined to be $\sim 10\text{ nm}$.



(a) 10 μm x 10 μm AFM scan of TiN; RMS roughness = 0.3 nm. (b) 3 μm x 3 μm AFM scan of TiN; RMS roughness = 0.4 nm.



(c) 1 μm x 1 μm AFM scan of TiN; RMS roughness = 0.4 nm.

Figure 4.1. Surface morphology for reactively sputtered TiN.

A low surface roughness of the bottom electrode is desirable in the application for both oxygen-vacancy based switches and FTJs. A high surface roughness was associated with a frequent non-reversible electrical breakdown in hafnia based MIM-stacks [67], which affects their use as both oxygen vacancy based, filamentary switches but also in FTJs. The current density depends strongly on the barrier thickness in tunnel junctions. When another film is deposited on a rough surface then significant divergence of the local thickness of said layer can occur. A low surface roughness is thus critical to manage intra-device variability [68]. A low grain size is desired, as grain boundaries function as nucleation sites for both conductive filaments but also for the polarization reversal in ferroelectric domains.

An X-ray reflectivity (XRR) measurement has furthermore been conducted to evaluate the film thickness. Figure 4.2 shows the diffractogram. The red vertical lines indicate the fringes used for the fit, which has yielded a film thickness of ~ 20 nm.

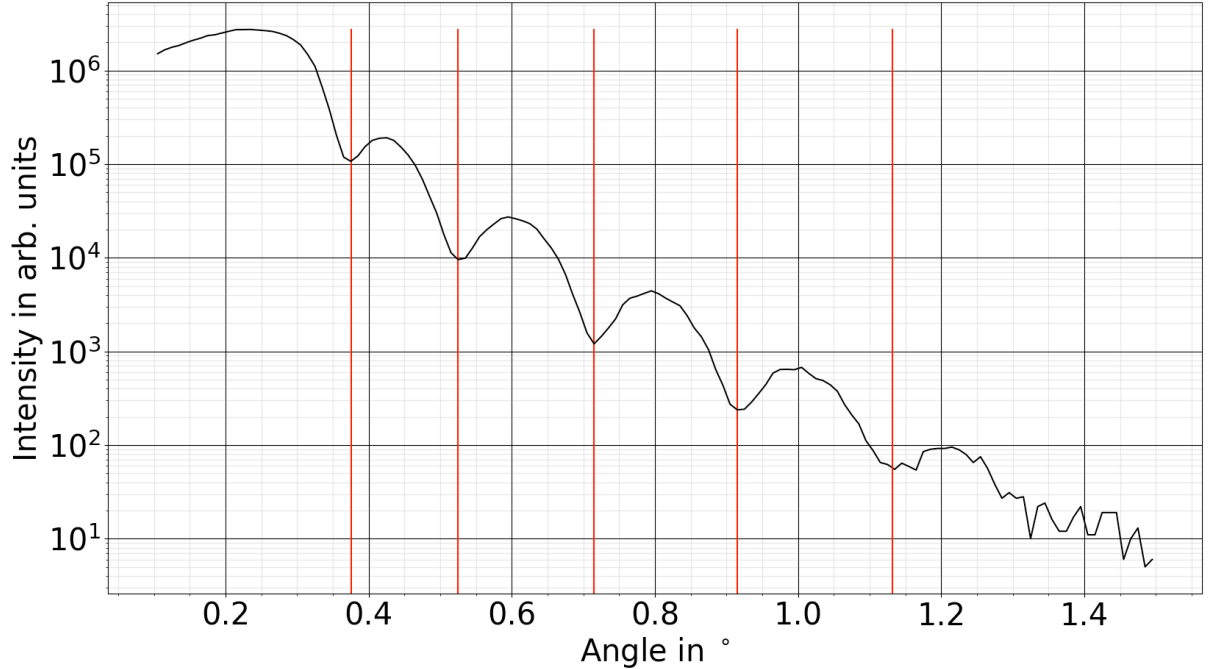


Figure 4.2. X-ray reflectivity (XRR) diffractogram used to measure the TiN film thickness. The fringes used for fitting are indicated by the red, vertical lines.

4.1.2. Hf_{0.5}Zr_{0.5}O₂ Dielectric

The hafnium zirconium oxide dielectric has been deposited from a ceramic Hf_{0.5}Zr_{0.5}O₂ target. The film has been grown directly onto the previously deposited TiN film without breaking vacuum. To control the initial oxygen vacancy concentration, a mixture of argon and oxygen gases has been used as the sputtering atmosphere. Argon was introduced at a flow rate of 1 sccm, and oxygen at 2 sccm, maintaining a chamber pressure of 5 mTorr. The sputtering power has been set to 20 W, and the substrate has been heated to approximately 270 °C. These parameters enable a low deposition rate, promoting the formation of polycrystalline films with large grain sizes and columnar growth that exhibit strong preferential directions in the film's lattice orientation. Before the 1.5 h deposition time started, the target has been pre-sputtered for 10 min.

X-ray reflectivity (XRR) has been used to determine the film's thickness and grazing incidence X-ray diffraction (GIXRD) has been used to investigate the present phase composition. The film used for these measurements was prepared by deposition of Hf_{0.5}Zr_{0.5}O₂ directly onto a cleaned silicon substrate with the aforementioned parameters.

The result of the XRR measurement is presented in Figure 4.3. The fit with the two fringes

which are indicated by the red, vertical lines yields a film thickness of approximately 4 nm.

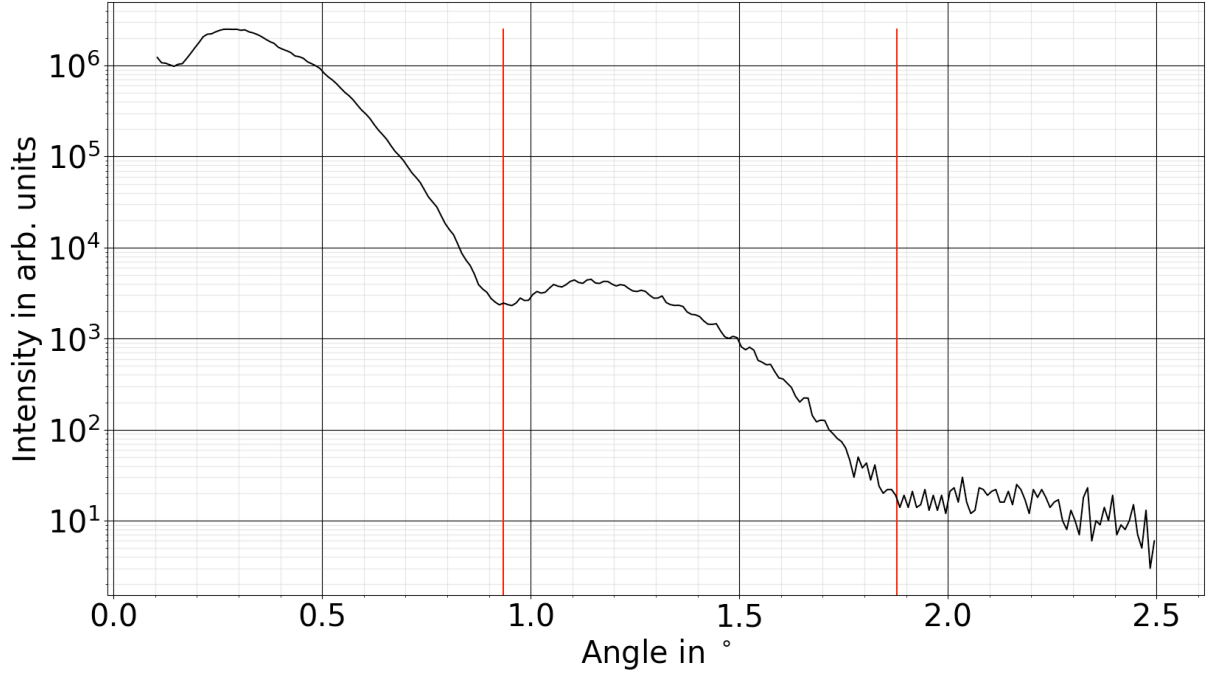


Figure 4.3. X-ray reflectivity (XRR)-diffractogram used to measure the HZO film thickness. The fringes used for fitting are indicated by the red, vertical lines.

Figure 4.4 highlights the range containing the most prominent XRD peaks of Hf_{0.5}Zr_{0.5}O₂ phases: the monoclinic (-111) at 28.2° and (111) at 31.7°, the tetragonal (101) at 30.3°, and the orthorhombic (111) at 30.4°. Black vertical lines indicate the monoclinic peak positions, while red and green lines mark the expected positions for the tetragonal and orthorhombic phases, respectively. Distinguishing between the orthorhombic and tetragonal phases is challenging due to significant peak overlap. However, no peaks associated with these phases are observed in the displayed diffractogram. The strong (-111) peak corresponding to the monoclinic phase suggests that the film exhibits a predominantly monoclinic structure, with minimal presence of other phases. The notable difference in intensity between the (-111) and (111) peaks results from the aforementioned strong preferential orientation within the early columnar growth. However, the prominent peak could also be associated with the (111) peak of the silicon substrate at 28.42°. In that case, no significant crystallinity of the deposited Hf_{0.5}Zr_{0.5}O₂ thin-film could be assumed. Since the ReRAM cells under investigation are based on oxygen-vacancy filaments, whereas the crystallinity plays a subordinate role, further investigation into the film's crystal structure are out of scope of this thesis.

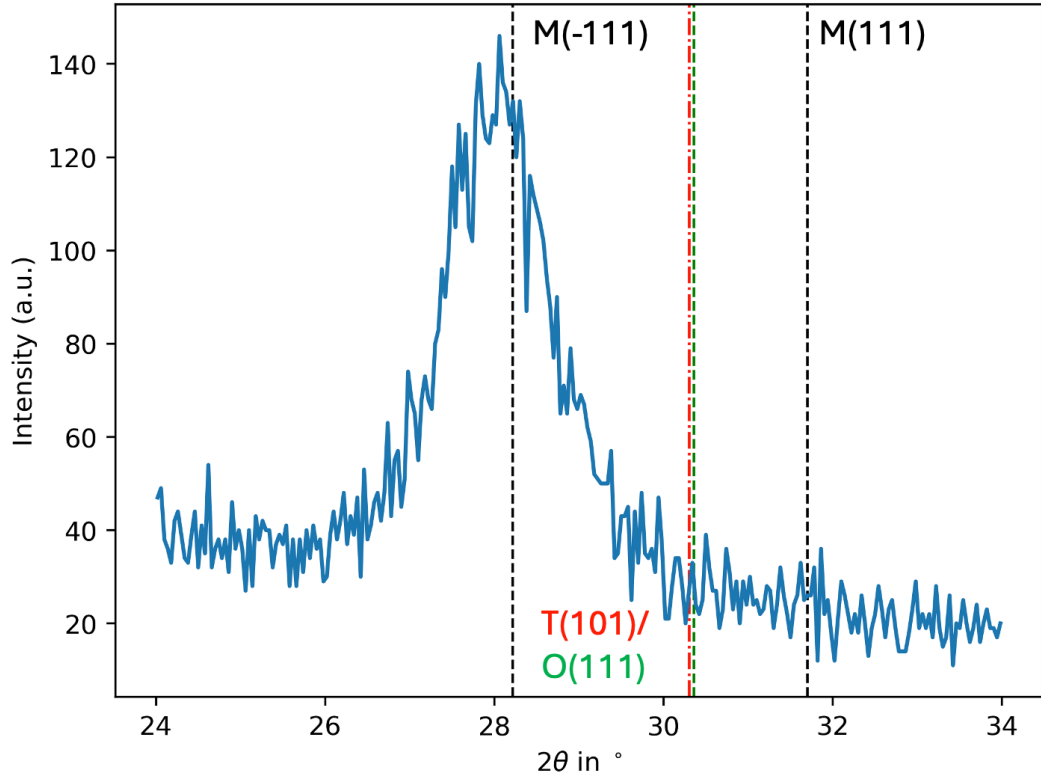


Figure 4.4. GIXRD-diffractogram of the deposited Hf_{0.5}Zr_{0.5}O₂ thin film. Only peaks, representing the monoclinic phase are observed.

As a deposition of significant fractions of the ferroelectric orthorhombic phase could not be achieved, the fabricated device, as deposited, are not suitable for the operation as FTJs. However, as their use as oxygen vacancy based filamentary switches is not bound to phase composition but solely to the oxygen vacancy structure, the MIM-stacks can still be used as such and negative feedback in their switching behavior will be investigated in this thesis.

4.1.3. Au Top Electrode

To grow the top electrode on the dielectric, the shadow mask technique has been employed. The substrates with previously deposited layers were allowed to cool to room temperature before venting the chamber. A stainless steel shadow mask with a thickness of 0.1 mm, showing square patterned circular openings of 300 μm in diameter and spaced 600 μm apart from center to center of each opening, has then been placed on the samples. The samples were returned to the deposition chamber and a new vacuum has been established. This setup allowed for the fabrication of 256 devices on a 1 cm x 1 cm silicon chip.

The top electrode has been deposited from a gold target using an argon plasma. Argon gas has been introduced at a flow rate of 5 sccm, maintaining a chamber pressure of 5 mTorr. A one-minute pre-sputtering step has been performed before the 10-minute deposition process began. A power of 20 W has been employed in both cases. The resulting circular top electrodes

are shown in the microscope image in Figure 4.5.

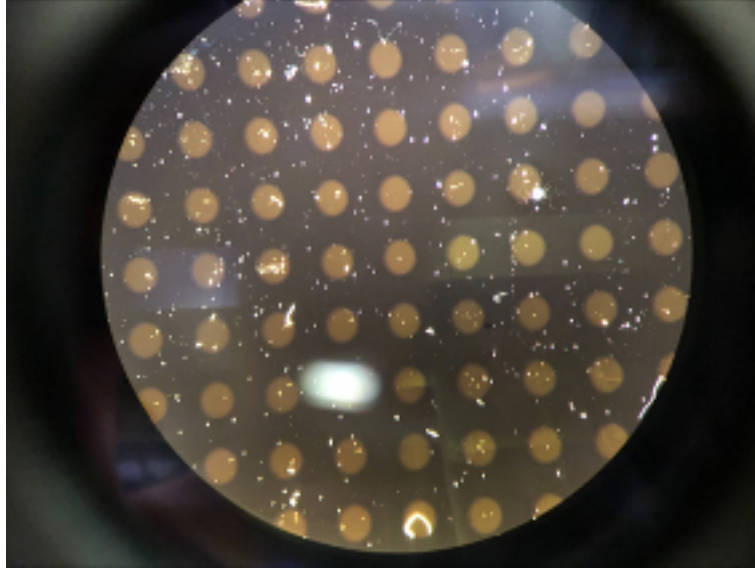


Figure 4.5. Top-view microscope image of the entire MIM-stack. The circular Au top electrodes can be seen.

The deposition of the top electrode marks the final step of the fabrication of the ReRAM devices.

4.2. TiN/Hf_{0.5}Zr_{0.5}O₂/Au Switching Behavior

This section presents the results of the electrical characterization of the fabricated TiN/Hf_{0.5}Zr_{0.5}O₂/Au MIM-stacks. subsection 3.3.4 details the setups for endurance, quasi-static and STDP measurements. Two tungsten needles – connected to a source/measurement unit (SMU) – have been brought into contact with the top and bottom electrode respectively. The SMU has controlled voltage sweeps and pulses, applied to the devices, while the resulting currents have been measured. From these results, conclusions about the devices switching behavior as well as emerging negative feedback mechanism are drawn.

4.2.1. General Electrical Characterization

Quasi-static measurements have been performed by applying triangular voltage sweeps to the memory cells and recording the resulting current. The sweep rate has been set to 1.75 V s⁻¹. Beginning from 0 V, the voltage has first been decreased to -1.5 V, then increased to 1.5 V, and finally returned to 0 V, completing the loop. The measurement has been conducted for a total of 100 periods.

Starting with a memory cell in its pristine state, a conductive filament must first form during an electroforming step. This process occurs during the initial voltage sweep from 0 V to -1.5 V and causes a deviation in this part of the hysteresis curve compared to later cycles. In the

fabricated cells, the electroforming completes quickly due to the thin Hf_{0.5}Zr_{0.5}O₂ film and no explicit electroforming step is required. Thus, no current-compliance has been employed here. In later switching events, only a small portion of the filament is dissolved and reformed.

Figure 4.6 shows the I(V) curve of one complete hysteresis loop for the pristine state cell (green), the second iteration (navy) and the 100th loop (orange). The loop starts at 0 V from where the voltage is gradually decreased. At ~ -0.67 V the resistance decreases in a SET operation and the trajectory of the I(V) characteristic follows this new path. Once -1.5 V has been reached the voltage is increased again, while the cell's current response is now dictated by its LRS state. RESET takes place at ~ 1.3 V where the cell jumps back into HRS. The voltage sweep reaching 0 V again marks the end of the hysteresis loop. The cell shows reliable switching behavior over the 100 cycles that were measured as no significant change in neither V_{SET} and V_{RESET} , nor the resistances for HRS and LRS respectively could be observed.

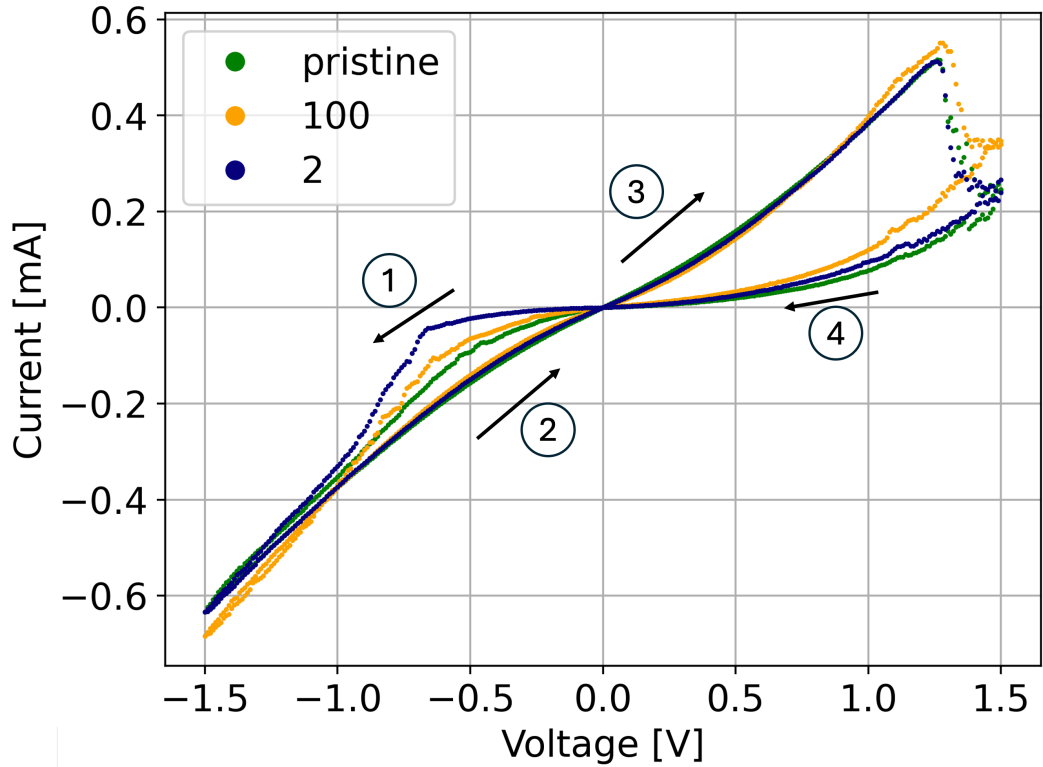


Figure 4.6. I(V) characteristic for quasi-static voltage sweep measurement. The curves for the first, second and 100th iteration are displayed.

