Arab American University Faculty of Graduate Studies Department of Health Sciences Ph.D. Program in Physics



Effects of Electrodes and Gd Doping on the Ferroelectric Properties of HfO₂ Thin Films Maisam Mohammed Ahmad Abdullah 201920348

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This Dissertation Was Submitted in Partial Fulfillment of the Requirements for the Doctor of Philosophy (Ph.D.) Degree in Physics

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Dissertation Approval

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Palestine, October/ 2024

Declaration

I declare that, except where explicit reference is made to the contribution of others, this dissertation is substantially my own work and has not been submitted for any other degree at the Arab American University or any other institution.

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Dedication

To my parents, brothers, sister. To my country Palestine, its martyrs, prisoners, and free people from the river to the sea.

Maisam Mohammed Ahmad Abdullah

Acknowledgments

Having this doctorate degree was one of my toughest personal challenges, it highlights how fortunate I am; even though this was my own effort on many aspects, it was not possible without the grace of Allah, teamworking and support of many people surrounded me. I would like to mention that this work has been done in a very limited period of time with much difficulties, what a challenge that was! I'm glad that I did it under a tight timeline.

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I hope you find this manuscript insightful. It was an honor and a pleasure to have such high-profile researchers on my final exam committee.

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Effects of Electrodes and Gadolinium-Doping on The Ferroelectric Properties of Hafnium (IV) Oxide Thin Films

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Abstract

Ferroelectrics have a wide range of applications relevant properties, such as spontaneous polarization that can be reversed by applying of electric field. This class of materials is represented by perovskites (ABX₃, which are used in sensors, actuators and non-volatile memories. The non-volatile memory application has crucial technological challenges; since perovskites are not easy to integrate into CMOS fabrication. The high annealing budget and instability of ferroelectric phase at ultrathin scale are two main issues that prevent aggressive scaling.

The discovery of ferroelectricity in hafnia-based films 13 years ago get the ferroelectric random-access memories (FeRAMs) back to the race. They are employed in CMOS technology and were evidenced to retain their ferroelectric properties down to few nanometers (5 nm or lower), controlling the limitations of perovskites class and bringing them as the ideal candidate for low power ferroelectric applications. Afterwards, research focused on the physics behind the polarization response, improving a reliable fabrication process for integration in memory devices. This work addresses intriguing and partially controversial points and contributes to CMOS-compatible processing of ferroelectric HfO₂.

In this thesis, the hafnia films are grown by plasma enhanced atomic layer deposition (PEALD) technique. The fabrication and characterizations of TiN/(Gd):HfO₂/SiO₂/Si metal/oxide/semiconductor (MOS) and TiN/Gd:HfO₂/TiN/SiO₂/Si metal/ferroelectric/ metal (MFM) are considered. The layers need high thermal budget to get ferroelectric properties. The three deposited layers and interfaces are studied by means of x-ray reflectometry (XRR), grazing incidence x-ray diffraction (GIXRD), in-plane and out-of-plane Bragg-Brentano x-ray diffraction, leakage current, positive up negative down and endurance measurements.

The ferroelectric properties evidenced on undoped hafnium oxide which are similar to those of doped HfO_2 are rather unexpected since it is believed that doping is a prerequisite to stabilize the HfO_2 ferroelectric behavior. Two different origins were invoked to account for this behavior. The first is related to thermodynamically HfO_2 orthorhombic/ferroelectric phase favored upon the monoclinic/non ferroelectric one by its lower surface energy in very small crystallites, i.e. in very thin layers. The second one is related to the existence of mechanical stress within the HfO_2 layer that allows the stabilization of non-centrosymmetric orthorhombic/ferroelectric phase.

The mechanical stress is due either to doping or to top and bottom metal layers in the metal/HfO₂/metal stack. The origin of undoped HfO₂ ferroelectric behavior is still under debate. In this work, additional evidence of the mechanical stress role in stabilizing the HfO₂ ferroelectric phase is presented. The effect of top and bottom TiN electrodes on the crystallization of Gd-doped and undoped HfO₂ layers were studied as a function of the layer thickness.

The results show that the HfO_2 orthorhombic phase of undoped HfO_2 disappears when the bottom TiN electrode is removed. In contrast, Gd-doped HfO_2 layers show intense orthorhombic phase even without the TiN bottom layer. The mechanical stress role is further evidenced by atomic planes interplanar distance measurements which show a large deformation between in-plane and out-of-plane x-ray diffraction geometries, only in the case of Gd-doped HfO_2 .

In addition to, the effect of annealing before and after capping TiN layer on TiN/Gd:HfO₂ /TiN/SiO₂/Si (MFM) stacks were presented structurally and electrically. Structurally, the orthorhombic/tetragonal phase peak can be seen in thickness range of 5-42 nm.

Electrically, it was observed that the total remnant polarization value $(2P_r)$ shrinks via over 24.8 and 29.7 nm-thick of Gd:HfO₂ layers due to orthorhombic phase relaxation into tetragonal phase, for MFM capacitor devices encapsulated with top TiN electrode before and after annealing, respectively. Furthermore, an evident gradual increase and decrease in total remnant polarization value $(2P_r)$ and coercive field (E_c) values, in respective, upon cycling were registered. Thus, such MFM devices can be employed as non-volatile memory applications.

Keywords: PEALD, hafnium oxide, ferroelectricity, Gd-doped HfO₂, remnant polarization.

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List of Definitions of Abbreviations

Abbreviations	Title
FeFET	Ferroelectric Field-Effect Transistor
FeRAM	Ferroelectric Random Acess Meomories
PLD	Pulsed Laser Deposition
PZT	Lead Zirconate Titanate
HZO	Hafnium Zirconium Oxide
BTO	Barium titanate
HfO ₂	Hafnium Oxide
Gd	Gadolinium
CMOS	Complementary Metal-Oxide-Semiconductor
CMOS	Metal-Oxide-Semiconductor
MFM	Metal/Ferroelectric/Metal
PEALD	Plasma Enhanced Atomic Layer Deposition
ALD	Atomic Layer Deposition
XRR	X-Ray Reflectometry
XRD	X-Ray Diffraction
GIXRD	Grazing Incidence X-Ray Diffraction

Chapter One: Introduction

The properties of ferroelectric materials make them very suitable for several technological applications. These days, they are employed in nonvolatile memory, capacitors, sensors and actuators and infrared detectors due to their hysteretic behavior, high permittivity, piezoelectric effect and high pyroelectric coefficient.

Ferroelectric Random Access Memory (FeRAM) is a non-volatile semiconductor application that has been reported intensively over the past few decades [S. J. Kim, Narayan, et al.,2017]; [Bondurant and Gnadinger,1989]; [Onishi et al.,1994]; [Kinam Kim and S. Lee,2006]; [Thomas Mikolajick et al.,2001]. FeRAMs are a promising type of non-volatile memories technology for data storage since the 1980s [Bondurant and Gnadinger,1989], which was successfully integrated into a Complementary Metal-Oxide Semiconductor (CMOS) environment [Onishi et al.,1994]. However, the earlier FeRAMs were based on the use of perovskite materials, mostly the lead zirconate titanate (PZT), which presents key shortcomings related to high temperature annealing process, complex crystal structure and the difficulty to scale down the PZT layer thickness below 70 nm [Kinam Kim and S. Lee,2006]; [Thomas Mikolajick et al.,2001].

In the early 2010s, Boscke et al. [Böscke et al.,2011] evidenced a ferroelectric behavior in Silicon-doped Hafnium Oxide Si:HfO₂, which revitalized the potential of FeRAM technology and opened an interesting pathway for new research and application perspectives, as a high k-dielectric material [S. J. Kim, Mohan, Harrison Sejoon Kim, et al.,2020]; [M. H. Park, Y. H. Lee, H. J. Kim, Y. J. Kim, et al.,2015]; [S. J. Kim, Mohan, Scott R Summerfelt, et al.,2019]; [Robin Materlik, Künneth, and Alfred Kersch,2015]. Although HfO₂ can crystallize in four different phases; cubic, monoclinic, tetragonal and orthorhombic, the monoclinic crystallographic phase is the most stable one.

The HfO_2 monoclinic phase is centrosymmetric that prevents it from being ferroelectric. In contrast, the HfO_2 orthorhombic phases with a space group of $Pca2_1$ is non-centrosymmetric and hence it is ferroelectric but its formation should be favored over the monoclinic phase.

Different approaches have been adopted to lead to a stable non-centrosymmetric ophase formation, among which doping with different elements like Si [Böscke et al.,2011], Al [Stefan Mueller et al.,2012], Y [Müller, Schröder, et al.,2011], Sr [Tony Schenk, Stefan Mueller, et al.,2013], Gd [Mueller et al.,2012]; [Adelmann et al.,2010]; [Reinke, Kuzminykh, and P. Hoffmann,2015]; [Hoffmann et al.,2015]; [Belahcen et al.,2020]; [Skopin et al.,2022]; [Alrifai et al.,2023], Zr [M. H. Park, H. J. Kim, Y. J. Kim, Y. H. Lee, Moon, Keum Do Kim, Hyun, Franz Fengler, et al.,2016], La [Chernikova et al.,2016] and N [Nishimura et al.,2016] was the most effective. Thus, it was evidenced that doping leads to the stabilization of HfO₂ orthorhombic phase, although the physical origin of this stabilization remained under debate.

While previous studies have investigated Gd-doped HfO₂ layers, they primarily focused on thin films, typically less than 12 nm in thickness [Mueller et al.,2012]; [Adelmann et al.,2010]; [Reinke, Kuzminykh, and P. Hoffmann,2015]; [Hoffmann et al.,2015]; [Belahcen et al.,2020]; [Skopin et al.,2022]; [Alrifai et al.,2023]. In contrast, my thesis explores Gd-doped HfO₂ across a larger thickness range, revealing ferroelectric behavior even at thicknesses that had not been studied before.

This work also aims to provide a contribution in understanding of HfO_2 thin films, which is a recently explored class of ferroelectric materials with unique properties that are expected to represent a new revolution in the field [Böscke et al.,2011]. The most challenging is to show ferroelectric behavior for ultrathin layer down to few nanometers. The theoretical study is mainly concerned with characterization of polarization, stabilization of ferroelectricity and factors affecting it.

The peculiar conditions that are related to the degradation of ferroelectric behavior in HfO₂-based thin films at very ultrathin layers (few nanometers) bring new challenges. In particular, the issues which were known in other family of ceramic ferroelectrics (perovskite) are supposed to be predominant role in this work.

At the same time, with the new class of ferroelectric material, it is potential to achieve a great step ahead in overcoming some of pressing technological challenges. Namely, the devices that are required by recent innovations; such as autonomous drive, demand reduction of power consumption and device scaling. The most promising application of these materials is in the field of non-volatile memories, super-capacitors, sensors and neuromorphic devices and more [A. Chen,2016]; [M. H. Park, Y. H. Lee, Thomas Mikolajick, et al.,2018].