Estimates for appropriate switching and read-out voltages for pulsed operation can be derived from quasi-static measurements. Given that pulse durations are significantly shorter than a sweep cycle, the required voltages must be set higher as vacancy migration already occurs at lower voltages during the sweep, leading to an earlier SET. For the following endurance measurements, the pulse height has therefore been set to 2 V. Similarly, a read-out voltage of 0.5 V has been deemed appropriate, as no significant alteration of the cell is expected at this

voltage.

After the quasi-static measurement, a train of voltage pulses, as shown in Figure 4.7, has been applied to the memory cell. V_{SET} and V_{RESET} have been set to 2 V and -2 V respectively, while the cell's resistance has been measured by a 0.5 V read-pulse following each switching event. The duration for each pulse has been set to 10 ms. Figure 4.7 displays the result of an endurance measurement over a total of 5,000 switching cycles. The measured resistances, corresponding to the LRS and HRS, are shown in navy and cyan, respectively. The cell exhibits relatively stable switching behavior, with an average HRS resistance of approximately 13.8 k Ω and an average LRS resistance of about 4.2 k Ω . This yields a pronounced relative resistance difference of roughly 2.3.

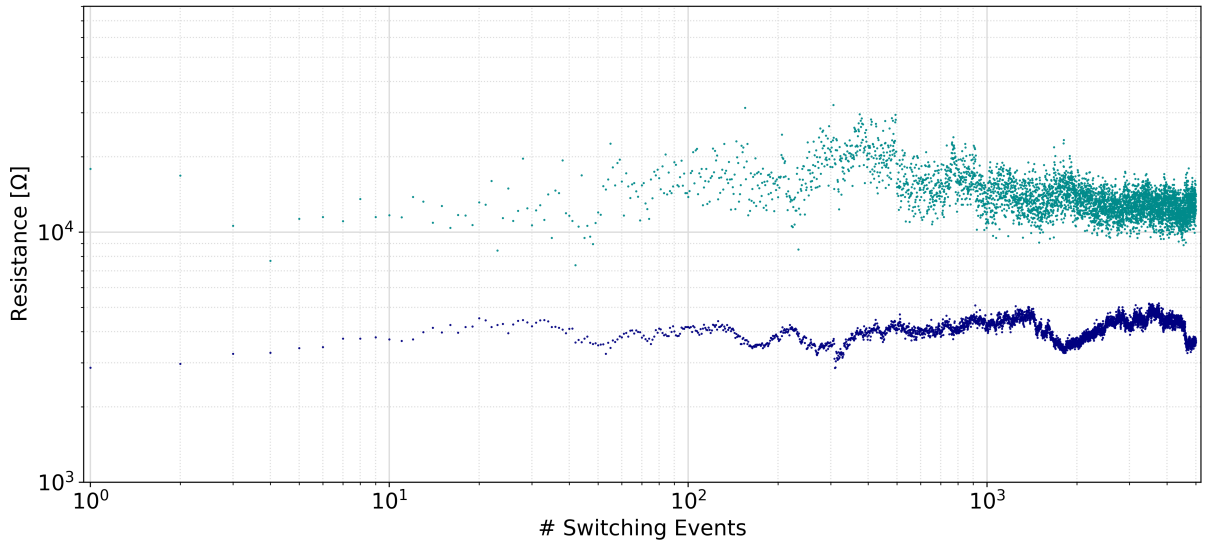


Figure 4.7. Endurance measurement for 5,000 switching cycles.

The presented measurements evaluate the suitability of the fabricated oxygen-vacancy based ReRAM devices in conventional memory fabrication. They show good stability for 100 cycles of swept switching as well as for over 5,000 periods of pulsed switching. However, this does not quite prove their viability for universal memory, as many million write cycles would be desirable here. Furthermore, only relatively low switching speeds have been investigated due to limitations of the used instruments and measurements concerning data retention were left out completely, as further investigation into the application of the fabricated devices for conventional memory are outside of the scope of this thesis.

4.2.2. Spike-Timing-Dependent Plasticity in ReRAM Cells

To analyze the spike-timing-dependent plasticity (STDP) of the fabricated memory devices, their response to different stimuli needs to be investigated, thus linking their behavior to synapses in biological neural networks. While the time delay with which the pre- and post-synaptic spike reach the synapse determine the response of the synapse (see subsection 2.1.3) voltages can be applied to the terminals of the ReRAM device freely. Thus, one terminal is grounded while a voltage pulse is applied to the other. As described in subsubsection 3.3.4.3, a train of voltage pulses with increasing height has been applied to the cell, while RESET was performed with a constant, negative voltage pulse with a height of -2 V . The resistance has been measured after both the SET and RESET operation with a 0.5 V pulse. The height of the applied positive SET pulses has been increased linearly from 1.5 V to 4 V in 1,000 steps with an increment of 2.5 mV , while the duration of each pulse – for both switching and measuring – has been set to 5 ms .

Figure 4.8 shows the result of the STDP measurement. The ordinate shows the relative difference between the HRS and LRS resistances while the abscissa displays the height of the applied voltage pulse with which the respective $\frac{\Delta R}{R_0}$ ratio was acquired. Up until approximately 2.2 V the expected characteristic from a memory cell showing STDP can be observed. When the height of the stimulus (the voltage pulse) increases, then the response and thus the difference between the measured resistances increases as well. However, for the fabricated memory cells, the response decreases for voltages higher than $\sim 2.2\text{ V}$ until no more response can be observed at around 3 V . This behavior indicates that a negative feedback mechanism must be at play as well, which counteracts the formation of a conductive filament until the cell does not react to the stimulus any more. This negative feedback in this highly non-linear system is a requirement for the emergence of deterministic chaos as seen in section 2.3.

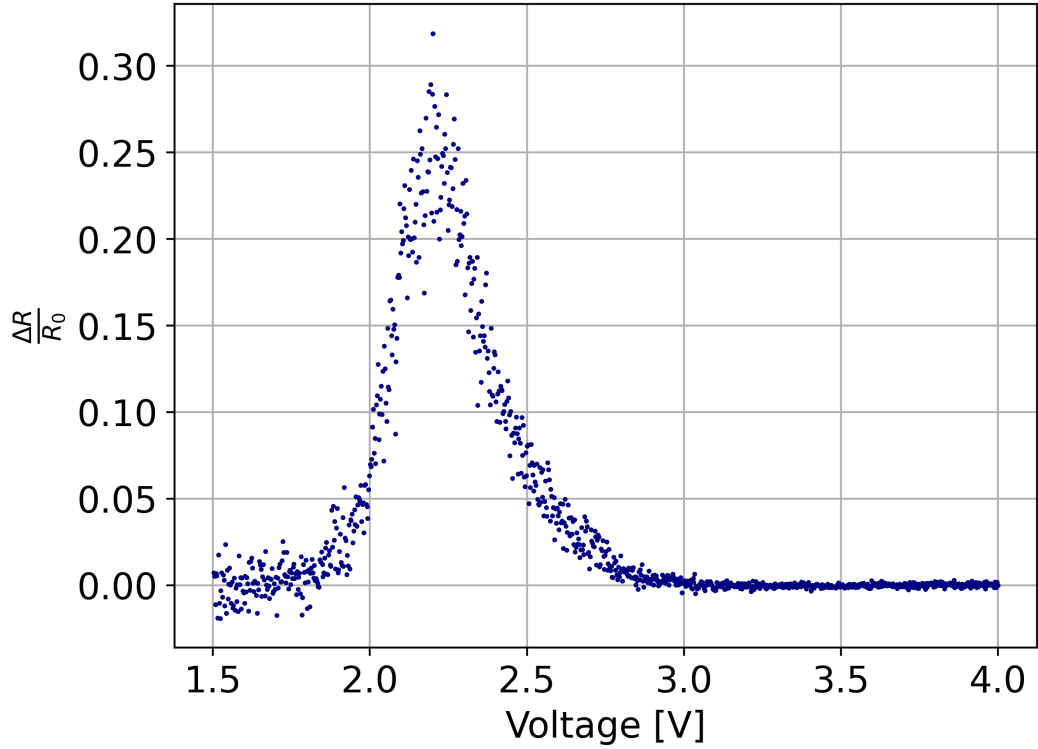


Figure 4.8. Spike-timing-dependent plasticity (STDP) measurement for our ReRAM cells. A negative feedback mechanism leads to the reduction of the cell's response for voltage pulses higher than ~ 2.2 V. This negative feedback constitutes a requirement for deterministic chaos in the cell's switching behavior.

The goal of section 4.3 is to deliver approaches to explain the cause of this negative feedback on a micro- and nanometer scale. Section 4.4 will deliver a mathematical investigation of prerequisites for chaotic behavior that show negative feedback as presented in Figure 4.8.

4.3. Microscopic Analysis of Negative Feedback Mechanisms

With the existence of a negative feedback mechanism established, this chapter aims to provide models for energy-dissipative effects, causing negative feedback at micro- and nanometer scales. Subsection 4.3.1 is dedicated to the influence of Joule heating on the dissolution of conductive filaments in oxygen-vacancy-based switches, a phenomenon that is often attributed to the RESET operation in unipolar ReRAM.

Subsequently, subsection 4.3.2 presents a potential feedback mechanism in FTJs, where the creation and recombination of oxygen vacancies are causing restrictions in the movements of domain walls. In this context, a higher density of oxygen vacancies increases ferroelectric domain-wall pinning, reducing polarization reversal during switching. This pinning effect reduces the fraction of the volume subject to switching and thus the cell's response to external

stimuli.

4.3.1. Influence of Joule Heating for Oxygen Vacancy Filamentary Switches

Joule heating, also known as Joule's first law, describes the phenomenon whereby current flowing through a resistance generates heat and serves as a mechanism to dissipate energy during ReRAM operation. The amount of dissipated power is given by:

$$P_{Joule} = I^2 \cdot R = \frac{V^2}{R} \quad (4.1)$$

where P is the power (dissipated energy per unit time) that is converted from electrical energy to thermal energy, I is the current flowing through the ReRAM element, V is the voltage drop over the memory cell and R is the cell's resistance.

The heat, generated by this conversion from electrical to thermal energy, increases the mobility for ion migration. The change in temperature due to the dissipated power P is given by:

$$\Delta T = \frac{I^2 R t}{mc} = \frac{V^2 t}{Rmc} \quad (4.2)$$

Here m denotes the mass that is subject to heating and c is the specific heat capacity of this mass. The power P is dissipated during the time t . This equation serves to illustrate the effect, but represents a considerable simplification, as the thermal conductivity is neglected.

This heating effect increases the mobility of oxygen ions, which migrate back towards the filament, resulting in partial recombination with oxygen vacancies. This recombination process causes a localized increase in resistance, thereby limiting further current flow and Joule heating. The result is a self-regulating feedback loop, where increased filament conductivity leads to enhanced recombination, which in turn reduces the conductivity.

The migration of oxygen ions follows a drift-diffusion model, incorporating both electric field-driven and thermally activated movement. The flux $\vec{J}_O$ of oxygen ions can be expressed as [69]:

$$\vec{J}_O = -D_O \cdot \left(\nabla C_O + \frac{C_O e \vec{E}}{kT} \right), \quad (4.3)$$

where $\vec{J}_O$ is the flux of oxygen ions, C_O is the concentration of oxygen ions, e is the elementary charge, k is the Boltzmann constant, and $\vec{E}$ is the externally applied electric field vector. The temperature dependence of the diffusivity D_O is described by an Arrhenius equation:

$$D_O = D_{O_0} \cdot \exp \left(-\frac{E_A}{kT} \right), \quad (4.4)$$

where D_{O_0} is the maximal diffusion coefficient (for $T \rightarrow \infty$) and E_A is the activation energy. An increase in temperature by ΔT (see Equation 4.2) enhances ion migration speed (Equation 4.3). With increased Joule heating, T rises, thus enhancing D_O and accelerating oxygen ion migra-

tion. This increased mobility increases the recombination rate with oxygen vacancies in the filament, which introduces a natural regulation of filament growth and conductivity [70]. An increasing voltage, applied to the terminals of the ReRAM device during SET operation does thus not necessarily lead to an increased response of the memory cell, as it increases the current through the conductive filament and thus the amount of dissipated energy. It therefore can lead to a partial dissolution of the filament during the SET operation. Effects, where rupture of the conductive filament is caused by Joule heating is discussed as the underlying mechanism for the RESET in unipolar resistive switches [71].

This negative feedback mechanism imposes a nonlinear influence on the filament's resistance. This feedback loop can be characterized by recursive modulation in the resistance of the conductive filament, which depends on vacancy concentration and can thus lead to the introductions of non-linearities and serve as a mechanism for the emergence of deterministic chaos in the cell's switching behavior as described in previous chapters of this thesis.

4.3.2. Influence of Domain Wall Pinning for FTJs

In the ferroelectric tunnel junction (FTJ), the generation and recombination of oxygen vacancies within each voltage cycle influence the switching behavior by interacting with the ferroelectric domain walls. The amplitude of the applied voltage pulse affects oxygen vacancy concentration as they are generated and removed due to high electric field strengths as in oxygen vacancy based filamentary switches.

Within the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ layer, oxygen vacancies influence the mobility of ferroelectric domain walls, thereby impacting the extent of polarization reversal under an electric field. During a positive voltage cycle, an increased field strength promotes oxygen vacancy generation as the displacement of oxygen atoms is accelerated, causing a temporary rise in vacancy concentration. These newly formed vacancies interact with the ferroelectric domain walls, pinning them and limiting their lateral movement. Consequently, the portion of the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ film that is subject to polarization reversal is reduced. This effect lowers the memory cell's overall response to the applied field and therefore constitutes a negative feedback mechanism.

In a subsequent cycle, when a negative voltage is applied, recombination of generated oxygen vacancies occurs and the vacancy density decreases again. This behavior causes the RESET in filament-based switches. This recombination reduces the pinning effect on domain walls, enhancing their mobility again and permitting a greater degree of polarization reversal across the $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ layer. As a result, the memory cell's responsiveness can be restored, making the effect reversible.

This reversibility in the generation and recombination of oxygen vacancies mirrors the behavior observed in oxygen-vacancy-based filamentary switches, where the formation and dissolution of a conductive path through the insulator create conductive and non-conductive states. However, while the gradual accumulation of oxygen vacancies in FTJs contributes to device fatigue and degradation over time [72], the vacancy generation and recombination discussed here occur

within each switching cycle. Although a long-term rise in vacancy density – ultimately leading to memory cell degradation – cannot be entirely ruled out, the focus here is on the immediate, reversible interactions between vacancies and domain walls in a single cycle.

By modulating vacancy concentration within the switching cycle, the applied voltage establishes an intrinsic feedback that reduces switching efficiency under high applied fields. Consequently, increasing the amplitude of the voltage pulse does not inherently lead to a proportional increase in the memory cell’s response. Instead, the generation of oxygen vacancies restrict the fraction of the film’s volume undergoing polarization reversal, leading to a decreased response.

Such a negative feedback mechanism is essential for period-doubling bifurcations, as observed by Gonzalez [5] (see Figure 2.7). These bifurcations represent a pathway to deterministic chaos, as previously discussed in subsection 2.3.2.

4.4. Chaotic Switching of ReRAM Cells

To further investigate the measured negative feedback, a mathematical expression for the curve presented in Figure 4.8 needs to be found. Thus, a fit with a modified log-normal distribution function was performed and is shown in Figure 4.9. The equation used for the fit is given by

$$f(x) = \frac{a}{(x - b)\sigma\sqrt{2\pi}} \cdot \exp\left(-\frac{(\log_{10}(x - b) - \mu)^2}{2\sigma^2}\right). \quad (4.5)$$

It should be stated that no physical relation can be drawn from this choice of equation and it was solely chosen due to the resemblance of this distribution and the measured dataset.

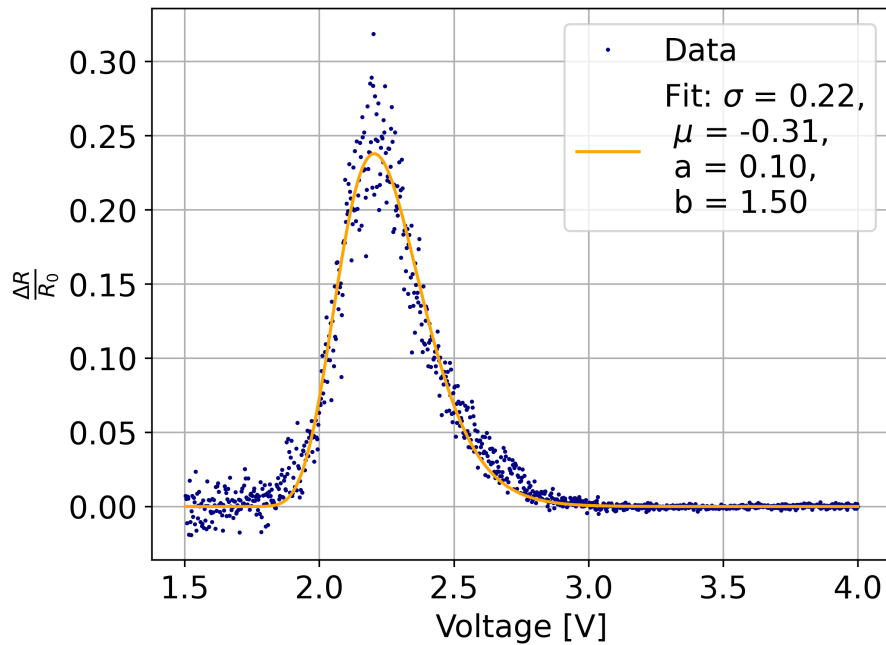


Figure 4.9. Fit of modified log-normal distribution function on acquired STDP measurement dataset.

With a mathematical expression now established that resembles the cell's STDP characteristic, a more rigorous mathematical investigation of the onset of chaos with the underlying feedback mechanism can be performed. To do so, a Feigenbaum diagram has been calculated by multiplying a variable growth factor r to the expression in Equation 4.5 with the parameters found with fit shown in Figure 4.9. The resulting diagram (shown in Figure 4.10) shows period-doubling bifurcations, consistent with the Feigenbaum route to deterministic chaos that has been shown earlier in this thesis with the logistic map. Since the period-doublings lead to possible populations in a very small range, a zoomed in version is shown in Figure 4.11 aswell. However, chaotic behavior in this system requires a multiplicative growth factor within a very narrow range, approximately 9.397 to 9.455. This small range, with a tolerance of just around 0.058, points out the precision necessary to achieve chaotic behavior. Additionally, the required growth rate is notably high, indicating that nearly an order of magnitude increase in the ON/OFF ratio would be necessary for this chaotic behavior to emerge.