There are several technological requirements that have to be achieved if someone wants to commercialize a ferroelectric device [Z. Li and Haas,2016], including: low operation

voltage in order to reduce power consumption, good retention (about 10 years), endurance 10^{15} cycles with minimal degradation, strong and stable polarization response, low thermal budget, and smooth integration into CMOS technology.

The amorphous films of HfO_2 films are used as high dielectric material since couples of years ago [Bohr et al.,2007]; [Guha and Narayanan,2009]. However, the required annealing step at temperature higher than 450-500 °C, to crystallize and stabilize the correct ferroelectric phase bring new challenges [M. H. Park, D. H. Lee, et al.,2020]. Additionally, the annealing step during fabrication for ultrathin layers leads to an interface effect, between electrode and ferroelectric materials; which has a crucial role in determining the functional properties and switching mechanism of the film.

Another sensitive point emerging from reported studies, that the operation voltage scaling seems to be interrupted for ultrathin layer (less than 10 nm), leading to difficulty in realization of sub-1 V devices [M. H. Park, D. H. Lee, et al.,2020]. Furthermore, the amount of strain level imposed to the film has a great importance to think about, the stress induced by annealing after growing the top electrode, the bottom electrode on which the film will be deposited on and doping are crucial points that significantly affect the crystallization and stabilization of non-centrosymmetric orthorhombic phase and will be presented hereinafter.

Overall, the retention of ferroelectric properties for extremely ultrathin layers acts like the greatest advantage of HfO_2 -based films. This renovated the interest in FeRAMs and lead to other applications in low-power consumption electronics. On the other hand, there are several hurdles in device commercialization; thus, this work is undertaking a wide approach in dealing the mentioned issues; by offering deep analysis of switching mechanisms in films of different thicknesses, coercive field scaling with different interface materials.

This thesis is divided into four chapters. The first chapter present a general introduction and motivation of this work. The second chapter starts introducing the fundamental terms of crystallography, an overview of electrical and structural properties of ferroelectrics in crystalline materials and the status of research on ferroelectric HfO₂-based films and some relevant quantities that will be used in this study.

The third chapter will present the fabrication process used to create the Metal-Oxide (ferroelectric)-Semiconductor (MOS) and Metal-Oxide (ferroelectric)-Metal (MFM) de-

vices that are investigated in this work. After that, the photolithography and etching steps to obtain the capacitor structures that were studied. The second and third sections of the chapter will describe, in respective, structural and electrical characterization techniques that were utilized to analyze the ferroelectric properties of HfO₂-based thin films.

The fourth chapter demonstrates the effect of TiN electrodes and Gd doping on crystallization of ferroelectric phase in HfO₂-based thin films. The first section presents a study on undoped and Gd doped HfO₂ films, which were deposited onto SiO₂/Si substrate, where the mechanical stress inside the material is explored by means of grazin incedence x-ray diffraction (GIXRD), in-plane and out-of-plane x-ray diffraction (XRD), and analyzed by using appropriate mathematical formulas.

The second section mainly presents the evolution of ferroelectric properties in TiN/ Gd:HfO₂/TiN/SiO₂/Si thin films in thickness range 5-40 nm. Furthermore, the endurance behavior of such films was explored by analyzing the progress of hysteresis behavior upon electrical cycling.

Chapter Two: Literature Review

This chapter starts by introducing, in the first section, the fundamental terms of crystallography and an overview of electrical and structural properties of ferroelectrics in crystalline materials. The second section presents the status of research on ferroelectric HfO₂-based films. The third and last section introduce some relevant quantities that will be used in this study.

2.1 Fundamentals of ferroelectricity

About a century ago, in 1921, the ferroelectric materials were reported as the first time. A permanent polarization was observed by Joseph Valasek [Valasek,1921]. The progress in this field was made in 1946 and after when ferroelectricity was discovered in $BaTiO_3$ (BTO) with perovskite structure. The last significant discovery was in 2011, when a permanent polarization appeared in Si:HfO₂ thin films [Böscke et al.,2011].

Different kinds of materials show a ferroelectric behavior; such as: ceramics (perovskite structures), which were the most investigated, thus, the BTO and PbZrO₃-PbTiO₃ (PZT) are the most important class of ferroelectric materials. This section will introduce ferroelectricity from electrical and structural point of view; the displacement of charges inside the material and crystal symmetry that makes ceramics to be ferroelectric. Then, the polarization switching and ferroelectric domains as well as structural defects will also be discussed.

2.1.1 Crystal structure: Fundamental terms of crystallography

Crystal structure refers, classically, to the atomic structure of solid material in thermodynamic equilibrium. It is the arrangement of atoms in an ordered pattern. By increasing the level of crystallinity, a solid is referred to: amorphous (no crystals and short-range order), polycrystalline (several crystalline areas of short- and long-range order, called grains) and monocrystalline (only one grain) [Sze, Y. Li, and Ng,2021].

To move from one point to another, only one discrete translation operations are possible.

Each point has a combination of three primitive vectors multiplied by an integer. The set of translation operations results in the Bravais lattice, which describes the positions of atoms in the crystal. There are 14-latices in 3D space, as tabulated in table 2.1.

The point group is a set of symmetry operations fixes one point and maps one lattice point onto another one. The possible symmetry operations involve rotation, rotary inversion and reflection. They are 32-crystallographic point groups, since the crystal has to display a 3D translation symmetry. Each crystal class describes all possible crystal symmetries. It is a combination of 32-point groups and 14-Bravais lattices enhanced with screw axis and glide plane symmetry operations.

The Hermann-Mauguin notation is the international standard to describe crystalline patterns [Sze, Y. Li, and Ng,2021]. Space groups are assigned by a set of 4-symbols, with the first symbol represents the center of lattice parameters, as it is seen in table 2.2. The following 3-symbols are based on the symmetry operations that are visible when the lattice is placed along a high symmetry axis. Table 2.3 summarize the related symbols.



Table 2.1: Selection of Bravais lattices with the edge lengths along a, b, c axes and the angles between them.

Table 2.2: Hermann-Mauguin notation for symbolism of lattice centering [Sze, Y. Li, and Ng,2021].

Symbol	Name	Explanation
Р	primitive	no additional lattice points
Ι	body centered	additional lattice point in the center of the unit cell
F	face centered	additional lattice point in the center of each of the cell faces
A, B, C	base centered	additional lattice point at one pair of opposite cell faces
R	\mathbf{r} hombohedral	no additional lattice points; special case of P

Table 2.3: Hermann-Mauguin notation for symbolism of symmetry operations [Sze, Y. Li, and Ng,2021].

Symmetry Element	Symbol	Examples
<i>n</i> -fold rotation axis	n	$1, 2, 3, 4, 5, 6, 7, 8, \ldots$
<i>n</i> -fold rotoinversion axis	\overline{n}	$\overline{1}, \overline{2}, \overline{3}, \overline{4}, \overline{5}, \overline{6}, \overline{7}, \overline{8}, \dots$
mirror plan \parallel or \perp to rotation axis	m or /m	
screw axis with a rotation angle of $\frac{360^{\circ}}{n}$ and	\mathbf{n}_m	$2_1, 3_1, 3_2, 4_1, 4_2, 4_3, 6_1, 6_2, \ldots$
translation along the rotation axis of $\frac{m}{n}$ -th of		
the lattice vector		
glide plane with a glide translation along half	a, b, c	
the respective lattice vector		
glide plane with a glide translation along a quar-	d	
ter of a face diagonal		
glide plane with two glides along the half of two	е	
different lattice vectors		
glide plane with glide translation along with half	n	
a face diagonal		

2.1.2 An overview of electrical properties of ferroelectrics

Ferroelectrics are a unique subgroup among all dielectric materials. To fully explain ferroelectricity, we need first to define dielectric materials from an electrical standpoint and then, from crystallographic point of view, to explore the requirements that a material must meet to be classified as a ferroelectric material [Damjanovic,1998]. The application of an electric field, E_j (V/m) (j = 1,2,3) on an insulating material slightly separate positive and negative charges, this displacement is called polarization. The applied electric field and polarization are related by:

$$P_i = \chi_{ij} E_j \tag{2.1}$$

Where χ_{ij} (F/m) is dielectric susceptibility, a symmetrical second-rank tensor, and P_j is the polarization vector. The subscripts ij illustrate orthogonal directions in 3D space. The total surface charge density induced in an insulating material by an applied electric field can be represented by the dielectric displacement vector, D_i (C/cm²), which accounts for polarization of the material itself, P_i, and polarization of the free space, is the permittivity of free space ε_0 .

$$D_i = \varepsilon_0 E_i + P_i \tag{2.2}$$

By including these two equations, D_i provides a measure of the total charge density within the material due to the applied electric field E_i :

$$D_i = \varepsilon_0 E_i + \chi_{ij} E_j = \varepsilon_0 \delta_{ij} E_j + \chi_{ij} E_j = (\varepsilon_0 \delta_{ij} + \chi_{ij}) E_j = \varepsilon_{ij} E_j$$
(2.3)

Where ε_{ij} is the dielectric permittivity of the material, δ_{ij} is Kronecker delta. In the application-relevant plane capacitor configuration, where the insulator is surrounded by two conductive electrode plates, there is simplifications can be introduced. The first one; in ferroelectrics, χ_{ij} is greater than ε_0 , thus $\varepsilon_{ij} = \chi_{ij}$. Also, polarization is the dominant contribution to displacement D in ferroelectrics, $D \approx P$. The second one, it is assumed that electric field (E), polarization (P) and displacement (D) are all uniformly aligned alongside the vertical direction; accordingly, i = j = 3 and subscripts are omitted together. Equation 2.3 can be rewritten for a ferroelectric in plane capacitor structure as:

$$D = \frac{q}{A} = \varepsilon E = \varepsilon_0 \ \varepsilon_r \ E \tag{2.4}$$

Where q is the charge at capacitor surface and A is the area of metallic electrodes. The relative permittivity is (ε_r) is the dielectric constant of the material $(\frac{\varepsilon}{\varepsilon_0})$.

Ferroelectric material is different from other dielectrics due to a spontaneous polarization P_s even in the absence of an external electric field E. Such a polarization can be switched if it is affected by a field, in the opposite direction, that is stronger than coercive field E_c . This conduct implies the insurgence of hysteresis in the polarization response while sweeping the electric field, as shown in Fig. 2.1 (b).

The intercept point on the y-axis is called remnant polarization P_r , which is a bit different from P_s in the practical case where ferroelectric domains are formed withinside the material. This difference can be ignored for now, it will be explained later in more details. The P-E curve is obtained as time integration of the transient current, which is measured across the capacitor as electric field is applied (higher than E_c). Figure 2.1 (a) shows the I-E curve plotted from this measurement [Damjanovic,1998].



Figure 2.1: (a) Displacement current versus electric field dependency of a ferroelectric material. (b) Typical hysteresis loop extracted from it.