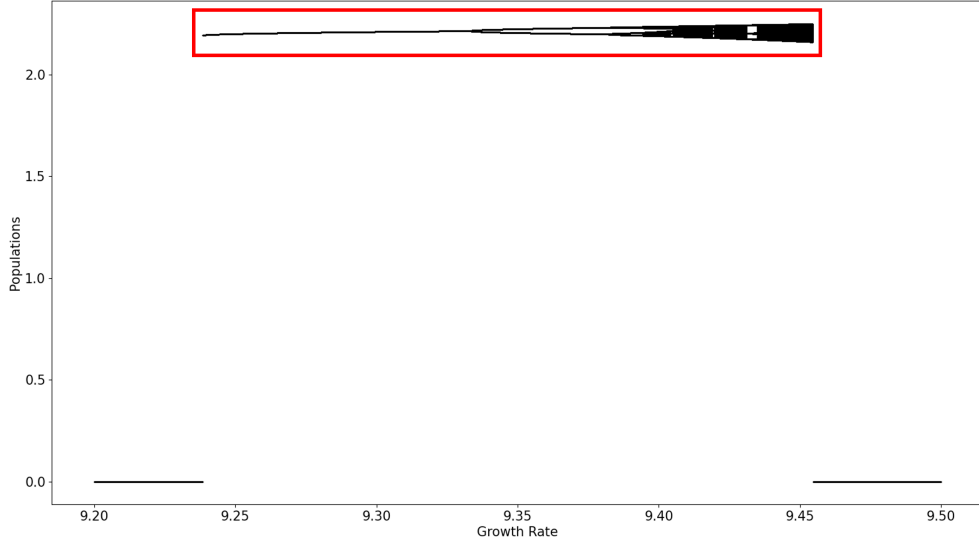


Figure 4.10. Feigenbaum diagram of the log-normal function found with the fit shown in Figure 4.9. The growth rate is multiplied to the function shown in Equation 4.5. The diagram is shown for growth factors between 9.2 and 9.5. A zoomed in version of the region, which is indicated by the red rectangle is presented in Figure 4.11.

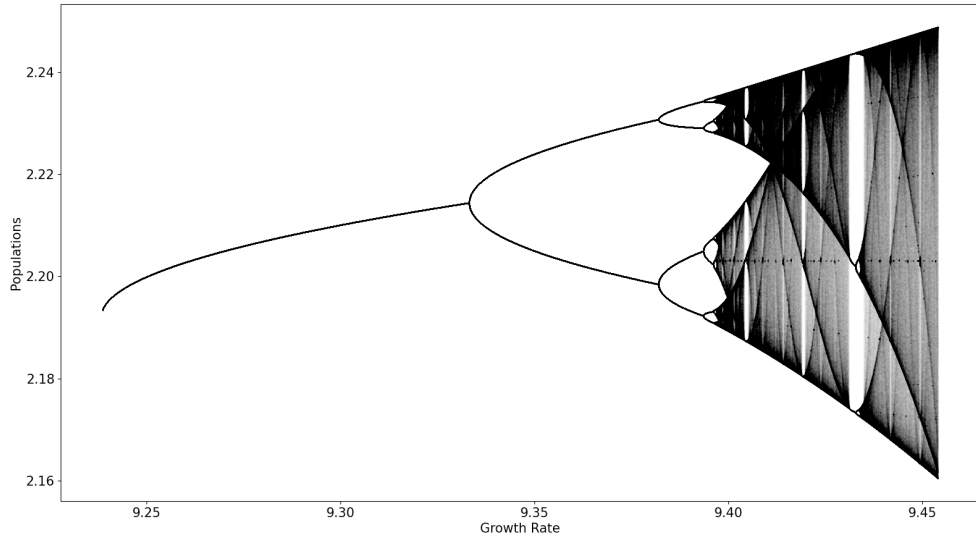


Figure 4.11. Feigenbaum diagram of the log-normal function found with the fit shown in Figure 4.9. The growth rate is multiplied to the function shown in Equation 4.5. The diagram is shown for a narrow range of growth factors to illustrate the period-doublings more clearly

The corresponding Lyapunov exponents, shown in Figure 4.12, were calculated as a function of the growth rate. The resulting graph reaffirms the previous observation. Chaotic behavior only emerges for a narrow range of specific values of r , while the map quickly converges to stable attractors for other values.

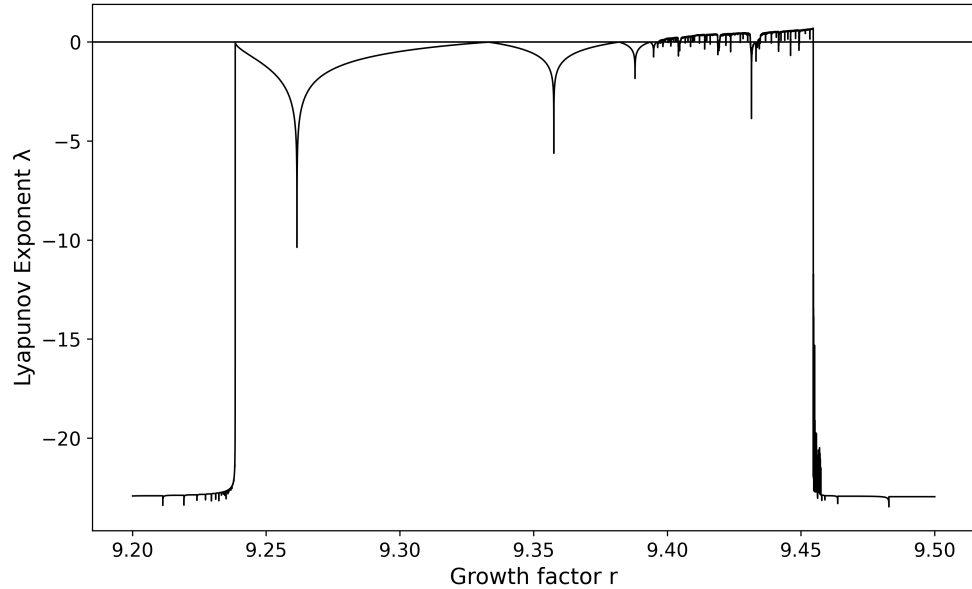


Figure 4.12. Lyapunov exponents corresponding to the Feigenbaum diagram depicted in Figure 4.11.

To harvest these effects for chaotic switching, devices need to be fabricated that utilize the found

results to operate in the chaotic regime. It remains to be discussed how the cells could be altered to exhibit this characteristic. The definition of the Lyapunov exponent (Equation 2.5) indicates that it is not the height of the considered map but rather its slope that determines the onset of chaos. Therefore, various approaches should be considered to increase both the ON/OFF ratio and the memory cell's sensitivity to external stimuli. This increased sensitivity could be driven by accumulation of oxygen vacancies near the region of the conductive filaments that are disrupted during the RESET operation, thus providing faster access to close the filament during a SET operation. This evolving vacancy distribution under operational conditions may ultimately drive the transition to chaotic behavior. Period-doubling bifurcations could thus only be triggered during device operation as observed in Figure 2.7.

5. Summary and Outlook

This chapter provides an overview of the findings of this thesis. The main investigation was concerned with negative feedback, emerging in the switching behavior of ReRAM cells. Here, both FTJs as well as oxygen vacancy based filamentary switches were considered. Furthermore, potential applications and directions for further research are outlined. Random number generation (RNG) and the modeling of neurodegenerative pathologies with the artificial neural network (ANN), showing chaotically changing nodes, are discussed.

5.1. Summary

This thesis has investigated the characteristics and dynamics of resistive switching in ReRAM cells, with a particular focus on the emergence of chaotic behavior through a negative feedback mechanism. This feedback mechanism was investigated using STDP measurements, where a modified log-normal distribution was used to fit the data. This distribution provides a purely empirical model for the cells' spike-timing-dependent plasticity (STDP) characteristics.

ReRAM cells, consisting of a $\text{TiN}/\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{Au}$ metal-insulator-metal (MIM) stacks were fabricated using radio frequency (RF)-magnetron sputtering. Since a desired substrate temperature during the deposition process could not be reached, no $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ thin films with a ferroelectric orthorhombic phase could be fabricated. Thus, only resistive switches based on oxygen vacancy filaments could be subjected to experiments, revealing their negative feedback behavior.

A Feigenbaum diagram was then calculated for the obtained model, showing period-doubling bifurcations typical of a route to deterministic chaos as in the logistic map. Furthermore, it was demonstrated that chaos in the fabricated ReRAM cells may only emerge within a narrow range of growth factors. The values for the growth factor that are necessary to induce chaos, indicate that almost an order of magnitude increase in the ON/OFF ratio would be needed for chaotic behavior to emerge. Furthermore, Lyapunov exponents were calculated, providing the specific values of the growth rate that lead to chaotic dynamics.

The analysis of chaotic behavior was extended to explore how oxygen vacancy distributions within the switching cycle may influence the behavior of the device, particularly during RESET and SET operations. This dynamic process, involving the accumulation and redistribution of vacancies, was proposed as a potential driver for the onset of chaos in ReRAM devices.

The findings suggest that improving the sensitivity of ReRAM cells to external stimuli – through factors such as oxygen vacancy distribution – could facilitate the transition to chaotic behavior, which could be harnessed for applications in random number generation and modeling of

pathologic neural networks.

5.2. Outlook

In this section, potential future routes for research and development based on the findings of this thesis are looked into. It examines how the observed chaotic switching behavior in resistive switching devices can be leveraged in practical applications, including random number generation (RNG) and the modeling of complex biological systems like neural networks that are subject to neurodegenerative pathologies.

5.2.1. Random Number Generation

The generation of random numbers is a foundation that many fields, including cryptography, simulations, statistical modeling, and secure communications, rely on. Traditionally, RNG methods are employed, using algorithms or physical processes that generate sequences of numbers that approximate true randomness. RNG methods are classified into two main categories. While pseudo-random number generation (PRNG) is based on algorithms or physical processes of deterministic nature, true random number generation (TRNG) exploits inherently unpredictable physical processes which are rooted in principles of quantum mechanics. Someone who attacks a system that is secured by using pseudo-random numbers could, theoretically, find the underlying mechanism that is used for their generation which constitutes a weakness of the system. In TRNG systems this is not possible as there is no mechanism determining the generated number. While TRNG is currently employed in quantum communications, its realization is often difficult [73]. The emergence of chaos that has been treated in this thesis is based on deterministic processes and thus only allows for an application as PRNG. However, an attacker would be required to have precise knowledge about the state of the memory cell which is not possible in practice. The suggested technique thus constitutes a very secure way of generating random number using deterministic chaos.

Chaotic systems, including those driven by negative feedback mechanisms as seen in resistive switching devices, exhibit a high degree of sensitivity to initial conditions, making it unfeasible to predict the evolution of the system. These systems, as described in this thesis, exhibit non-linear dynamics that can evolve into deterministic chaos under certain conditions. In a chaotic system, nearby trajectories in phase space diverge exponentially with minute changes in the system's initial conditions, making the output highly unpredictable. This sensitivity forms the basis of randomness, as even a tiny variation in the initial state can result in entirely different outcomes. By measuring the voltage, current, or resistance fluctuations in a resistive switching device operating in a chaotic regime, one can extract random sequences of numbers.

One of the advantages of using resistive switching devices for RNG is their inherent hardware-based nature, which can provide randomness without relying on computational algorithms or external noise sources. By utilizing the chaotic switching behavior of resistive memory cells, it is possible to develop compact, energy-efficient, and fast random number generators that could

even be integrated into embedded devices. This approach overcomes some of the weaknesses inherent in traditional RNG methods, such as vulnerabilities to algorithmic predictions or external interference. Furthermore, the integration of such devices can contribute to more secure, efficient, and scalable RNG solutions.

5.2.2. Modeling of Neurodegenerative Pathologies

The intersection of neuromorphic computing and the study of neurodegenerative pathologies constitutes a promising path for further research. Neuromorphic computing aims at emulating the behavior of biological neural networks, and resistively switching devices, such as ReRAM cells, have been proposed as a potential building block for being employed as the nodes in hardware-based ANNs due to their STDP behavior. Given their proposed ability to exhibit chaotic switching behavior under certain conditions, these devices could be employed to model neurological disorders that arise from chaotic firing patterns in biological neurons.

In many neurodegenerative diseases, the brain's electrical activity becomes erratic or dysfunctional, often resulting in abnormal firing patterns of neurons. For example, in epilepsy, neurons in the brain fire in rapid, uncontrolled bursts, leading to seizures [74]. Similarly, Alzheimer's disease has been associated with abnormal neural activity, including neural hyperexcitability [75]. Autism, on the other hand, is thought to involve irregularities in the synchronization of neural networks, resulting in altered patterns of neuronal firing that affect cognition, behavior, and sensory processing [76, 77]. These pathological firing patterns can be understood as forms of chaos in the brain's electrical activity, and resistive switching devices offer an opportunity to simulate such dynamics.

The chaotic switching behavior of ReRAM devices, driven by negative feedback mechanisms can mimic the erratic firing behavior of neurons in diseases. Using chaotically switching ReRAM cells in hardware-based ANNs could model how neurons transition between stable states, undergo bifurcations, and eventually exhibit chaotic dynamics. These models could then be used to study how these pathologies emerge, such as the sudden onset of seizures in epilepsy or the cognitive decline seen in Alzheimer's disease. The sensitivity of chaotic systems to initial conditions could also provide insights into how abnormal neural behaviors appear and the thresholds at which these transitions occur.

Furthermore, chaotic resistive switches, integrated in ANNs could offer the potential for testing intervention strategies that might mitigate or reverse the effects of chaotic firing patterns in neurological diseases. For example, therapeutic approaches aimed at restoring stability to neuronal networks could be simulated by adjusting the feedback mechanisms or operational parameters of the underlying system. Such simulations could provide some insights into the development of treatments that target the fundamental, neuronal dynamics of diseases, potentially leading to novel therapeutic strategies.

6. Sommaire récapitulatif en français

6.1 Introduction

En 1965, Gordon Moore a formulé une loi empirique prévoyant que la densité des transistors dans les circuits intégrés doublerait tous les 18 mois [1], entraînant une réduction des coûts de fabrication et augmentant l’accessibilité des dispositifs microélectroniques. Cependant, cette évolution a également conduit à une demande accrue en stockage de données et en efficacité de calcul. Un exemple frappant est l’augmentation du temps d’entraînement des réseaux de neurones artificiels (ANN), notamment les modèles de langage (LLM) tels que ChatGPT. Sevilla et al. rapportent un doublement du temps d’entraînement tous les 5 à 6 mois pour les modèles de taille régulière entre 2010 et 2022, et tous les 9 à 10 mois pour les modèles à grande échelle entre 2015 et 2022 [2]. Cette tendance dépasse les capacités de la loi de Moore, notamment en raison des limitations physiques des processus nanométriques.

Face à cela, un changement de paradigme devient essentiel pour poursuivre l’évolution des algorithmes d’apprentissage automatique. Actuellement, les ANN sont simulés de manière inefficace en utilisant l’architecture binaire de Von Neumann, ce qui entraîne une dissipation énergétique élevée, car l’information doit être transférée de manière répétée entre l’unité de traitement et la mémoire externe.

Les systèmes neuromorphiques, inspirés des synapses biologiques, suscitent un intérêt croissant pour résoudre ce problème. Dans ces systèmes, le stockage et le calcul se déroulent au même endroit, réduisant ainsi la dissipation d’énergie. Un exemple prometteur est la « resistive random-access memory (ReRAM) », qui peut fonctionner dans une « cross-bar structure » similaire à celle des réseaux de neurones. Les états résistifs des cellules ReRAM peuvent directement représenter les paramètres du réseau de neurones dans cette application [3, 4].

6.2 Objectifs

L’objectif principal de cette thèse est d’étudier les mécanismes de rétroaction négative dans les dispositifs à commutation résistive, en particulier leur rôle en tant que précurseur d’un comportement chaotique. Cette étude se concentre sur une structure métal-isolant-métal MIM TiN/Hf_{0.5}Zr_{0.5}O₂/Au, fabriquée par pulvérisation magnétron à radiofréquences, pour explorer ces mécanismes. Une caractérisation détaillée des couches du dispositif a été réalisée par microscopie à fore atomique (AFM) et par diffraction à rayons X afin de comprendre les propriétés structurales et évaluer la morphologie de surface. Des mesures électriques ont été effectuées pour analyser le comportement de commutation résistive et identifier des indices de rétroaction

négative.

Ce mécanisme de rétroaction négative est proposé comme une condition nécessaire au chaos, offrant ainsi des perspectives sur la dynamique non linéaire des dispositifs à commutation résistive. Les mécanismes possibles responsables de cette rétroaction sont explorés en détail, en tenant compte des phénomènes spécifiques aux matériaux, tels que le mouvement des ions d'oxygène et la formation de lacunes. Une analyse mathématique est également présentée pour démontrer comment cette rétroaction pourrait conduire le dispositif vers un comportement chaotique dans certaines conditions d'exploitation. Cette analyse vise à poser les bases pour des études futures sur les applications du chaos dans la commutation résistive, avec des implications pour l'informatique neuromorphique et les systèmes de communication sécurisés.

6.3 Fondamentaux

Ce chapitre présente les bases des commutateurs résistifs et de leur utilisation dans les applications de mémoire. Ils promettent d'être utilisés comme mémoire universelle non volatile et rentable. De plus, ils offrent la possibilité d'informatique neuromorphique grâce à leur spike-timing-dependent plasticity (STDP) similaire aux synapses.

Sur cette base, leur réalisation est décrite dans le système matériau $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$, à la fois comme commutateur filamentaire à lacunes d'oxygène et jonction tunnel ferroélectrique (FTJ). Le comportement de leurs propriétés de commutation nécessite le développement des bases de la théorie du chaos. Ici, le comportement chaotique dans les systèmes non linéaires est examiné, avec une attention particulière portée à la route de Feigenbaum vers le chaos déterministe.

6.3.1 Commutateurs résistifs

Les structures à commutation résistive présentent des résistances modulables où la commutation est induite par l'application d'un biais électrique externe. Le changement de conductivité est généralement provoqué par l'un des quatre mécanismes suivants [3] :

1. Réactions électrochimiques (par exemple, redox et migration des ions)
2. Changements de phase (par exemple, transition amorphe-cristalline)
3. Magnétorésistance tunnel (par exemple, «spin dependent tunnelling»)
4. Ferroélectricité (par exemple, barrière de tunneling modulée par la polarisation du réseau)

Les discussions de cette thèse se limiteront aux changements de résistivité dus à la modulation de la barrière de tunneling causée par l'inversion de la polarisation ferroélectrique et la réaction redox dans sous-sections 2.2.1 et 2.2.2.

Le resistive random-access memory (ReRAM) consiste en une structure MIM simple et peut fonctionner en mode binaire, multi-niveaux et analogique. En mode binaire, la résistance des cellules passe entre le high-resistive state (HRS) et le low-resistive state (LRS), ce qui les

rend utilisables comme cellules mémoire classiques. En mode multi-niveaux, la résistance est commutée entre 2^n | $n \geq 1$ niveaux pour encoder plusieurs bits par état [6]. Enfin, en mode analogique, les valeurs de résistance sont obtenues de manière continue. Ce mode est utilisé pour l'informatique neuromorphique. Les cellules ReRAM ont suscité un grand intérêt en raison de leur évolutivité, de leur non-volatilité, de leur grande endurance et de leur lecture non destructive [4].