2.1.3 Ferroelectric domains and polarization switching

Polarization is considered as a macroscopic effect that can be identified by surface charges on a material. Going back to Fig. 2.1 (b), one can observe the two stable polarization states, also, the switching from one polarization state to the other doesn't occur abruptly, it is punctual and occurring at one precise value of the field. The points where the loop cross the positive and negative x-axis are called coercive fields. However, the polarization reversal process starts before and continues after these field values.

As discussed before, the spontaneous polarization appears along one or more crystal axes that allow phase transition during cooling down the crystalline material. However, these crystal axes and polarization can be oriented in different directions throughout the material, since the boundary conditions are different in electrical and mechanical properties. Ferroelectric materials include small continuous regions that contribute small orientation of spontaneous polarizations called domains. Such domains possess its own hysteretic behavior of different bias and coercive fields leading to a switching shift along the field axis. Splitting the material into domains leads to a spread of polarization switching with respect to applied field.

For more qualitatively details, the P-E hysteresis loop is presented in Fig. 2.2. When a

positive electric field is firstly applied across the material, part of the domains switch until the coercive electric field is achieved, where most of the ferroelectric response is already appeared (from A to C). At this point, the domains are left to switch is less and polarization is saturating (from C to D), where the relationship between P and E is approximately linear. After that, the applied field to the ferroelectric decreases and accordingly (from D to F); the polarization reduces, due to switching back some domains very early on.

Polarization crosses the point of zero electric field with a positive remnant polarization value P_r and only becomes zero at the negative coercive field ($-E_c$). The polarization is reversed completely with more negative applied field (from F to G). Afterward, polarization reduces until it switches at the positive E_c upon increasing the field (from G to D). One can see hexagons at the critical points, which represent the domain configurations, where E and P are zeros and at saturation.

A mixed domain configuration is seen at the positive and negative coercive fields, while a monodomain state is achieved for high applied field. One can observe the difference between the saturation polarization P_s and the remnant polarization (P_r), respectively, (P_r is less than P_s); which is attributed to some domains that already start switching back when the applied field is decreased. This loop is supposed to be symmetric with respect to x and y axes (ideally), but there are many reasons that affect this symmetry, as will be discussed hereinafter.



Figure 2.2: Ferroelectric hysteresis loop conducted on a PZT sample. The hexagons sketch domain configuration of the material at different points of the loop, reproduced and adapted from [Damjanovic,2006].

Formation of the domains occur due to the minimization of Gibbs energy; two oppositely charged surfaces would appear if the polarization is uniformly aligned everywhere in the material. Consequently, a depolarization field E_d is created proportionally withinside the material in an opposite direction to polarization, which has high energy cost.

This effect can be cancelled by the creation of opposite ferroelectric domains, as it is seen in Fig. 2.3 (b), which are separated by 1-10 nm fine region (ferroelectric domain wall). The direction of such polarization changes oppositely from that of domain to that of another next domain, with 180° domain wall between them. However, domain walls with different angles exist if the domains are aligned differently. In such a case, there is a strain associated to them and the walls become ferro-elastic domain walls.



Figure 2.3: (a) A ferroelectric material has a uniformly aligned polarization P_s , which leads to a depolarization field E_d , b) a more favorable lower energy configuration with ferroelectric domains of opposite P_s , that ideally enables the cancellation of E_d [Damjanovic,2006].

Suppose there is no sufficient screening and charges don't compensate. In that case, the insurgence of E_d is an unavoidable result: The displaced charges always create a field that is opposite to the polarization direction, leading to an increase in Gibbs free energy inside the material. The compensation can be occurred internally or externally: at the outer surface, compensation can be achieved by the outcoming electrons from a conductive electrode or ions in the air [Kalinin et al.,2018].

Although the domain walls act like interfaces and appear imperfect, splitting into domains costs energy. Then, the result of a complex energy minimization process is domain formation upon phase transition, considering the surface energy associated to electric and elastic field, and that of domain walls [Damjanovic,2006]; [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019]. The real picture of polarization inside the material includes multiple domains with different alignment states. However, ideally, in single crystalline structure can have a monodomain configuration, whereas in a polycrystalline material, many domains with different alignments can be observed, oriented as possible close as the polarization direction or along it.

It is worth mentioning that the applied field increases up to a point, where it leads to instability in the crystal, which switches suddenly to opposite stable state; this is called intrinsic switching (or thermodynamic). On the other hand, in reality, Domains of opposite direction start forming at the interface and polarization reversal occurs gradually; such a switching is called extrinsic. The mechanism includes domain nucleation and growth parts [Damjanovic,2006].

At the end, the mechanism of main domain formation and how different polarization switching processes contribute, when the material is polycrystalline thin film of bulk state, were introduced simply. The interfaces, charged species, inclusions and other kind of defects are important to be understood for complete explanation of ferroelectricity. Thus, the effect of defects on ferroelectricity will be presented in the next subsection.

2.1.4 Structural defects and their impact on ferroelectric properties

This subsection shows that defects are a must in real ferroelectric materials and have a crucial role in identifying properties. There are several kinds of impurities; such as: point defects like atoms of foreign elements, which can be neutral or charged with respect to the substituted element in the crystal. This affects the material when it is exposed to electric field. Furthermore, they can be smaller or larger in diameter affecting the strain of crystal lattice.

It is worth noting that materials are engineered to differ from perfect crystal to enhance the ferroelectric properties; such engineering is called doping. One more example of point defects are oxygen vacancies; they were the most reported defects and are formed to compensate dopant charge in the material fabrication process. Their amount and distribution can be changed by phase transition and electrical cycling [Pešić et al.,2016].