Les sous-sections suivantes explorent davantage les propriétés et applications des commutateurs résistifs. Tout d'abord, la promesse qu'ils représentent en tant que mémoire binaire universelle. Ensuite, leurs propriétés neuromorphiques sont étudiées avec une attention particulière portée sur la spike-timing-dependent plasticity (STDP).

6.3.1.1 Mémoire Universelle

Dans l'approche actuelle axée sur les données pour les progrès technologiques (informatique en nuage, intelligence artificielle), la demande des industries et des consommateurs pour des capacités de stockage d'information toujours plus grandes, tant pour les fermes de serveurs à grande échelle que pour les systèmes embarqués, ne cesse de croître. Les mémoires à semi-conducteurs dominantes de nos jours – qui stockent des informations binaires – peuvent être divisées en trois catégories [7] :

1. static random-access memory (SRAM) – basée sur des circuits de verrouillage
2. dynamic random-access memory (DRAM) – basée sur la charge électrique d'un condensateur
3. Flash – basée sur le passage d'électrons entre les grilles flottantes d'un transistor

Chacune de ces technologies présente des inconvénients, ce qui conduit à la nécessité de combiner plusieurs d'entre elles pour offrir de bonnes performances à coût raisonnable. Cela entraîne toutefois des complexités supplémentaires en matière de fabrication et de mise en œuvre. Le SRAM offre des vitesses de lecture et d'écriture rapides et nécessite peu de puissance pour la rétention de la mémoire. Cependant, il requiert une grande taille de cellule, typiquement six transistors, et n'est donc pas adapté aux applications embarquées nécessitant une grande capacité de mémoire dans un espace réduit. Il est donc principalement utilisé pour la mémoire cache des processeurs, où l'accès rapide aux données est crucial. En revanche, le DRAM offre une taille de cellule plus petite puisqu'il ne consiste qu'en un seul transistor et un condensateur de stockage, ce qui le rend adapté aux applications nécessitant une grande densité énergétique de mémoire. Toutefois, cette technologie présente des fuites de courant à partir du condensateur, ce qui nécessite une réécriture des cellules toutes les quelques millisecondes, augmentant ainsi la consommation d'énergie et le rendant inadapté aux appareils portables.

Contrairement aux SRAM et DRAM, la mémoire Flash offre une solution non volatile, ce qui signifie que l'information est conservée même en l'absence d'alimentation. La durée de

conservation de l'information dans une cellule Flash, sans réécriture, est d'au moins 10 ans. Dans cette technologie, un bit est enregistré comme l'état de charge de la grille flottante d'un MOSFET. Cependant, malgré sa petite taille et ses temps d'accès rapides, la mémoire Flash présente des temps d'écriture lents et une dégradation progressive de l'isolant dans la jonction de tunnel après des cycles répétés, réduisant ainsi la longévité des cellules mémoire [8].

Ainsi, toutes ces technologies de mémoire, bien qu'elles possèdent des avantages, présentent aussi des inconvénients. C'est pourquoi une combinaison des trois est souvent intégrée dans le même dispositif [7]. Le SRAM permet des vitesses de lecture et d'écriture rapides, mais au prix d'une complexité d'intégration et d'un grand encombrement. Le DRAM permet une grande densité de mémoire grâce à sa petite taille de cellule, mais avec une consommation d'énergie plus élevée. Enfin, bien que la mémoire Flash soit non volatile, elle ne supporte qu'un nombre limité de cycles de lecture et d'écriture. C'est dans le but de combiner les avantages de ces technologies, à savoir une haute densité d'intégration, la non-volatilité, et des vitesses de lecture/écriture rapides, tout en atténuant leurs limitations, que le concept de mémoire universelle a émergé.

La ReRAM est considérée comme un fort candidat pour la mémoire universelle en raison de sa grande évolutivité, grâce à sa structure simple, ses faibles tensions de fonctionnement, et sa commutation rapide et durable [9, 10, 11].

6.3.1.2 Informatique Neuromorphique

L'informatique neuromorphique vise à utiliser des composants électroniques analogiques pour imiter, au moins partiellement, les comportements et les fonctionnalités des réseaux neuronaux biologiques, tels que les cerveaux de mammifères [13]. Le désir d'utiliser des structures semblables à celles du cerveau pour imiter ses remarquables capacités de calcul a conduit au développement des réseaux neuronaux artificiels (artificial neural network (ANN)) comme plateforme pour une variété de tâches, y compris la reconnaissance de formes, mais aussi la génération de contenu textuel, visuel et auditif. Dans ces systèmes logiciels, qui fonctionnent sur l'architecture de Von Neumann, les données doivent être constamment transférées entre la mémoire externe et l'unité logique de l'ordinateur, ces deux entités étant strictement séparées. Ce transfert de données est nécessaire tant pour le processus d'apprentissage que pour le fonctionnement du réseau neuronal, et concerne à la fois les données traitées et les paramètres du ANN. Ce transfert nécessite de l'énergie supplémentaire et constitue un goulot d'étranglement pour le débit du système [14]. Dans l'approche neuromorphique récemment proposée, basée sur du matériel, les données — sous forme de poids du réseau neuronal — sont stockées, manipulées et utilisées pour les calculs dans le même endroit physique, éliminant ainsi l'overhead mentionné et introduisant une parallélisation inhérente [15]. La ReRAM est un candidat prometteur pour ce type de calcul en mémoire, car les poids des réseaux neuronaux peuvent être représentés par leurs résistances. Ainsi, la force d'une connexion dans le réseau neuronal dépend de la fréquence de stimulation durant le processus d'apprentissage. De plus, ils peuvent être configurés

en réseaux croisés, connectant les neurones entre eux [13] et représentant la structure du ANN en «hardware». Dans ce cas, l'entrée du ANN est représentée par les tensions appliquées. Le courant, constituant la sortie d'un calque, est alors directement déterminé par la loi d'Ohm et la loi des courants de Kirchhoff [4]. En se connectant aux deux bornes de l'élément ReRAM, le moment des impulsions appliquées aux connexions respectives peut être également appris grâce à leur spike-timing-dependent plasticity (STDP), permettant ainsi l'utilisation en tant que spiking neural network (SNN) [15].

6.3.1.3 Spike-Timing-Dependent-Plasticity (STDP)

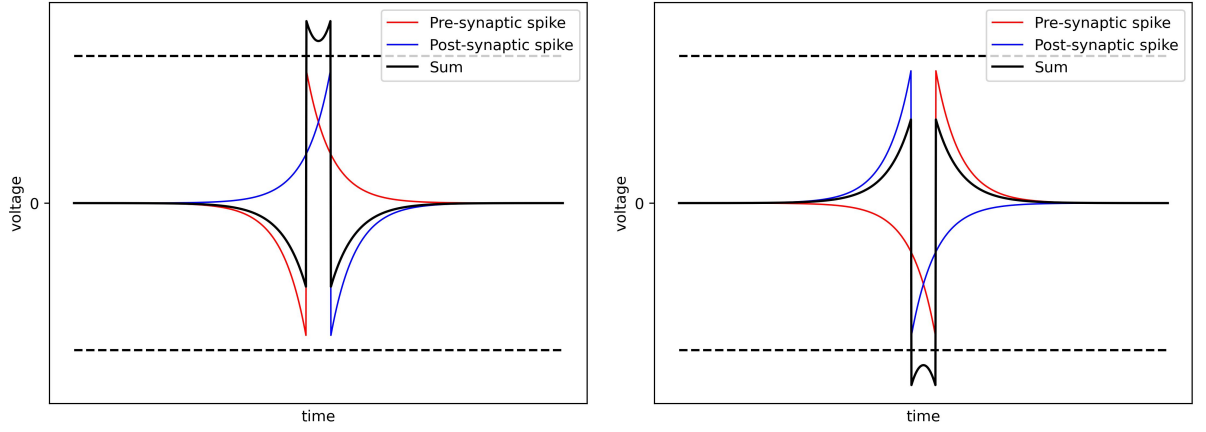
Dans les réseaux neuronaux, une synapse est la connexion directionnelle entre deux neurones, désignée respectivement comme pré-synaptique et post-synaptique. Ces neurones «déclenchent» des potentiels d'action pré- et post-synaptiques qui sont appliqués à la synapse. La forme temporelle de ces potentiels d'action varie selon la fonction des neurones dans les cerveaux de mammifères [16], et c'est la somme des deux qui est effectivement appliquée à la synapse. Selon le temps de décalage Δt entre l'arrivée des potentiels d'action pré- et post-synaptiques, la conductivité de la synapse peut augmenter, entraînant ainsi un renforcement de la connexion entre les deux neurones, diminuer, affaiblissant ainsi la connexion, ou ne pas influencer la connexion si le voltage résultant ne dépasse pas un seuil. Cette plasticité synaptique, dépendante du délai entre les potentiels d'action, est appelée spike-timing-dependent plasticity (STDP). Figure 6.1 montre l'influence des différents délais des potentiels d'action sur le potentiel résultant à travers la synapse. Les fonctions par morceaux avec deux branches exponentielles ont été utilisées pour représenter les spikes individuels, en référence à [4] :

$$V_{spike}(t) = \begin{cases} A \cdot \exp\left(\frac{-t}{B}\right), & t > 0 \\ -A \cdot \exp\left(\frac{t}{B}\right), & t \leq 0. \end{cases} \quad (6.1)$$

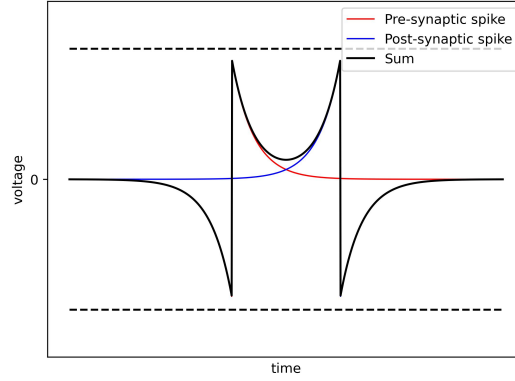
L'impulsion résultante, en fonction du décalage temporel Δt , est ensuite calculée comme suit :

$$V_{res} = V_{spike}\left(t + \frac{\Delta t}{2}\right) + V_{spike}\left(-t + \frac{\Delta t}{2}\right) \quad (6.2)$$

Dans 6.1a, le spike pré-synaptique arrive peu avant le spike post-synaptique, ce qui entraîne un potentiel accumulé dépassant un seuil arbitrairement choisi. Cela conduit à une diminution de la résistance de la synapse et renforce ainsi la connexion des neurones. Cela peut être comparé à une opération SET partielle des cellules ReRAM. D'autre part, dans 6.1b, le spike pré-synaptique arrive après le spike post-synaptique. L'impulsion résultante est donc négative, ce qui affaiblit la connexion des neurones, de manière analogue à une opération RESET en ReRAM. Enfin, dans 6.1c, le potentiel d'action pré-synaptique arrive longtemps avant le spike post-synaptique, de sorte que la somme ne dépasse pas le seuil et n'affecte donc pas la conductivité de la connexion des neurones.



(a) Spike pré-synaptique avant le spike post-synaptique. (b) Spike post-synaptique avant le spike pré-synaptique.



(c) Spike pré-synaptique bien avant le spike post-synaptique.

FIGURE 6.1. Spike-timing-dependent plasticity (STDP) avec différents délais.

À partir d'un long délai négatif, lorsque le spike pré-synaptique arrive bien avant le spike post-synaptique, la réponse de la synapse augmente de manière monotone au début, à mesure que la hauteur des impulsions augmente, jusqu'à ce que la largeur des pulses diminue. Comme le potentiel est appliqué pendant une durée de plus en plus courte, l'effet sur la synapse diminue. À $\Delta t = 0$, les deux spikes s'annulent complètement et le signe de l'impulsion STDP, et donc la réponse de la synapse, passe de SET à RESET. Lorsque le délai positif augmente, la réponse de la synapse augmente à nouveau, car la largeur de l'impulsion augmente. Enfin, la hauteur des impulsions diminue jusqu'à ce qu'elle ne dépasse plus le seuil, réduisant ainsi la réponse de la synapse. Cette transition est illustrée dans Figure 6.2, où l'intégrale des parties où l'impulsion STDP dépasse le seuil est montrée en fonction du délai temporel respectif. Des courbes similaires ont été mesurées dans les cellules ReRAM par Mittermeier *et al.* [4] et sont présentées en Annexe A, mais aussi dans des synapses biologiques, comme les neurones hippocampiques de rat [17], où l'influence du délai des spikes sur la conductivité des synapses est directement montrée, suggérant ainsi que seules les impulsions qui dépassent le seuil modifient la configuration des

synapses. Il est donc possible d'approximer la superposition des spikes pré- et post-synaptiques par une fonction rectangulaire lors de l'étude du comportement STDP des structures ReRAM.

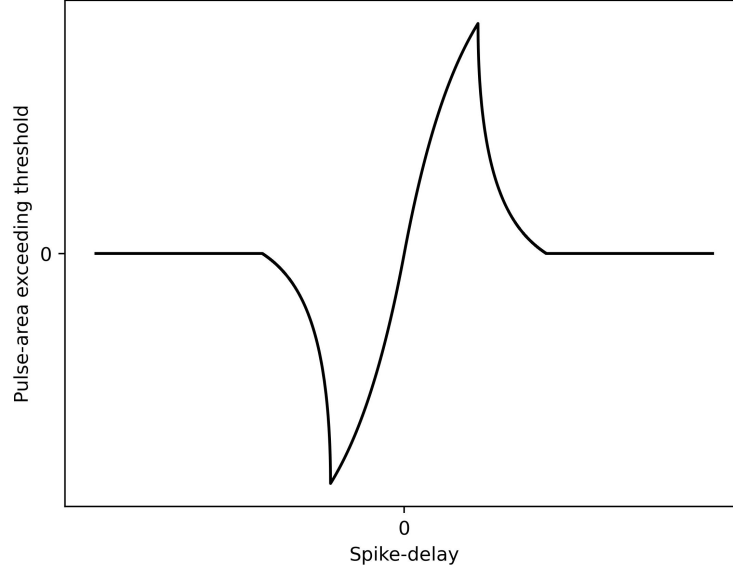


FIGURE 6.2. Surface excédant le seuil en fonction du délai temporel des spikes.

6.3.2 Commutation dans le $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$

L'oxyde d'hafnium (HfO_2) a été introduit en tant que diélectrique de grille à haute permittivité pour le nœud technologique de 45 nm en 2007 [18], car sa phase amorphe offre une combinaison d'une constante diélectrique élevée (~ 25) et d'une bande interdite d'environ 5.7 eV. Ce matériau est donc bien établi dans l'industrie des semi-conducteurs depuis de nombreuses années. HfO_2 cristallise dans une phase monoclinique à température ambiante, subit une transition vers une phase tétragonale à environ 2000 K, puis une autre transition vers une phase cubique autour de 2870 K [19]. En 2011, une phase orthorhombique de HfO_2 dopée à l'oxyde de silicium a été rapportée, montrant un comportement ferroélectrique et antiferroélectrique [20]. Depuis, de nombreux dopants ont été étudiés pour stabiliser cette phase orthorhombique. Le zirconium est un candidat prometteur, ayant des propriétés chimiques similaires à celles de l'hafnium, et la polarisation ferroélectrique maximale dans le $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ (HZO) est atteinte pour $x = 0,5$. Cela permet un dépôt facile du HZO par dépôt de couches atomiques (ALD) en alternant les précurseurs respectifs. De plus, les propriétés ferroélectriques des couches minces de HZO peuvent être obtenues à des températures de dépôt relativement faibles, réduisant ainsi la contrainte thermique sur le procédé [21].

La ferroélectricité désigne la propriété d'un réseau cristallin qui subit une polarisation spontanée réversible lorsqu'un champ électrique lui est appliqué. De plus, lorsque le champ externe est supprimé, la polarisation rémanente reste non nulle [5]. Ces deux états distincts peuvent être utilisés pour stocker des informations binaires. Pulvari [22] a proposé en 1951 une mémoire

permanente à base de titanate de baryum utilisant la polarisation rémanente du pérovskite. Une autre méthode de stockage d'information basée sur la ferroélectricité a été proposée par Esaki *et al.* [23] sous la forme de la jonction tunnel ferroélectrique (FTJ), où la modulation de la barrière de tunnel, causée par les charges d'écran induites par l'état de polarisation du diélectrique, est utilisée pour la commutation résistive. Le HfO_2 ferroélectrique constitue un candidat intéressant pour les mémoires ferroélectriques grâce à sa compatibilité CMOS. De plus, il ne présente pas l'effet de couche morte, qui est inhérent aux ferroélectriques pérovskites [24], facilitant ainsi son utilisation dans les jonctions tunnel.

En outre, la formation et la rétraction d'un filament déficient en oxygène peuvent être exploitées pour présenter des propriétés de commutation résistive dans les oxydes à base d'hafnium. Dans ce cas, l'oxygène est retiré d'un filament dans le réseau cristallin, et la conduction électronique se fait via les lacunes d'oxygène [25].

6.3.2.1 Jonctions Tunnel Ferroélectriques

Une jonction tunnel ferroélectrique (FTJ) est une mémoire à résistance variable (ReRAM) dans laquelle un matériau ferroélectrique mince et isolant est placé entre deux électrodes métalliques. L'isolant doit être suffisamment fin pour permettre un effet de tunnel quantique entre les deux électrodes. En 2009, Garcia *et al.* ont démontré que l'inversion de polarisation ferroélectrique est responsable de la commutation résistive des FTJ [26]. Ainsi, la polarisation rémanente, pouvant être dirigée vers l'électrode supérieure ou inférieure en appliquant un champ électrique, modifie la barrière de tunnel par interaction avec les charges induites aux interfaces des matériaux asymétriques des électrodes.

La direction de la polarisation influence la hauteur de la barrière de tunnel. Si elle pointe vers l'électrode ayant une fonction de travail plus élevée, la barrière de potentiel est réduite, facilitant le tunnel d'électrons et conduisant à un état de faible résistance. À l'inverse, si la polarisation est orientée vers l'électrode à fonction de travail plus faible, la barrière augmente, réduisant ainsi le tunnel d'électrons et entraînant un état de haute résistance [27]. Les FTJ nécessitent donc des électrodes asymétriques, mais cette asymétrie peut aussi être induite par des effets interfaciaux lors du dépôt des couches [28].

Les FTJ ont été largement étudiées dans notre groupe, avec une attention portée à la fabrication de structures MIM [29], la modélisation théorique de leur comportement de commutation [30] et l'influence des lacunes d'oxygène [5]. Dans la thèse de Gonzalez [5], un comportement inhabituel a été observé : lors de mesures d'endurance, un dédoublement des états de faible et de forte résistance a émergé, une forme de bifurcation périodique qui peut précéder un chaos déterministe [31, 32]. Ce phénomène pourrait mener à une commutation chaotique dans les ReRAM, nécessitant une rétroaction négative. L'étude d'autres ReRAM, comme celles à base de lacunes d'oxygène, est prometteuse en raison des effets dissipatifs qui y interviennent, tels que les processus thermiquement activés.

6.3.2.2 Commutation par Lacunes d'Oxygène

Les interrupteurs à lacunes d'oxygène sont constitués de structures MIM, similaires aux FTJ, mais avec une couche isolante pouvant atteindre plusieurs dizaines de nanomètres d'épaisseur, car le mécanisme de conduction n'est pas basé sur l'effet tunnel quantique. Une panne diélectrique douce et contrôlée est employée pour créer un filament conducteur reliant les deux électrodes. Ce processus implique une modification chimique partielle de la couche isolante, plus précisément une réduction pour l'opération de SET et une oxydation pour celle de RESET, ce qui provoque un changement d'état de résistance. L'application d'une tension externe entraîne la migration des atomes d'oxygène, formant un filament conducteur dans une phase sous-stœchiométrique ou même métallique.

Un schéma exemplaire du fonctionnement de la ReRAM bipolaire basé sur la commutation filamentaire par lacunes d'oxygène est illustré dans la figure 6.3. À l'état initial (a), les lacunes d'oxygène sont distribuées de manière aléatoire dans le diélectrique. Après une étape d'électroformation (b), l'application d'une tension positive à une électrode entraîne la migration des atomes d'oxygène vers cette électrode, ce qui provoque une croissance progressive du filament reliant les deux électrodes. Une fois ce filament complété, un chemin conducteur est créé, et la cellule passe de l'état HRS à l'état LRS. Lorsque la polarité est inversée (c), le filament se rompt partiellement et la résistance de la structure MIM augmente. Ce processus est réversible dans une cellule mémoire fonctionnelle, les opérations de SET et RESET étant associées à la fermeture et la rupture du filament.

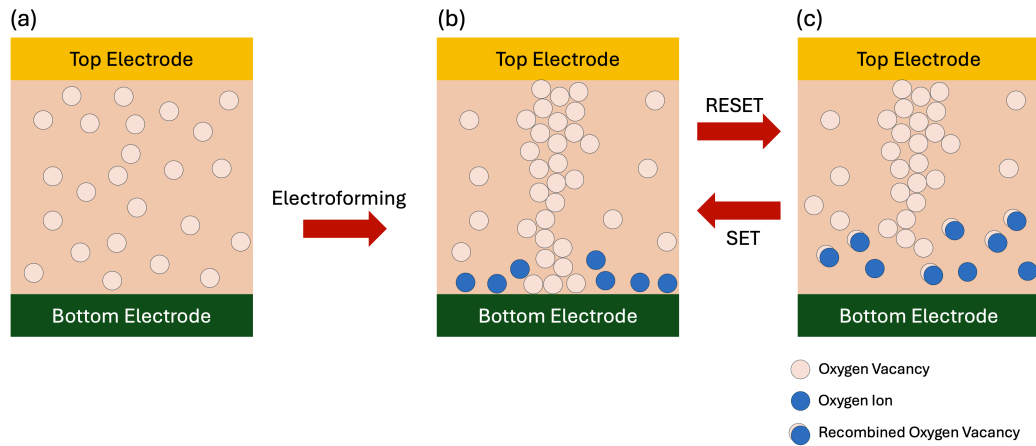


FIGURE 6.3. Schéma de la commutation par lacunes d'oxygène dans une ReRAM.

La performance de ces dispositifs dépend fortement de la densité et de la distribution des lacunes d'oxygène, qui sont elles-mêmes influencées par les conditions de fabrication. À cet égard, des recherches approfondies ont été menées pour améliorer le contrôle de la concentration de lacunes d'oxygène durant la fabrication, dans le but d'assurer un comportement de commutation plus stable et reproductible. Par exemple, Gonzalez a étudié l'impact de la pression partielle d'oxygène et des méthodes de recuit sur la densité de lacunes et le comportement de commu-

tation qui en résulte. De plus, l'insertion d'une couche métallique de Hf entre le diélectrique et l'électrode supérieure a été explorée pour promouvoir la formation de lacunes, et l'utilisation d'une électrode en titane, ayant une forte affinité pour l'oxygène, a montré une réduction des tensions de formation et de commutation. Un dopage avec ZrO_2 pourrait également améliorer le comportement de commutation, en augmentant le rapport on/off et en réduisant les tensions et courants de fonctionnement.

En ce qui concerne les bifurcations de doublement de période mentionnées précédemment, la ReRAM à commutation par lacunes d'oxygène peut présenter des effets dissipatifs responsables de la rétroaction négative nécessaire. Par exemple, dans le cas de la commutation unipolaire, l'énergie thermique produite par l'échauffement joule peut dissoudre le filament conducteur par diffusion latérale, ce qui diminue le ratio on/off à mesure que la température augmente.

6.3.3 Chaos Déterministe

Le concept de chaos est souvent associé au désordre et à l'imprévisibilité. Cependant, dans le contexte du chaos déterministe, il se réfère à un type spécifique de comportement au sein des systèmes dynamiques, qui est à la fois déterministe et extrêmement sensible aux conditions initiales. Contrairement au hasard traditionnel, le chaos déterministe émerge d'équations bien définies régissant l'évolution du système, produisant des résultats qui semblent aléatoires et imprévisibles.

Le chaos déterministe est un phénomène où des systèmes régis par des lois déterministes affichent un comportement si sensible aux conditions initiales que des prédictions à long terme deviennent impossibles en raison du bruit et de la sensibilité limitée des instruments de mesure. Bien que la nature de ces systèmes soit déterministe – c'est-à-dire que leurs états futurs sont entièrement déterminés par leurs conditions initiales – de légères variations dans ces conditions peuvent mener à des résultats très différents. Ce phénomène, appelé l'« effet papillon », a été popularisé par Edward Lorenz, qui a démontré que des changements infimes dans les conditions de départ des modèles météorologiques pouvaient conduire à des prévisions complètement divergentes [39].

L'étude du chaos déterministe a émergé au 20^e siècle, bien que ses racines conceptuelles remontent à des travaux antérieurs. Henri Poincaré a fait des contributions significatives à la compréhension de l'instabilité des systèmes, notamment dans son étude du problème des trois corps. Il a découvert que même des systèmes simples pouvaient présenter un comportement très complexe, apparemment désordonné, posant les bases de la théorie moderne du chaos [40]. Ce n'est cependant qu'à partir des années 1960 que le chaos déterministe a commencé à susciter un intérêt plus large. Le travail d'Edward Lorenz sur les modèles atmosphériques a permis d'identifier un comportement chaotique dans les systèmes déterministes, donnant naissance au célèbre attracteur de Lorenz [41]. Un attracteur est la représentation en espace de phase d'un système dynamique vers laquelle il évolue de manière asymptotique avec le temps, indépendamment des conditions initiales. Un attracteur simple, par exemple, serait un point unique où

un système finit par se stabiliser. Cependant, en raison de la dépendance des systèmes chaotiques aux conditions initiales, les attracteurs simples ne suffisent pas pour les décrire, d'où le concept d'attracteurs étranges, dont l'attracteur de Lorenz est un exemple. Comme les attracteurs simples, les attracteurs étranges attirent les trajectoires du système dynamique, mais avec la particularité que la distance entre deux points voisins dans l'espace de phase diverge exponentiellement avec le temps [32], rendant le système imprévisible en raison de sa sensibilité aux conditions initiales. De plus, ces attracteurs ont une nature fractale, c'est-à-dire qu'ils forment une structure complexe ayant une dimension fractionnaire, supérieure à leur dimension topologique mais inférieure à celle de l'espace qu'ils occupent [42]. Cette nature fractale permet à l'attracteur de contenir une infinité de détails dans une zone finie. Le modèle utilisé par Lorenz pour décrire des phénomènes météorologiques où il a découvert le chaos déterministe est donné dans l'équation 6.3 [41] et a permis de calculer la courbe représentée dans la figure 6.4 avec $\sigma = 10$, $\beta = \frac{8}{3}$ et $\rho = 28$.

$$\begin{aligned}\dot{X} &= \sigma X + \sigma Y \\ \dot{Y} &= -XZ + \rho X - Y \\ \dot{Z} &= XY - \beta Z.\end{aligned}\tag{6.3}$$

Cette découverte a révolutionné la compréhension des systèmes dynamiques, révélant que le chaos pouvait être présent dans une grande variété de systèmes physiques, allant de la dynamique des fluides [43] aux circuits électriques [44], et même aux processus biologiques [45].

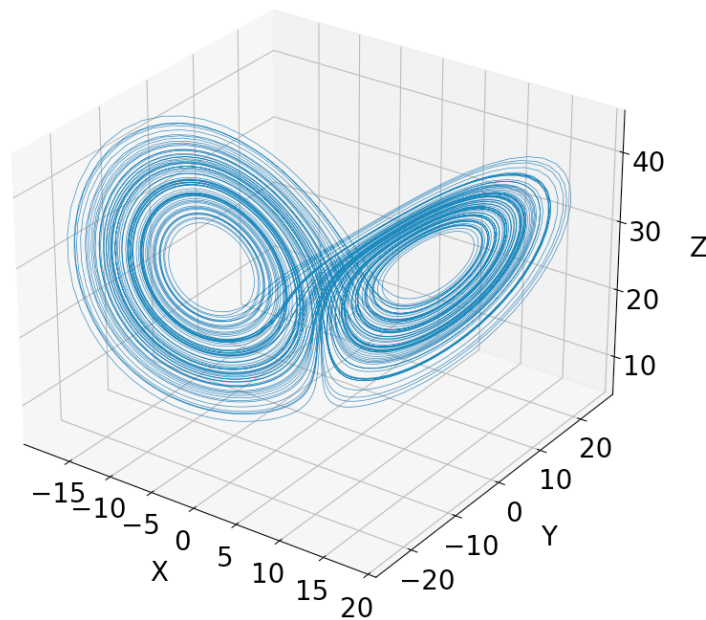


FIGURE 6.4. Attracteur de Lorenz

6.3.3.0.1 Exposants de Lyapunov Les exposants de Lyapunov sont essentiels pour comprendre le chaos, car ils quantifient la sensibilité d'un système à ses conditions initiales. Ils mesurent le taux moyen exponentiel de divergence (ou de convergence) des trajectoires voisines dans l'espace de phase. Si l'on considère deux trajectoires dans l'espace de phase qui commencent très proches l'une de l'autre, la distance entre elles croît de manière exponentielle dans les systèmes chaotiques. L'exposant de Lyapunov λ est défini comme le taux de cette divergence selon [32] :

$$\varepsilon e^{t\lambda(x_0)} = |f(t, x_0 + \varepsilon) - f(t, x_0)|, \quad (6.4)$$

où ε est la distance entre les positions initiales dans l'espace de phase, t est le temps du système et f est le modèle qui décrit le système. Pour $\varepsilon \rightarrow 0$ et $t \rightarrow \infty$, cela conduit à la définition formelle de l'exposant de Lyapunov :

$$\begin{aligned} \lambda(x_0) &= \lim_{t \rightarrow \infty} \lim_{\varepsilon \rightarrow 0} \frac{1}{t} \ln \left| \frac{f(t, x_0 + \varepsilon) - f(t, x_0)}{\varepsilon} \right| \\ &= \lim_{t \rightarrow \infty} \frac{1}{t} \ln \left| \frac{\partial f(t, x)}{\partial x} \right|_{x=x_0}. \end{aligned} \quad (6.5)$$

L'exposant de Lyapunov fournit une mesure directe de la manière dont de petites erreurs ou incertitudes dans l'état initial d'un système se propagent au fil du temps. Si $\lambda > 0$, les trajectoires voisines divergent de manière exponentielle, ce qui indique un comportement chaotique. Si $\lambda < 0$, les trajectoires convergent, menant à des points fixes ou des orbites dans des systèmes dissipatifs et donc à un comportement prévisible (par exemple, oscillation amortie) [46]. Si des trajectoires proches dans l'espace de phase restent à la même distance moyenne, alors $\lambda = 0$ (par exemple, oscillation non amortie). Ce comportement est également prévisible et donc non chaotique. Il peut donc être conclu que l'exposant de Lyapunov fournit une mesure de la «rapidité» avec laquelle un système apparaîtra chaotique en indiquant la vitesse à laquelle les trajectoires proches divergeront.

6.3.3.0.2 Entropie de Kolmogorov-Sinai Par analogie avec l'entropie en mécanique statistique, Shannon a introduit le concept dans la théorie de l'information [47]. Alors que l'entropie est une mesure du désordre dans les systèmes physiques, dans la théorie de l'information, elle mesure le manque d'information que l'on a sur le système et est alors définie par :

$$S = -C \sum_i p_i \log p_i, \quad (6.6)$$

où S est l'entropie de Shannon, p_i sont les probabilités d'un ensemble d'événements et C est une constante positive que l'on fixe à $C = 1$ pour les considérations suivantes, sans perte de généralité. S est une mesure de l'information du système nécessaire pour le localiser dans l'état i [32]. Si une trajectoire $\vec{x}(t)$ dans un espace de phase d -dimensionnel, qui est divisé en éléments i_i de taille l^d , est considérée, alors les probabilités que la trajectoire $\vec{x}(t)$ passe par l'élément i_0

à $t = 0$, par l'élément i_1 à $t = \tau$, et ainsi de suite jusqu'à ce qu'elle passe par l'élément i_n à $t = n\tau$, sont données par p_i . L'entropie de Shannon est alors donnée par :

$$S_n = - \sum_i^n p_i \log p_i. \quad (6.7)$$

Ainsi, l'entropie du système est donnée par Equation 6.7 et est proportionnelle à l'information nécessaire pour trouver le système sur une trajectoire i_i . Ainsi, $S_{n+1} - S_n$ est l'information nécessaire pour trouver la trajectoire dans l'élément i_{n+1} si elle était auparavant dans les éléments i_i , ce qui résulte dans le changement d'information lors de la transition de l'élément i_n à i_{n+1} . L'entropie de Kolmogorov-Sinai est alors le taux moyen auquel l'information sur le système est perdue :

$$K = \lim_{\tau \rightarrow 0} \lim_{l \rightarrow 0} \lim_{N \rightarrow 0} \frac{1}{N\tau} \sum_{n=0}^{N-1} (S_{n+1} - S_n). \quad (6.8)$$

L'entropie de Kolmogorov-Sinai est une métrique appropriée pour le comportement chaotique dans les systèmes dynamiques, un peu comme les exposants de Lyapunov. Pour $K = 0$, aucune information n'est perdue le long de la trajectoire, ce qui fait que les points proches dans l'espace de phase restent également proches. Pour les systèmes stochastiques, véritablement aléatoires, K devient infini et pour les systèmes chaotiques, K devient une constante positive qui mesure la rapidité avec laquelle l'information est perdue. Il n'est donc pas surprenant que l'entropie de Kolmogorov-Sinai puisse être liée aux exposants de Lyapunov d'un système [32].

6.3.3.1 Scénario de Feigenbaum

Après avoir établi des métriques utiles pour le comportement chaotique dans les systèmes non linéaires, l'accent est mis sur le chaos déterministe dans les cartes non linéaires. Une carte est définie par la relation :

$$x_{n+1} = f(x_n) \quad (6.9)$$

dans le cas non linéaire, lorsque $f(x)$ présente au moins un terme non linéaire. Pour les considérations suivantes, un système simple d'ordre deux est utilisé :

$$x_{n+1} = rx_n(1 - x_n). \quad (6.10)$$

Cette carte est appelée carte logistique et a été utilisée pour la première fois par Pierre Verhulst en 1845 pour modéliser la dynamique des populations dans un espace confiné. La variante discrète de la carte logistique peut être utilisée pour modéliser l'évolution d'une population d'une année à l'autre. Dans cette équation, r représente un facteur de croissance qui modélise le taux de reproduction de l'espèce, tandis que le terme $1 - x_n$ introduit une rétroaction négative cruciale pour le comportement chaotique. Lorsque r est augmenté, des bifurcations apparaissent,

marquées par un doublement de période dans la séquence de population, ce qui mène à une transition vers le chaos au-delà d'un certain seuil $r \approx 3.569945$. Ce comportement chaotique est illustré dans le diagramme de Feigenbaum, comme montré sur la Figure 6.5.

Pour étudier la transition vers le chaos, les exposants de Lyapunov en fonction du facteur de croissance r sont calculés, comme indiqué dans la Figure 6.6. Au fur et à mesure que r augmente, les bifurcations deviennent de plus en plus fréquentes et l'exposant de Lyapunov devient positif à $r = r_\infty$, signalant le début du chaos déterministe. Ce phénomène de transition est communément appelé scénario de Feigenbaum.

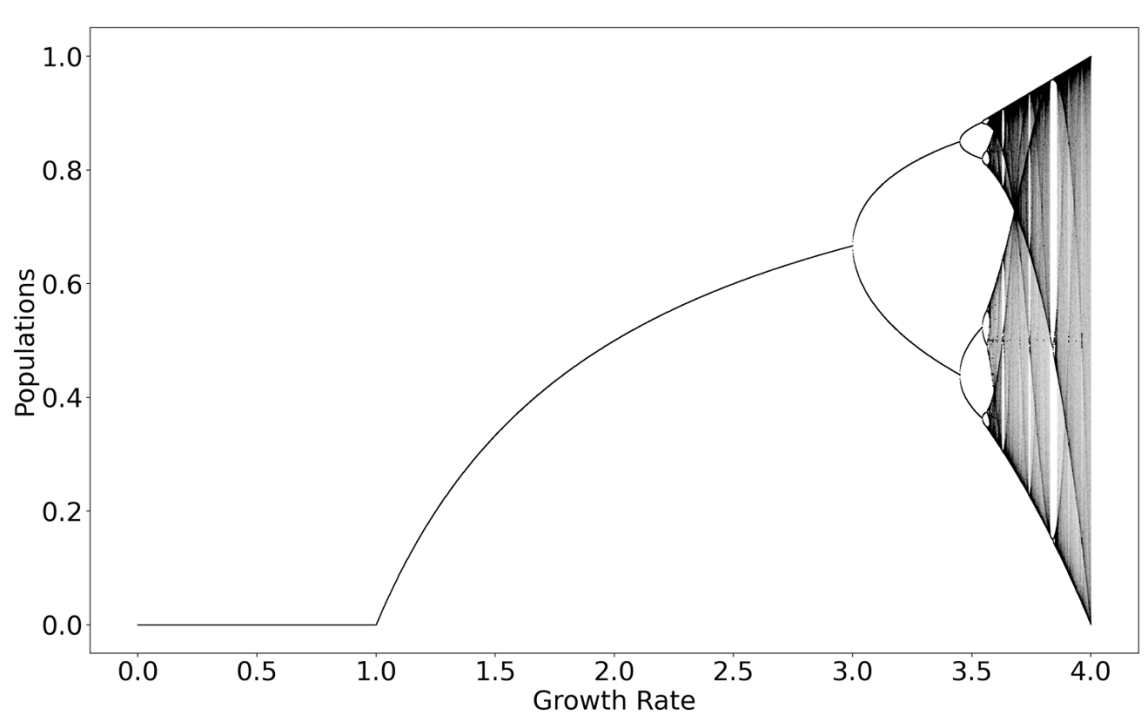


FIGURE 6.5. Diagramme de Feigenbaum de la carte logistique

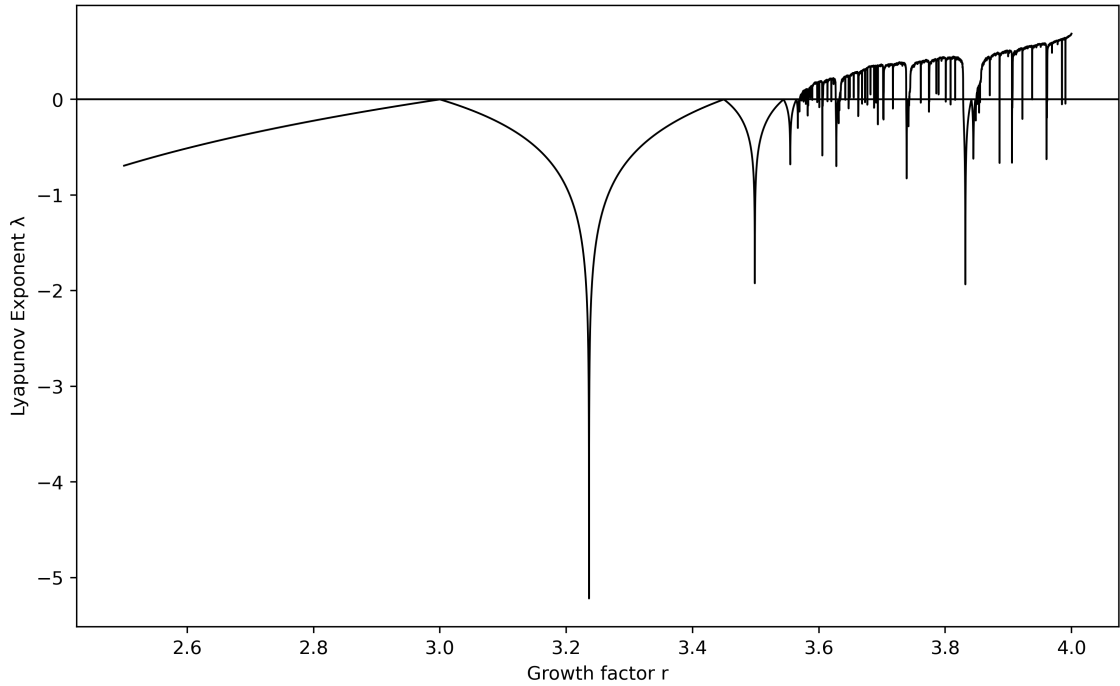


FIGURE 6.6. Exposants de Lyapunov de la carte logistique

6.4 Matériaux et Méthodes

Ce chapitre détaille les matériaux utilisés dans les dispositifs resistive random-access memory (ReRAM), ainsi que les techniques de dépôt de couches minces employées pour créer les empilements structures métal-isolant-métal (MIM). En outre, les procédures de caractérisation seront abordées.