Dislocations, as another kind of defects with higher dimensionality, occur when there is an error in the stacking of atoms leads to modification from one atomic layer to another. Thus, the stress increases and the ability of the material to deform becomes higher due to the dislocation. Grain boundaries are surface defects due to the polycrystalline material (not single crystals). The more smaller grain size, the more grain boundaries exist and vice versa, which is related to the film thickness; it is considered as an important factor to control to modify the ferroelectric properties [Hyuk Park, Joon Kim, Jin Kim, Moon, et al.,2014]; [D. Ye et al.,2014]; [Ihlefeld et al.,2016].

Another example of surface defect is the interfaces with other materials (top and bottom electrodes), where a lot of attention was paid here due to vital effect on both electric fields withinside the ferroelectric and stress [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019]. In HfO₂-based thin films, sometime there is a region which is not stabilized in the desired ferroelectric phase is called volume defect [Shiraishi et al.,2016].

All these kinds of defects and its effect should be taken into account when one need to enhance ferroelectric properties. On the other hand, defects have side effects that will now be discussed.

In ferroelectric devices, imprint is one of the problems that hinders the technological development; the coercive voltage shift to lower or higher values or the loop's shift in the horizontal direction as shown in Fig. 2.4 (a). This means that a higher electric field is required, since one of the two polarization directions is more difficult to switch. Thus, the material prefers to polarize in one direction more than the other [Tony Schenk, Michael Hoffmann, et al.,2015]; [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019].

In memory applications, this is undesired phenomena, because more voltage has to be applied to have a functional device. Moreover, when no voltage is applied, the material might switch back to the preferential polarization direction; it one more problem that hinder the technological development. The origin of imprint is attributed to the interface defects and trapped charges that lead to pinning the domains in its current state. Applying a field in the opposite direction leads to a need for more activation energy to switch the domains.

Imprint also might occur as a result of phase transition from non-polar phase, especially if stress and electric field constraints are present [Pešić et al.,2016]. In addition to that, imprint originates from the incomplete screening of charges at the interface; that leads to in-built field inside the material; when the two different electrode materials are present. To greatly overcome these problems, electrical cycling (continuous alternation of positive and negative fields) is the consistent way to redistribute defects homogeneously within the material [Pešić et al.,2016]; [Michael Hoffmann, F. P. Fengler, et al.,2019]; [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019].



Figure 2.4: (a) Hysteresis loop for imprinted ferroelectric material. (b) typical endurance diagram of three regions: wake up (I), stable (II) and fatigue (III).

Figure 2.4 (b) exhibits the typical plot of endurance in literature, where one can see three different regions during cycling: (I) wake up, (II) stable and (III) fatigue. Cycling plays a vital role in building up the ferroelectric properties. Wakeup effect arise if the formation of ferroelectric phase didn't cause a uniform distribution of defects, which are located mostly at the interfaces. During cycling, the mobile defects are moved from interfaces to bulk and distribute homogeneously inside the material; leading to homogeneous field distribution across the ferroelectric and switching large portion of the material; consequently, higher P_r values is observed [M. H. Park, Y. H. Lee, Thomas Mikolajick, et al.,2018]; [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019]; [Pešić et al.,2016].

Moreover, repeating domain reversal leads to continuous migration of charged imperfections; consequently, domain walls become denser and have high-energy regions. By having a high defects concentration inside the material, the domain walls don't have enough energy to move and might be remained pin. Furthermore, defects can prevent domain nucleation and growth, lowering the switching area and the measure P_r . Both phenomena can be seen at the bias of fatigue [M. H. Park, Y. H. Lee, Thomas Mikolajick, et al.,2018]; [Tagantsev et al.,2001].

Now, it is time to pay more attention to the ferroelectric material that is the subject of this study; HfO_2 -based films. The next section will present the state of art of HfO_2 films in the research field. Much progress was done in this field; similarities will be presented to PZT and perovskites, since they are strongly well characterized since long time ago.

2.2 State of the art of HfO₂-based ferroelectrics

Hafnium Oxide (HfO₂) is a ceramic oxide of 5.5 eV band gap. It is a compound formed from 0.67 atomic percent O^{-2} anions to Hf^{+4} cations. It has been known as fluorite crystal structure, where the Hf^{+4} cations occupying the corners and faced of a parallelepiped and anions O^{-2} on the eight tetrahedral interstitial sites. The structure's coordination number (CN) for the Hf^{+4} and O^{-2} is 8 and 4, respectively [Johnson and Jones,2019].

The monoclinic (m-) phase is the stable crystal structure of bulk material at room temperature, while increasing the temperature up to 1700 °C or more induces a phase transformation into tetragonal (t-) and then into cubic phase at higher temperature of 2600 °C or more. The orthorhombic (o-) phase, between monoclinic (m-) and tetragonal (t-), could be developed at high applied enough pressure [D. Shin, Arróyave, and Z.-K. Liu,2006]. In addition to that, it was reported that doping can lead to stabilization of cubic and tetragonal phases to lower temperature [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019].

Although HfO₂ was commonly used as high κ dielectric layer in electronics, ferroelectricity was not immediately discovered, since neither of these phases is non-centrosymmetric [Bohr et al.,2007]; [Guha and Narayanan,2009]. The authors claimed, in the early report of ferroelectric Si:HfO₂ film, the stabilization of previously undetectable noncentrosymmetric *Pbc*2₁ orthorhombic phase. It was developed instead of (or together with) the well-known reported tetragonal and monoclinic phases [Böscke et al.,2011]. This was attributed, in their study, to annealing after capping with top TiN electrode. This annealing step was built an in-plane strain which stabilize the unstable orthorhombic phase [Böscke et al.,2011], as shown in Fig. 2.5.