Dans la première section, les matériaux d'électrode utilisés pour la structure $\text{TiN}/\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{Au}$ sont discutés. Le nitrure de titane et l'or servent d'électrodes. Par conséquent, leur épaisseur n'est pas aussi critique que celle de l'isolant $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$. Cependant, pour l'électrode inférieure en TiN, une faible rugosité de surface ainsi que de petites tailles de grains sont importantes pour offrir des conditions optimales au dépôt du $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$. Ensuite, le principe de la technique de fabrication des couches minces par pulvérisation, et plus spécifiquement la pulvérisation magnétron à radiofréquences, est abordé. Cette technique est un standard industriel car elle permet un contrôle précis de l'épaisseur des éléments de la structure et une bonne évolutivité. Enfin, les moyens de caractériser les structures fabriquées et les couches individuelles sont présentés. Des techniques pour analyser la composition des matériaux, l'épaisseur des couches, la morphologie de surface ainsi que la caractérisation électrique des dispositifs complets sont décrites.

6.4.1 Matériaux

Les dispositifs fabriqués dans le cadre de cette thèse sont constitués d'empilements à trois couches : l'électrode inférieure en nitrure de titane, la couche active et commutante en $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$

et l'électrode supérieure en or. La combinaison de ces matériaux présente des avantages détaillés dans les sections suivantes.

6.4.1.1 Électrode Inférieure en Nitrure de Titane

Le nitrure de titane est un matériau favorable pour une électrode inférieure en raison de son faible coût, de sa résistance élevée à la température, de sa stabilité mécanique et de son excellente conductivité électrique. De plus, il a été montré à plusieurs reprises que les électrodes en nitrure de titane stabilisent la phase orthorhombique ferromagnétique dans les couches minces de $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$. Le titane a une affinité très élevée pour l'oxygène, ce qui conduit à une élimination de l'oxygène lors du dépôt de $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$. Cela introduit des lacunes d'oxygène dans le diélectrique, ce qui stabilise la phase ferromagnétique dans l'hafnia. Ces vacants d'oxygène sont également utilisés dans la construction de filaments conducteurs dans les interrupteurs à vacants d'oxygène. Ainsi, l'utilisation d'une électrode inférieure en nitrure de titane présente des avantages pour le fonctionnement des jonction tunnel ferroélectrique (FTJ) et des interrupteurs à filament de lacunes d'oxygène.

6.4.1.2 Électrode Supérieure en Or

L'or (Au) a été choisi comme matériau pour l'électrode supérieure dans l'empilement $\text{TiN}/\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{Au}$ en raison de ses propriétés matérielles et électriques spécifiques essentielles aux applications ReRAM. L'or a été choisi pour son inertie chimique intrinsèque, minimisant les risques de réactions à l'interface électrode/isolant. Cette stabilité est cruciale dans les dispositifs ReRAM, où les appareils subissent des événements de commutation répétés qui pourraient autrement dégrader les matériaux des électrodes, affectant ainsi la performance et la durée de vie du dispositif. La résistance de l'or à l'oxydation et à d'autres changements chimiques garantit la stabilité de l'interface avec la couche $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$, favorisant un comportement de commutation cohérent sur plusieurs cycles.

En plus de sa stabilité, la fonction de travail élevée de l'or (5.3 eV) correspond bien aux exigences fonctionnelles d'une électrode ReRAM. Une électrode avec une fonction de travail élevée génère une barrière de Schottky bénéfique à l'interface avec $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$, permettant une injection et extraction contrôlées des charges.

Bien que le platine (Pt) présente également une fonction de travail élevée et soit souvent envisagé pour les applications d'électrodes, il n'a pas été choisi pour ce dispositif en raison de sa grande perméabilité à l'oxygène. Le platine permet aux ions d'oxygène de pénétrer à travers l'électrode, ce qui peut déstabiliser le dispositif en modifiant la distribution des lacunes d'oxygène dans la couche commutante. La perméabilité à l'oxygène plus faible de l'or garantit que les ions d'oxygène restent confinés dans la couche $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$, contribuant à un mécanisme de commutation résistif plus stable et prévisible.

6.4.2 Dépôt de Couches Minces

Chacune des couches mentionnées précédemment (nitrure de titane, hafnium-zirconium-oxyde et or) a été déposée par pulvérisation magnétron à radiofréquences. Cette section détaille cette technique de dépôt. L'empilement a été déposé sur des substrats en silicium avec une couche d'oxyde naturel, bien que son influence soit négligeable en raison de la polycristallinité et de l'épaisseur relativement élevée des électrodes inférieures en TiN.

6.4.2.1 Pulvérisation Magnétron à Radiofréquences

La pulvérisation magnétron à radiofréquences est une méthode de dépôt polyvalente et largement utilisée, faisant partie des techniques de dépôt physique par phase vapeur (PVD). Dans ces techniques PVD, un vaporisateur d'ions et d'atomes du matériau cible est généré. Ce vaporisateur se répand ensuite dans la chambre et se condense sur le substrat pour former une couche mince.

Un exemple de technique PVD est la pulvérisation. Ici, un plasma est allumé près de la cible, entraînant un bombardement de sa surface par des ions issus du plasma. Les ions incidents éjectent des atomes de la surface de la cible par transfert de moment, ce qui permet le dépôt des atomes de la cible sur le substrat et les parois de la chambre. Un ou plusieurs gaz sont pompés dans une chambre précédemment évacuée, et un plasma est allumé entre les deux électrodes, la cible étant placée sur une électrode et le substrat sur l'autre. Les ions issus du plasma sont accélérés vers la cible et «frappent» sa surface, éjectant des atomes de la cible qui «pleuvent» ensuite sur le substrat pour former une couche mince. La pulvérisation est largement utilisée dans les domaines académiques et industriels en raison de son application à grande et petite échelle. De plus, les paramètres de dépôt tels que la pression, la puissance et la température du substrat peuvent être contrôlés précisément.

Dans la pulvérisation, un plasma peut être allumé à l'aide d'une alimentation en direct current (DC) ou en radiofréquences (RF). Cependant, la pulvérisation DC entraîne une accumulation de charge pour les matériaux cibles isolants, car les porteurs de charge ne peuvent pas être évacués par l'électrode. Cette accumulation de charge finit par protéger l'électrode, entraînant des instabilités du plasma et la perturbation du dépôt [58]. En revanche, avec la pulvérisation RF, le dépôt de matériaux isolants, semi-conducteurs et conducteurs peut être réalisé. Des fréquences supérieures à 1 MHz sont suffisantes pour générer une décharge presque suffisante, mais la plupart des systèmes fonctionnent à une fréquence de 13.56 MHz afin de ne pas interférer avec les protocoles de communication radio [59].

Placer des aimants derrière la cible et immerger ainsi la cible dans un champ magnétique peut être utilisé pour augmenter la vitesse de dépôt. Ce processus, appelé «pulvérisation magnétron», entraîne un confinement des électrons primaires et secondaires près de la surface de la cible, augmentant ainsi la probabilité de collisions avec les atomes de gaz et augmentant la densité d'ionisation du plasma près de la cible. L'efficacité d'ionisation accrue conduit à une densité de courant ionique plus élevée vers la cible, où plus d'atomes seront «éjectés», car le nombre

moyen d'atomes extraits de la cible par ion de gaz incident reste constant. Le résultat est un rendement de pulvérisation accru par rapport à la pulvérisation non magnétron [60].

De plus, un gaz réactif avec le matériau cible peut être présent dans la chambre pendant le processus de dépôt, en l'introduisant dans la chambre pendant le dépôt. Le plasma peut être généré à partir de ce gaz ou être présent en plus du gaz à partir duquel le plasma est formé. Cette technique est appelée «pulvérisation réactive» et peut être utilisée pour assurer la stœchiométrie du matériau cible (par exemple dans le cas des cibles oxydes). De plus, ce processus peut être utilisé pour modifier la composition de la couche mince par rapport au matériau cible. Par exemple, des oxydes ou des nitrures peuvent être déposés en utilisant une cible métallique lorsque les gaz respectifs sont présents dans la chambre.

6.4.2.2 Outil de Pulvérisation SPT310-TT

Un outil de pulvérisation RF-magnétron SPT310-TT de Plasmionique Inc. a été utilisé pour la fabrication des dispositifs étudiés dans cette thèse. L'unité est équipée de trois magnétrons montés à un angle au-dessus du support du substrat. Cette configuration permet la co-pulvérisation en utilisant deux magnétrons simultanément. L'outil est équipé de deux contrôleurs de débit massique permettant de contrôler le flux de deux gaz dans la chambre. La distance entre le substrat et les cibles est relativement grande, d'environ 11 cm, ce qui entraîne un faible taux de dépôt et permet un contrôle précis de l'épaisseur des couches déposées.

L'unité est équipée d'un élément chauffant pour contrôler la température du substrat. Cependant, pendant la période où les dispositifs détaillés dans cette thèse ont été fabriqués, l'élément chauffant a souffert de difficultés techniques, rendant impossible l'emploi des températures souhaitées d'environ 650 °C. Cette limitation a été particulièrement notable dans le dépôt des couches HZO avec une phase orthorhombique, car des températures élevées étaient nécessaires. Par conséquent, il n'a pas été possible de produire un jonction tunnel ferroélectrique (FTJ) dans le cadre de ce travail. Cependant, comme les bifurcations à double période ont été observées pour la première fois dans ces dispositifs (voir sous-section 6 et [5]), un modèle du retour négatif dans leur comportement de commutation sera tout de même discuté dans sous-section 6.

6.4.3 Techniques de caractérisation

Dans la fabrication de ces couches, une enquête approfondie de leurs propriétés est essentielle, constituant un retour pour l'optimisation des performances des dispositifs fabriqués. Les couches individuelles ainsi que les structures complètes ont été analysés en termes de leur épaisseur, leur morphologie de surface ainsi que leurs propriétés électriques, telles que le comportement de commutation.

6.4.3.1 Réflectométrie de Rayons-X

Les rayons X, formes de radiation électromagnétique avec des longueurs d'onde allant de 0,01 à 10 nm, pénètrent profondément dans divers matériaux, permettant l'analyse de la densité électronique et de l'épaisseur des films. Cette méthode, non destructive, est utilisée pour déterminer l'épaisseur, la densité et la rugosité des films fins, en observant les motifs d'interférence issus des rayons X réfléchis sur la surface et les interfaces du film.

6.4.3.2 Diffraction X à incidence rasante

La diffraction X à incidence rasante (GIXRD) est une technique spécialisée pour l'analyse des films minces, en permettant de sonder la structure à la surface du matériau avec une influence minimale du substrat sous-jacent. Elle utilise un angle d'incidence faible afin de concentrer l'interaction des rayons X sur la surface du film, ce qui permet d'analyser la structure cristalline.

6.4.3.3 Microscopie à force atomique

La microscopie à force atomique (AFM) est une technique permettant d'étudier la topographie et la morphologie de surface des matériaux. Cette méthode repose sur un processus de balayage d'un probe au-dessus de la surface du matériau, mesurant les interactions de celui-ci avec la surface. Trois modes de fonctionnement sont couramment utilisés : mode contact, mode tapotement et mode non-contact.

6.4.3.4 Caractérisation électrique

La caractérisation électrique des structures métal-isolant-métal (MIM) est cruciale pour l'évaluation de leurs performances en tant que dispositifs de mémoire. Plusieurs techniques de caractérisation ont été employées dans ce travail, incluant des mesures de balayage de tension quasi-statique, des mesures d'endurance avec des impulsions de tension alternées et l'étude du comportement de la cellule en réponse à des variations de largeur et d'amplitude d'impulsion.

6.5 Résultats et Discussion

Tous les résultats obtenus sont présentés, suivis d'une discussion concluant le chapitre suivant. Tout d'abord, la fabrication et la caractérisation des couches individuelles ainsi que de la structure complète $\text{TiN}/\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2/\text{Au}$ métal-isolant-métal (MIM) seront détaillées. Toutes les couches sont déposées par pulvérisation magnétron à radiofréquences, et leurs propriétés sont examinées par microscopie à force atomique (AFM) et réflexion des rayons X, lorsque cela est applicable. De plus, les propriétés électriques des structures complètes, y compris le comportement quasi-statique, l'endurance et le comportement STDP, sont discutées. Ce dernier révèle un mécanisme de rétroaction négative dans le comportement de commutation de la cellule. La deuxième partie de ce chapitre explorera les facteurs microscopiques influençant l'émergence

de ce mécanisme de rétroaction. Enfin, ces résultats seront utilisés pour examiner mathématiquement le potentiel de déclenchement d'une commutation chaotique dans les cellules ReRAM. Des méthodes telles que le diagramme de Feigenbaum et les exposants de Lyapunov seront utilisées pour analyser les conditions menant à la transition vers le chaos déterministe dans les commutateurs résistifs.

6.5.1 Structure TiN/Hf_{0.5}Zr_{0.5}O₂/Au

Cette section détaille la fabrication de la structure TiN/Hf_{0.5}Zr_{0.5}O₂/Au métal-isolant-métal (MIM) ainsi que sa caractérisation structurale. Une sous-section est consacrée à chaque couche individuelle de l'empilement. Un outil RF-Magnetron sputtering SPT310-TT de Plasmionique Inc. a été utilisé pour déposer chaque couche.

Des puces en silicium (1 mm x 1 mm) avec une couche d'oxyde natif ont été utilisées comme substrats. Avant le dépôt, les substrats ont subi un processus de nettoyage chimique. Ils ont été placés dans un bécher et immergés successivement dans une série de solvants polaires et non polaires, suivis d'une sonication de cinq minutes dans chaque solvant. Les étapes de nettoyage ont inclus de l'acétone, de l'isopropanol, de l'éthanol et de l'eau déionisée, dans cet ordre. Ensuite, le substrat a été séché sous un flux d'azote pur sous pression.

L'Hf_{0.5}Zr_{0.5}O₂ a été déposé directement sur le TiN sans casser le vide afin de minimiser la pollution externe. La chambre de dépôt a ensuite été ventilée pour placer des masques de type ombre sur le diélectrique afin de fabriquer plusieurs dispositifs sur une seule puce. La chambre a été évacuée à une pression de base de 10⁻⁵Torr entre chaque dépôt.

6.5.2 Comportement de commutation TiN/Hf_{0.5}Zr_{0.5}O₂/Au

Cette section présente les résultats de la caractérisation électrique des MIM-piles TiN/Hf_{0.5}Zr_{0.5}O₂/Au fabriquées. Deux aiguilles de tungstène, reliées à un source/measurement unit (SMU), ont été mises en contact avec les électrodes supérieure et inférieure respectivement. Le SMU contrôlait les balayages de tension et les impulsions appliquées aux dispositifs, tandis que les courants résultants étaient mesurés. À partir de ces résultats, des conclusions sur le comportement de commutation des dispositifs ainsi que sur le mécanisme de rétroaction négative émergent ont pu être tirées.

6.5.2.1 Caractérisation électrique générale

Les mesures quasi-statiques ont été effectuées en appliquant des balayages de tension triangulaires aux cellules mémoire et en enregistrant le courant résultant. Le taux de variation a été fixé à 1.75 V s⁻¹. Partant de 0 V, la tension a d'abord été réduite à -1.5 V, puis augmentée à 1.5 V, avant de revenir à 0 V, complétant ainsi la boucle. La mesure a été réalisée sur un total de 100 périodes.

Lorsqu'une cellule mémoire est dans son état initial, un filament conducteur doit d'abord se former lors d'une étape d'électroformation. Ce processus se déroule pendant le premier balayage de tension de 0 V à -1.5 V et provoque une déviation de cette partie de la courbe d'hystérésis par rapport aux cycles suivants. Dans les cellules fabriquées, l'électroformation se termine rapidement en raison de l'épaisseur réduite du film $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$. Aucun contrôle de courant n'a donc été utilisé ici. Lors des événements de commutation ultérieurs, seule une petite portion du filament est dissoute et reformée.

Figure 6.7 montre la courbe $I(V)$ d'une boucle complète d'hystérésis pour la cellule dans son état initial (vert), la deuxième itération (marine) et la 100^{ème} boucle (orange). La boucle commence à 0 V, à partir duquel la tension est progressivement réduite. Vers -0.67 V, la résistance diminue brusquement lors d'une opération SET, et la trajectoire de la caractéristique $I(V)$ suit ce nouveau chemin. Une fois -1.5 V atteint, la tension est de nouveau augmentée, tandis que la réponse en courant de la cellule est maintenant dictée par son état LRS. Un RESET a lieu vers 1.3 V, où la cellule revient dans l'état HRS. Le balayage de tension atteignant à nouveau 0 V marque la fin de la boucle d'hystérésis. La cellule montre un comportement de commutation fiable sur les 100 cycles mesurés, aucune variation significative de V_{SET} , V_{RESET} , ni des résistances en HRS et LRS respectivement n'ayant été observée.