Figure 2.5: An XRD patterns for two Si:HfO₂ films annealed before and after capping (reproduced from [Böscke et al.,2011]), (b) phase transition that leads to o-phase formation (reproduced from [Böscke et al.,2011]).

The common ferroelectric ceramics, such as: PZT or BTO, have a perovskite structure, where the displacement of the central Zr^{+4} or Ti^{+4} cations in the unit cell's octahedral interstitial sites determines the polarity. Therefore, the discovery of ferroelectric behavior in Si:HfO₂ was unexpected, it was the first example of fluorite structure ceramics, involving the movement of O^{-2} anions inside the tetrahedral interstitial sites of orthorhombic unit cell. Figure 2.6 shows the HfO₂ flourite structure and PZT perovskite unit cells, where the polarization direction is clear, by looking at the O^{-2} and Zr/Ti^{+4} positions, respectively.



Figure 2.6: Sketch of fluorite HfO_2 and perovskite PZT unit cells, which were created with Avogadro v1.2.0 [Hanwell et al.,2012], exhibiting the elements positions and polarization direction.

The recent discovery of ceramic ferroelectrics brought the nonvolatile memory and FeFET applications back into the race. PZT-based technology scaled down to 130 nm in 2007 due to its instability of the material at smaller thicknesses [M. H. Park, Y. H. Lee, Thomas Mikolajick, et al.,2018]; [Hanwell et al.,2012]; [S. Summerfelt et al.,2007]. On the other hand, the first discovery of ferroelectricity in Si:HfO₂ films was for 10nm-thick layer only. This material was immediately investigated by many researchers. They explored the factors that affect the structural properties and ferroelectric response, rather than top electrode and chemical composition of HfO₂, such as: film thickness, annealing conditions, electrode material and oxygen vacancies.

Afterwards, different dopants such as Al [Stefan Mueller et al.,2012], Gd [Mueller et al.,2012], La [Müller, Böscke, S. Müller, et al.,2013], Sr [Tony Schenk, Stefan Mueller, et al.,2013] and Y [Olsen et al.,2012] were investigated, since the dopants make displacement of atoms from their original positions and distort the lattice structure, which probably leads for stabilization of the orthorhombic phase observed in Si:HfO₂, therefore enabling ferroelectricity. Such lattice distortion is basely caused by the both differences in ionic radius and valency of dopant and Hf^{+4} cation. The ionic radius of Hf^{+4} is 0.83 Å, with a valency of 4+ Hf [Johnson and Jones,2019], as well as the trivalent Gd^{+3} cation has an ionic radius of 1.05 Å, which is larger compared to that of Hf^{+4} .

The larger ionic radius requires elongation of the trivalent metal bond with the O^{-2} ion. Once the trivalent Gd^{+3} dopant substitutes for the Hf^{+4} in the monoclinic or tetragonal HfO₂ lattices, a charge deficiency occurs. Consequently, oxygen vacancies can be created to maintain the neutrality of the crystal structure. Thus, the coordination number around the Hf^{+4} decreases forming a favorable environment for developing and stabilizing the non-centrosymmetric orthorhombic phase [Johnson and Jones, 2019].

For each dopant, there is an optimal concentration window where the o-phase stabilizes. This window is kind of wide for La and lower for other dopants. Figure 2.7 shows plotted polarization as a function of dopant concentration of various elements [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019]. HZO is one of the HfO₂-based chemical compound that was the most studied and reported among ferroelectrics. It has higher tolerance to concentration changes, high remnant polarization, high endurance and low thermal budget for fabrication. All these properties are pretty promising for applications and make it the most studied over all the HfO₂-based ferroelectrics [S. J. Kim, Mohan, Scott R Summerfelt,

et al.,2019]; [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019]; [Müller, Böscke, Bräuhaus, et al.,2011]; [M. H. Park, Y. H. Lee, H. J. Kim, Tony Schenk, et al.,2017]; [Lehninger et al.,2020].



Figure 2.7: Hysteresis loops of HfO₂ thin films with different doping concentrations of Si and La dopants (A, B, C). remnant polarization upon dopant concentration for elements smaller (D) and larger (E) than Hf (reproduced from [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019]).

HfO₂ based thin films experience an important trend showing lower amount of o - phase and remnant polarization with increasing thickness [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019]; [Ekaterina Yurchuk et al.,2013]; [H. J. Kim, M. H. Park, Y. J. Kim, Y. H. Lee, Jeon, et al.,2014]. It was studied that the determination of the favorable phase in a thin film depends on different parameters, including the grain free energy [M. H. Park, Y. H. Lee, H. J. Kim, Tony Schenk, et al.,2017]; [Robin Materlik, Künneth, and Alfred Kersch,2015], which is dependent on the grain size and film thickness. When the grain size is small, the o - phase is more favorable than m - phase, since the former has lower interface energy [M. H. Park, Y. H. Lee, H. J. Kim, Tony Schenk, et al.,2017]; [Robin Materlik, Künneth, and Alfred Kersch,2015].
Thus, the authors explored that HZO films could be stabilized in o - phase by effectively inserting 1 nm layer of AL_2O_3 in the middle, thus smaller grain size [Robin Materlik, Künneth, and Alfred Kersch,2015]. Figure 2.8 represents o-phase ratio/(o - phase + m - phase) and grain size as a function of film thickness for HZO and HZAHZ (with 1 nm layer of AL_2O_3 at exact half thickness), and formation energy of crystalline phases of Gd:HfO₂ as a function of oxygen vacancy concentration.