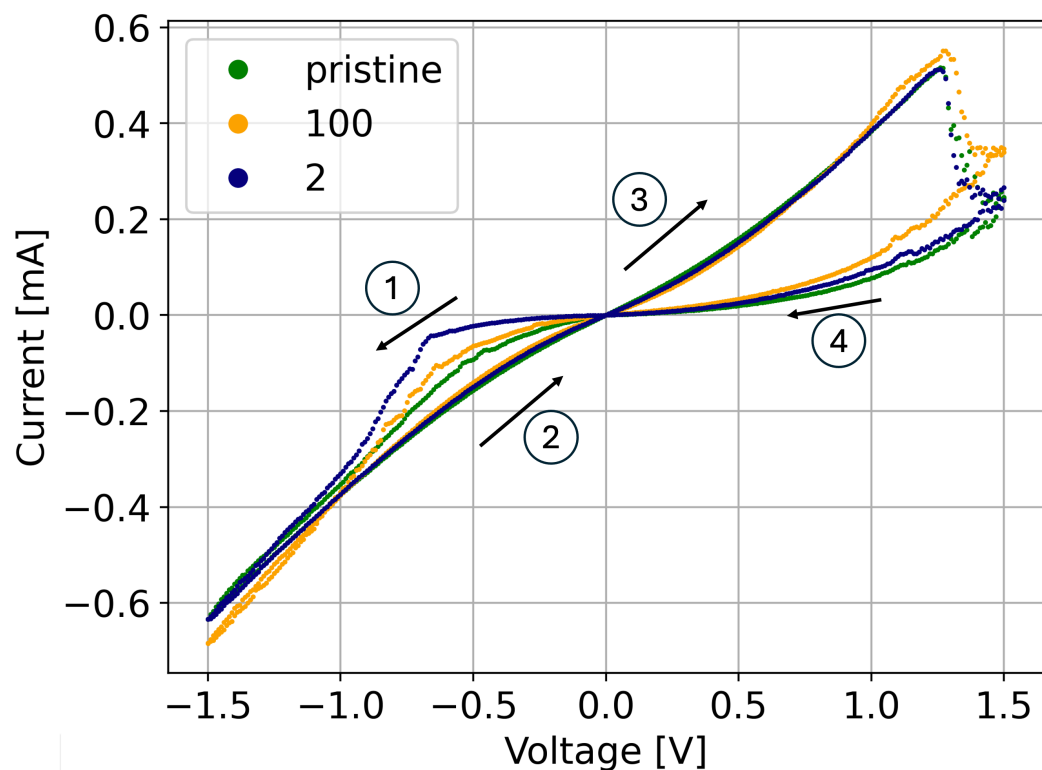


FIGURE 6.7. Caractéristique $I(V)$ pour la mesure de balayage de tension quasi-statique. Les courbes pour la première, la deuxième et la 100^{ème} itération sont affichées.

Des estimations des tensions de commutation et de lecture appropriées pour une opération

par impulsions peuvent être dérivées des mesures quasi-statiques. Étant donné que la durée des impulsions est bien plus courte qu'un cycle de balayage, les tensions requises doivent être réglées plus haut. Pour les mesures d'endurance suivantes, la hauteur de l'impulsion a donc été fixée à 2 V. De même, une tension de lecture de 0.5 V a été jugée appropriée, car aucune altération significative de la cellule n'est attendue à cette tension.

Après l'électroformation, un train d'impulsions de tension a été appliqué à la cellule mémoire. V_{SET} et V_{RESET} ont été réglés à 2 V et -2 V respectivement, tandis que la résistance de la cellule était mesurée en appliquant une impulsion de lecture de 0.5 V après chaque événement de commutation. La durée de chaque impulsion a été fixée à 10 ms. Figure 6.8 montre le résultat d'une mesure d'endurance sur un total de 5,000 cycles de commutation. Les résistances mesurées, correspondant respectivement aux états LRS et HRS, sont affichées en bleu marine et cyan. La cellule présente un comportement de commutation relativement stable, avec une résistance moyenne de HRS d'environ 13.8 k Ω et une résistance moyenne de LRS d'environ 4.2 k Ω . Cela donne une différence de résistance relative marquée d'environ 2.3.

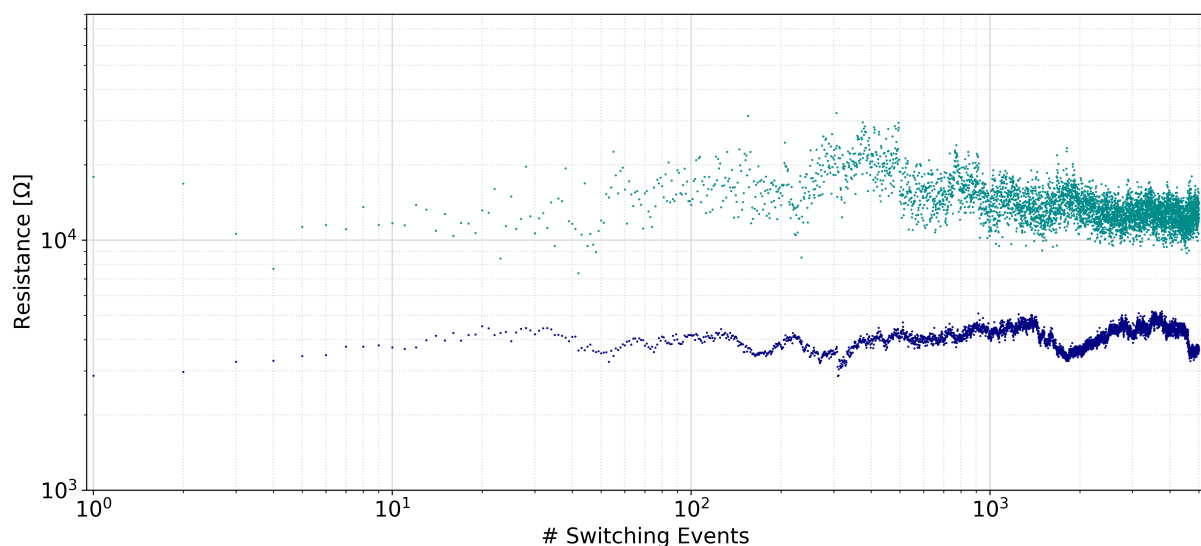


FIGURE 6.8. Mesure d'endurance sur 5 000 cycles de commutation.

Les mesures présentées évaluent la pertinence des dispositifs ReRAM fabriqués à base de lacunes d'oxygène pour la fabrication de mémoires conventionnelles. Elles montrent une bonne stabilité pour 100 cycles de commutation balayés ainsi que pour plus de 5 000 périodes de commutation par impulsions. Cependant, cela ne prouve pas encore leur viabilité pour une mémoire universelle, car de nombreux millions de cycles d'écriture seraient souhaitables. De plus, seules des vitesses de commutation faibles ont été étudiées et les mesures concernant la rétention des données ont été complètement omises, car une investigation plus poussée sur l'application des dispositifs fabriqués pour la mémoire conventionnelle sort du cadre de cette thèse.

6.5.2.2 Spike-Timing-Dependent Plasticity dans les Cellules ReRAM

Pour examiner la spike-timing-dependent plasticity (STDP) des dispositifs mémoire fabriqués, il est nécessaire d'étudier leur réponse à différents stimuli, établissant ainsi un lien entre leur comportement et celui des synapses dans les réseaux neuronaux biologiques. Alors que le retard temporel avec lequel les spikes pré- et post-synaptiques atteignent la synapse détermine la réponse de la synapse, les bornes du dispositif ReRAM peuvent être manipulées librement. Ainsi, une borne est mise à la terre tandis qu'une impulsion de tension est appliquée à l'autre. Un train d'impulsions de tension avec une hauteur croissante a été appliqué à la cellule, tandis que RESET a été effectué avec une impulsion de tension négative constante de -2 V . La résistance a été mesurée après les impulsions positives et négatives avec une impulsion de lecture de 0.5 V . La hauteur des impulsions positives appliquées a été augmentée linéairement de 1.5 V à 4 V en 1 000 étapes, tandis que la durée de chaque impulsion — pour la commutation et la mesure — était fixée à 5 ms .

Figure 6.9 montre le résultat de la mesure STDP. L'ordonnée montre la différence relative entre les résistances HRS et LRS, tandis que l'abscisse affiche la hauteur de l'impulsion de tension appliquée avec laquelle le rapport $\frac{\Delta R}{R_0}$ a été acquis. Jusqu'à environ 2.2 V , le comportement attendu d'une cellule mémoire montrant de la STDP peut être observé. Lorsque la hauteur du stimulus (l'impulsion de tension) augmente, la réponse et donc la différence entre les résistances mesurées augmentent également. Cependant, pour les cellules mémoire fabriquées, la réponse diminue pour les tensions supérieures à $\sim 2.2\text{ V}$ jusqu'à ce qu'aucune réponse ne puisse être observée autour de 3 V . Ce comportement indique qu'un mécanisme de rétroaction négative doit également être en jeu, qui contrecarre la formation d'un filament conducteur jusqu'à ce que la cellule ne réagisse plus du tout au stimulus. Cette rétroaction négative dans ce système hautement non linéaire est une condition nécessaire à l'émergence du chaos déterministe et explique également les bifurcations de doublement de période observées dans les mesures d'endurance par Gonzalez [5].

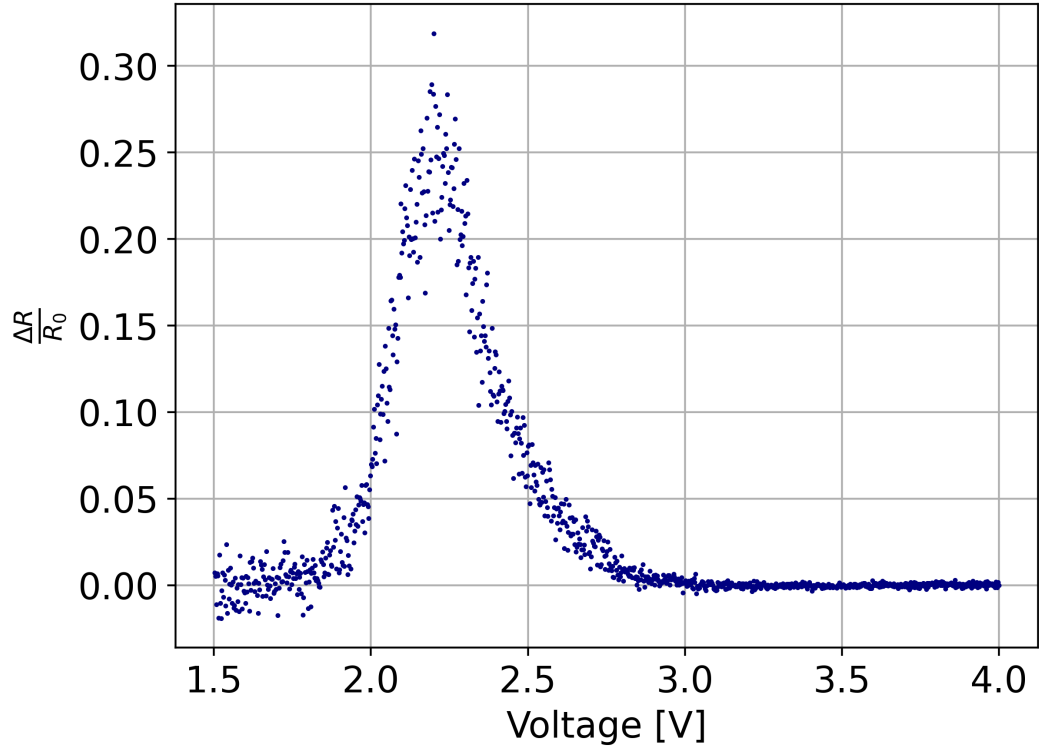


FIGURE 6.9. Mesure de la spike-timing-dependent plasticity (STDP) pour les cellules ReRAM fabriquées. Un mécanisme de rétroaction négative conduit à la réduction de la réponse de la cellule pour les impulsions de tension supérieures à ~ 2.2 V. Cette rétroaction négative constitue une condition préalable au chaos déterministe dans le comportement de commutation de la cellule.

6.5.3 Analyse microscopique des mécanismes de rétroaction négative

Cette section examine les effets énergétiques dissipatifs à l'échelle micro et nanométrique, qui contribuent aux mécanismes de rétroaction négative. Elle débute par l'analyse de l'influence du chauffage Joule sur la dissolution des filaments conducteurs dans les dispositifs à mémoire résistive basés sur les lacunes d'oxygène, un phénomène utilisé dans les mémoires unipolaires à changement de résistance (ReRAM). Ce chauffage favorise la dissolution des filaments, créant ainsi un processus auto-limitant pour le passage du courant.

Ensuite, la section présente un mécanisme de rétroaction potentiel dans les jonctions tunnel ferroélectriques (FTJ), où la création et la recombinaison des lacunes d'oxygène jouent un rôle clé. Dans ce cas, une plus grande densité de lacunes d'oxygène entraîne un blocage des parois des domaines ferroélectriques, réduisant l'inversion de polarisation et donc la réponse du dispositif aux stimuli externes.

6.5.3.1 Influence du chauffage Joule pour les commutateurs à filaments de lacunes d'oxygène

Le chauffage Joule décrit l'effet de génération de chaleur par le passage du courant dans une résistance. Cette dissipation d'énergie augmente la mobilité des ions d'oxygène, facilitant leur migration et leur recombinaison avec les vacantes d'oxygène. Ce phénomène provoque une augmentation locale de la résistance, limitant ainsi le passage du courant et régulant la croissance du filament conducteurs. Ce mécanisme de rétroaction négative impose un contrôle non linéaire sur la résistance du filament conducteur.

6.5.4 Commutation chaotique des cellules ReRAM

Afin d'examiner plus en détail la rétroaction négative mesurée, une expression mathématique pour la courbe présentée dans Figure 6.9 a été recherchée. Un ajustement avec une distribution log-normale modifiée a donc été effectué et est présenté dans Figure 6.10. L'équation utilisée pour cet ajustement est donnée par :

$$f(x) = \frac{a}{(x-b)\sigma\sqrt{2\pi}} \cdot \exp\left(-\frac{(\log_{10}(x-b)-\mu)^2}{2\sigma^2}\right). \quad (6.11)$$

Il est important de noter qu'aucune relation physique ne peut être tirée de ce choix d'équation, qui a été choisi uniquement en raison de la ressemblance de cette distribution avec l'ensemble de données mesurées.

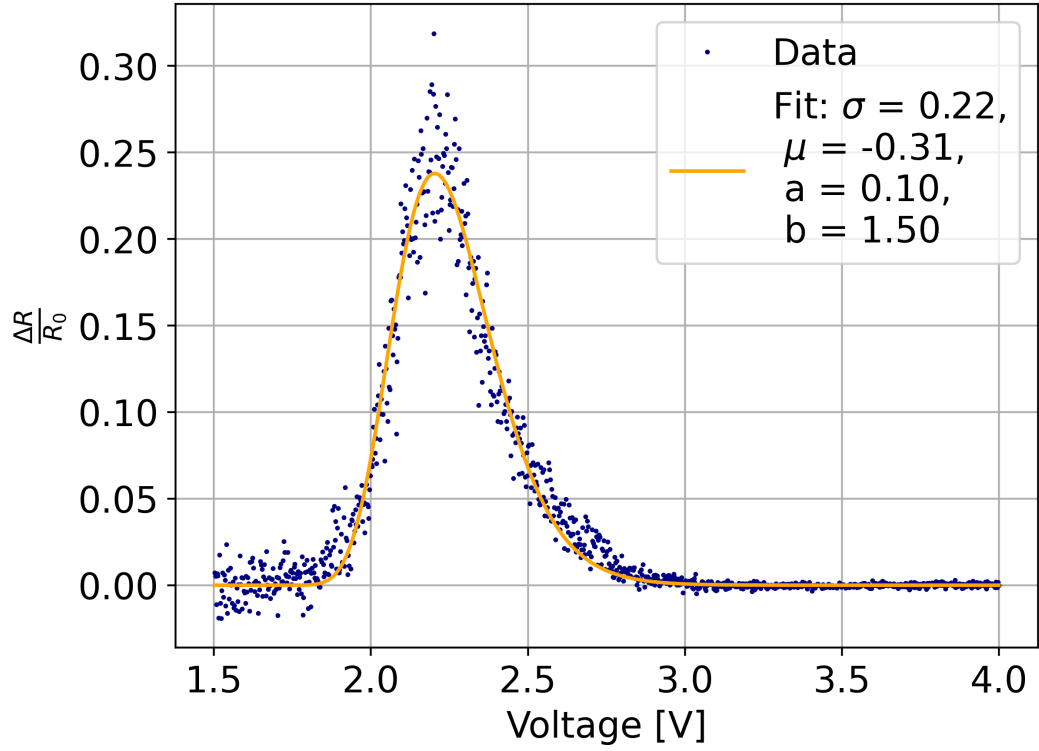


FIGURE 6.10. Fit de la fonction de distribution log-normale modifiée sur les données de mesure STDP.

Une fois une expression mathématique établie pour représenter la caractéristique STDP de la cellule, une exploration plus approfondie du début du chaos à travers le mécanisme de rétroaction négative sous-jacent est désormais possible.

Un diagramme de Feigenbaum a été calculé en appliquant un facteur de croissance variable r à cette expression, basé sur l'ajustement montré dans Figure 6.10. Le diagramme résultant (présenté dans Figure 6.11) illustre des bifurcations à double période, caractéristiques de la route classique vers le chaos déterministe observé dans la carte logistique. Cependant, le comportement chaotique dans ce système nécessite un facteur de croissance multiplicatif dans une plage très étroite, d'environ 9.397 à 9.455. Cette plage, avec une tolérance d'environ 0.058, met en évidence la précision nécessaire pour obtenir un comportement chaotique. De plus, le taux de croissance requis est particulièrement élevé, ce qui indique qu'une augmentation presque d'un ordre de grandeur du rapport ON/OFF serait nécessaire pour que ce comportement chaotique émerge.

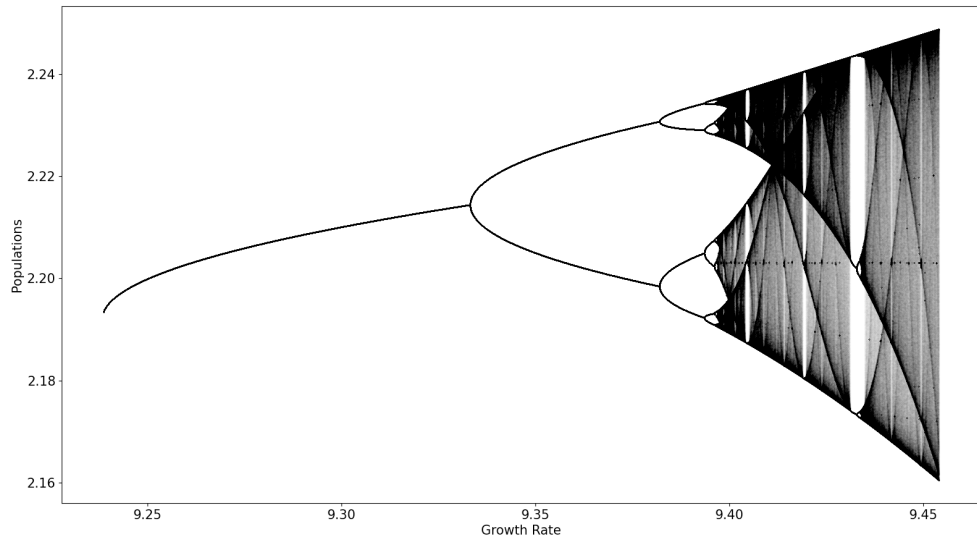


FIGURE 6.11. Diagramme de Feigenbaum de la fonction log-normale trouvée avec l'ajustement montré dans Figure 6.10. Le taux de croissance est multiplié à la fonction donnée dans Equation 6.11.

Les exposants de Lyapunov, montrés dans Figure 6.12, ont été calculés en fonction du taux de croissance. Le graphique résultant confirme cette idée : le comportement chaotique n'émerge que pour des valeurs spécifiques de r , tandis que la carte converge rapidement vers des attracteurs stables pour d'autres valeurs.

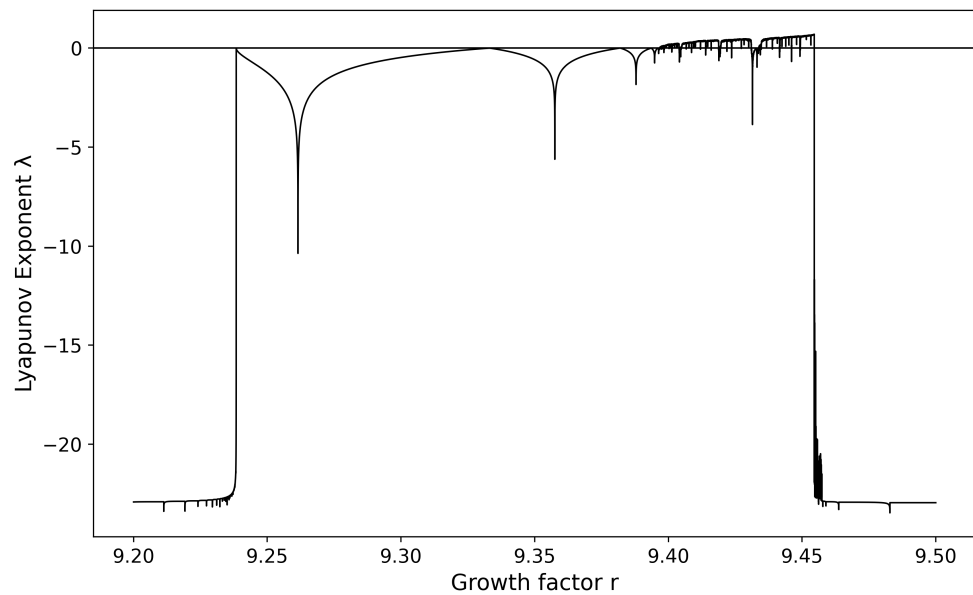


FIGURE 6.12. Exposants de Lyapunov correspondant au diagramme de Feigenbaum montré dans Figure 6.12.

La définition de l'exposant de Lyapunov indique que ce n'est pas la hauteur de la carte consi-

dérée, mais plutôt sa pente qui détermine l'apparition du chaos. Par conséquent, diverses approches devraient être envisagées pour augmenter à la fois le rapport ON/OFF et la sensibilité de la cellule mémoire aux stimuli externes. Cette sensibilité accrue pourrait être alimentée par l'accumulation de lacunes d'oxygène près de la région des filaments conducteurs perturbés pendant l'opération RESET, offrant ainsi un accès plus rapide à ces derniers pour fermer le filament lors de l'opération SET. Cette distribution évolutive des lacunes sous conditions opérationnelles pourrait finalement conduire à la transition vers un comportement chaotique, en faisant un processus dynamique enraciné dans l'opération du dispositif.

6.6 Résumé et Perspectives

Ce chapitre présente un aperçu des principales conclusions de cette thèse, en mettant en lumière les découvertes clés concernant le comportement chaotique des cellules ReRAM. Il propose également des pistes pour de futures recherches, notamment dans les domaines de la génération de nombres aléatoires, de la modélisation des pathologies neurodégénératives, et de l'amélioration des dispositifs de commutation résistive.

6.6.1 Résumé

Cette thèse explore les caractéristiques et la dynamique de la commutation résistive dans les cellules ReRAM, en mettant l'accent sur l'émergence d'un comportement chaotique à travers un mécanisme de rétroaction négative. L'étude examine le cadre mathématique sous-jacent régissant le processus de commutation, en utilisant une distribution log-normale modifiée pour ajuster les données mesurées. Cette distribution propose un modèle purement empirique pour les caractéristiques STDP des cellules, crucial pour comprendre la relation entre la tension appliquée et le changement de résistance.

Un diagramme de Feigenbaum est introduit, montrant des bifurcations par doublement de période typiques du chaos déterministe dans la carte logistique, et démontrant que le chaos dans les cellules ReRAM émerge dans une plage étroite de facteurs de croissance. Cette plage précise des valeurs du facteur de croissance est nécessaire pour induire le chaos, avec un taux de croissance élevé, indiquant qu'une augmentation presque d'un ordre de grandeur du rapport ON/OFF serait nécessaire pour manifester ce comportement chaotique. De plus, les exposants de Lyapunov sont calculés pour mettre en évidence les valeurs spécifiques du taux de croissance menant à des dynamiques chaotiques, renforçant l'idée que le chaos est extrêmement sensible aux paramètres du système.

L'analyse du chaos est étendue pour explorer comment les distributions de lacunes d'oxygène au cours du cycle de commutation peuvent influencer le comportement du dispositif, notamment lors des opérations de RESET et de SET. Ce processus dynamique, impliquant l'accumulation et la redistribution des vacanciers, est identifié comme un facteur potentiel déclencheur du chaos dans les dispositifs ReRAM.

Les résultats suggèrent que l'amélioration de la sensibilité des cellules ReRAM aux stimuli

externes—via des facteurs tels que la distribution des lacunes d’oxygène—pourrait faciliter la transition vers un comportement chaotique, pouvant être exploité pour des applications telles que la génération de nombres aléatoires et la modélisation de systèmes complexes.

6.6.2 Perspectives

Cette section explore les avenues futures de recherche et de développement issues des résultats de cette thèse. Elle examine comment le comportement chaotique observé dans les dispositifs à commutation résistive, tels que les cellules ReRAM, peut être exploité dans des applications pratiques, notamment la génération de nombres aléatoires et la modélisation de systèmes biologiques complexes tels que les pathologies neurodégénératives. En identifiant ces opportunités, cette perspective offre une vision de l’évolution de ces technologies et de leur contribution à un large éventail de domaines scientifiques et techniques.

6.6.2.1 Génération de Nombres Aléatoires

La génération de nombres aléatoires est un élément fondamental de nombreuses applications cryptographiques et statistiques, et son efficacité est cruciale pour garantir la sécurité et la performance des systèmes modernes. L’utilisation de dispositifs de commutation résistive (ReRAM), en particulier ceux montrant des comportements chaotiques, offre une voie innovante pour générer des nombres aléatoires véritablement imprévisibles. Ces dispositifs exploitent les mécanismes de rétroaction négative, tels que la migration et la recombinaison des lacunes d’oxygène, pour produire des transitions entre états stables et chaotiques. Le comportement chaotique observé dans ces dispositifs peut être utilisé pour générer des séquences de nombres aléatoires dont l’imprévisibilité est directement liée à la dynamique non linéaire du système. Les diagrammes de Feigenbaum et les exposants de Lyapunov calculés pour les cellules ReRAM illustrent comment de petites variations des paramètres du système peuvent provoquer des transitions vers des comportements chaotiques, fournissant ainsi une base robuste pour la génération de nombres aléatoires. Cette approche offre un avantage potentiel pour les applications de cryptographie, où la qualité et l’imprévisibilité des nombres générés sont essentielles pour assurer la sécurité des communications.

6.6.2.2 Modélisation des Pathologies Neurodégénératives

La convergence de l’informatique neuromorphique et de l’étude des pathologies neurodégénératives ouvre de nouvelles perspectives pour la recherche. Les dispositifs de commutation résistive, tels que les cellules ReRAM, exhibent des comportements chaotiques pouvant simuler les troubles neurologiques associés à des décharges neuronales irrégulières, comme dans la maladie d’Alzheimer, l’épilepsie et l’autisme.

Ces pathologies sont caractérisées par des décharges neuronales anormales, souvent chaotiques. Les cellules ReRAM, en raison de leur sensibilité aux conditions initiales et de leur comporte-

ment chaotique, peuvent modéliser ces dynamiques. En ajustant leurs paramètres, il est possible d'étudier des modèles de dysfonctionnement neuronal, comme l'excitabilité altérée et la perte de synchronisation. Cette approche permet de simuler les transitions entre états stables et chaotiques, analogues aux comportements observés dans ces maladies, et pourrait offrir de nouvelles avenues pour comprendre et traiter ces pathologies.

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Appendices

A. STDP curve acquired by Mittermeier et. al.

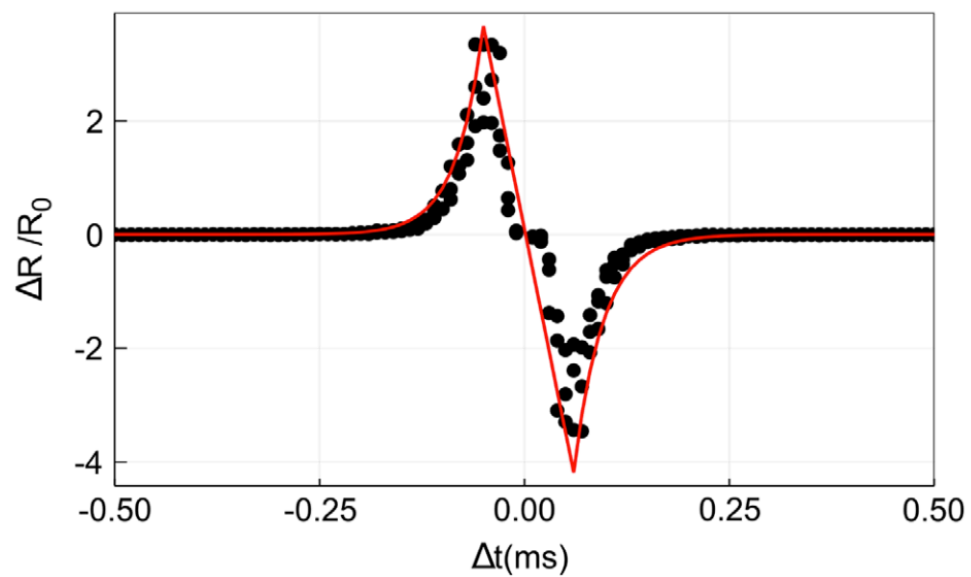


Figure A.1. STDP-curve for TiN/HZO/Pt stack. Adapted from Mittermeier *et. al.* (2019).

B. Exemplary Feigenbaum Diagrams for Non-Linear Maps

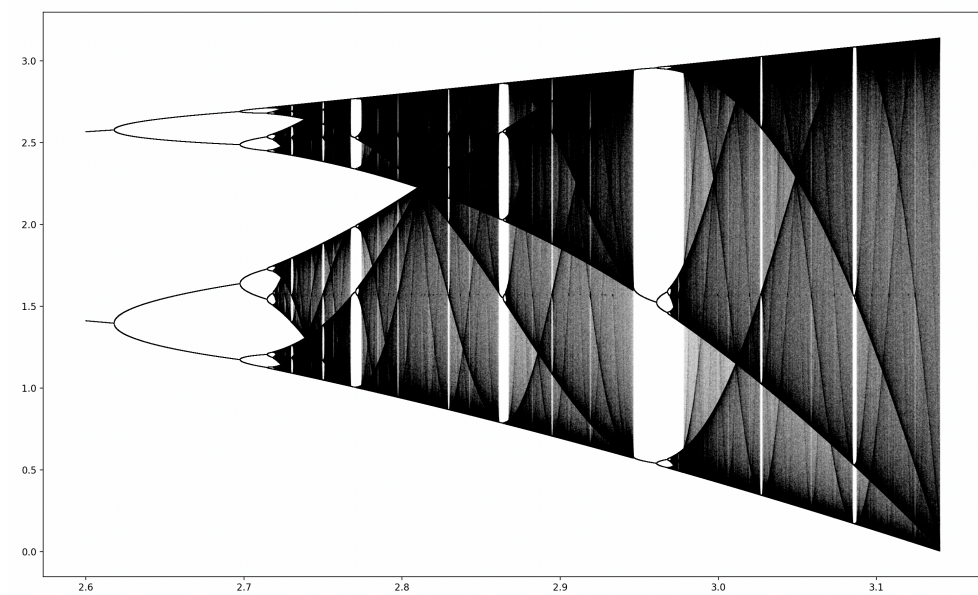


Figure B.1. Feigenbaum Diagram for $x_{n+1} = r \cdot \sin(x)$

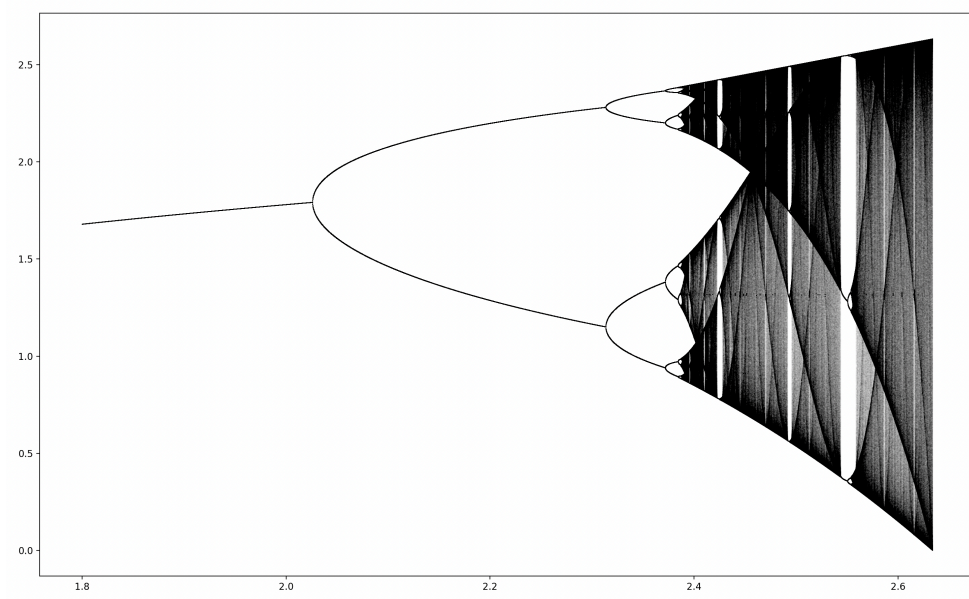


Figure B.2. Feigenbaum Digram for $x_{n+1} = r \cdot (-\cosh(x_n - 1.317) + 2)$

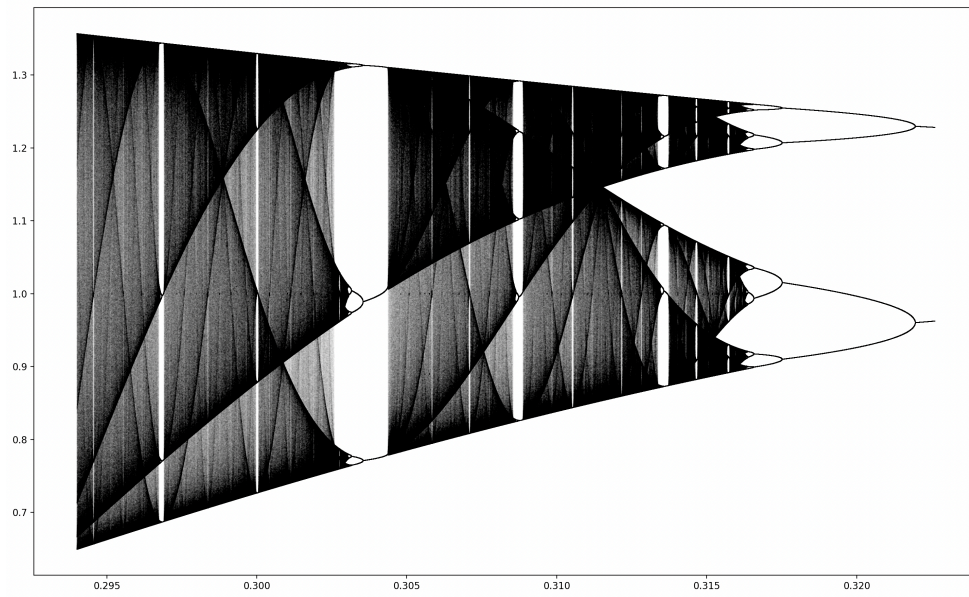


Figure B.3. Feigenbaum Digram for $x_{n+1} = \frac{r}{\sqrt{2\pi} \cdot \exp(-0.5 \cdot (x_n - 1)^2)}$

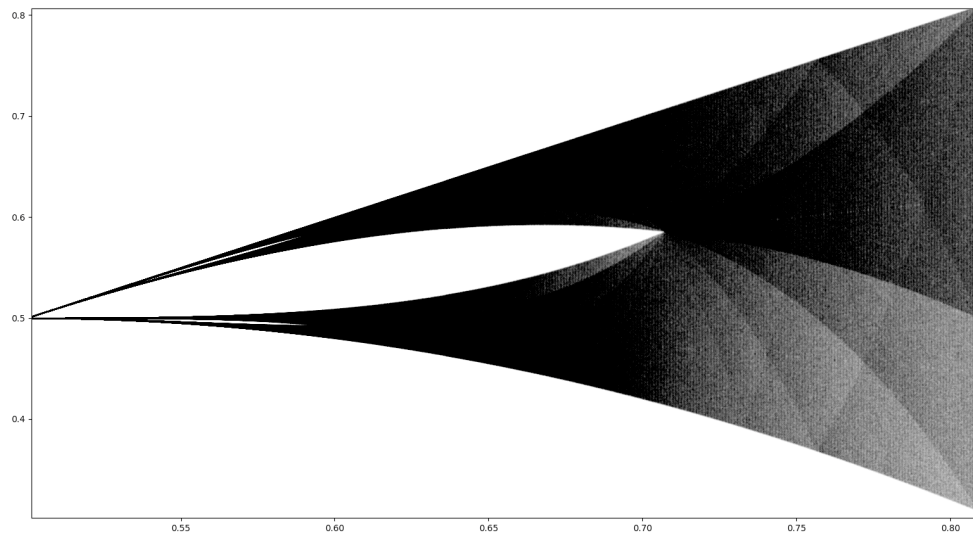


Figure B.4. Feigenbaum Digram for $x_{n+1} = r \cdot (1 - 2 \cdot |0.5 - x|)$