Figure 2.8: (a) O-phase ratio/(o-phase + m-phase) and (b) grain size as a function of film thickness for HZO and HZAHZ (with 1 nm layer of AL_2O_3 at exact half thickness), (reproduced from [H. J. Kim, M. H. Park, Y. J. Kim, Y. H. Lee, Jeon, et al.,2014]) and (c) formation energy of crystalline phases of Gd:HfO₂ as a function of oxygen vacancy concentration for different crystalline structure (reproduced from [Hoffmann et al.,2015]).

Additionally, researches in HfO₂-based ferroelectric films, as well as in PZT, investigated the crucial effect of O vacancies. The existence of large amount of O vacancies leads to difficulty in crystallization the m-phase, whereas too many O vacancies favor the development of t-phase, as it is seen in Fig. 2.8. Moreover, the oxygen vacancies were reported to form preferentially at the electrode interfaces in perovskite ferroelectrics. It migrates to grain boundaries, leading to degradation of ferroelectric properties and progression in non-ferroelectric dead layer [Ihlefeld et al.,2016]; [Lou,2009]; [Genenko et al.,2015]; [F. P. Fengler et al.,2017].

The distribution of O vacancies in HfO_2 -based films are dependent on the electrodes, where a crucial annealing step is needed to get ferroelectricity. TiN electrode is reported as the most widely used electrode, which is very suitable to CMOS technology, since its high quality electrical and mechanical properties and chemical and thermal stability [Guha and Narayanan,2009]. It is easy for TiN to bind with O atom forming TiO_xN_y or TiO₂, since it is in a direct contact with HfO₂ layer during the annealing step [H.-Y. Chen and F.-H. Lu,2005].

This creates an interfacial dead layer, rich of O vacancies and majority in the t-phase [Pešić et al.,2016]; [M. H. Park, H. J. Kim, Y. J. Kim, Jeon, et al.,2014]; [Hamouda et al.,2020]. Reducing the film thickness strongly enhances these effects, where the size of the film is comparable with that of the dead layer. Such effects increase the coercive voltage, decreases the remnant polarization and endurance [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019].

Following to interface effect between ferroelectric and electrodes, the thermal budget and atmosphere play a vital role in the ferroelectric response of thin films [Chernikova et al.,2016]; [Hyuk Park, Joon Kim, Jin Kim, W. Lee, et al.,2013]; [Lomenzo et al.,2016]; [M. H. Park, Chung, et al.,2018]. It was explored that annealing process in inert atmosphere (N_2) at temperatures between 450 and 800 °C gives the best results for ALD HfO₂ films [M. H. Park, Chung, et al.,2018]. Figure 2.9 exhibits the complex phase formation process according to thermal budget during annealing, film thickness and dopant content.



Figure 2.9: A summary of phase formation trends of HfO₂-based films with thermal budget during annealing, film thickness and dopant content (reproduces from [Hoffmann et al.,2015]).

It has been discussed that the top electrode is significant in twofold; firstly, it affects the interfacial layer and controls oxygen vacancies amount, furthermore, it induces stress withinside the thin film during annealing by imposing the mechanical constraint. It was discussed before that oxide electrode can prevent the formation of dead layer in HZO [Goh et al.,2020]. The difference between electrode materials in thermal expansion coefficients vary the induced amount of stress upon annealing.

It was reported that lowering the thermal expansion coefficient leads to increase the tensile stress and remnant polarization of the ferroelectric film [Patrick Polakowski and Johannes Müller,2015]. Moreover, increasing the thickness of electrode increases the stress as well as the o-phase formation in the film.

The stress induced by annealing after growing the top electrode material can be better understood thinking about that even undoped HfO_2 was exhibited to be ferroelectric. This is an intrinsic effect and not dependent on doping [D. Ye et al.,2014].

It is clear now that we need to pay attention for the suitable amount of strain level imposed to the film, thus, it is great importance to think about the bottom electrode on which the film will be deposited, taking into consideration the lattice mismatch between the two materials. Many researchers explored that the deposition of thin films by PLD at a temperature higher than 700 °C on engineered substrates that leads to a favorable o-phase formation [Takao Shimizu et al.,2016]; [T. Li et al.,2018]; [Yoong et al.,2018]; [Lyu, Fina, Fontcuberta, et al.,2019]. Such films no longer need top electrode deposition and annealing to show ferroelectric trend.

As discussed so far, the P_r value depends on the amount of o-phase in the film; it was mentioned previously that this transform with electrical cycling, thus P_r value changes with the creation and distribution of imperfections in the film. It intensely reported that ALD HfO₂ films present initially a wakeup effect before displaying a stable P_r , then undergoing fatigue [Hoffmann et al.,2015]; [Pešić et al.,2016]; [Tony Schenk, Michael Hoffmann, et al.,2015]; [F. Fengler et al.,2018]; [D. Zhou et al.,2013]; [M. H. Park, H. J. Kim, Y. J. Kim, Y. H. Lee, Moon, Keum Do Kim, Hyun, and C. S. Hwang,2015]; [H. J. Kim, M. H. Park, Y. J. Kim, Y. H. Lee, Moon, et al.,2016]; [T. Y. Lee et al.,2018]. However, the epitaxial ferroelectric thin films grown by PLD at high temperature and already in the o-phase don't need a wakeup procedure [Takao Shimizu et al.,2016]; [Lyu, Fina, Fontcuberta, et al.,2019].

The hysteresis loop of a ferroelectric HfO_2 thin film in its pristine state mostly exhibits a pinched hysteresis, where the current (I)-electric field (E) characteristic shows double peak. This is attributed mainly to the accumulation of charged defects (O vacancies) at the interface between the electrodes (especially the top) and ferroelectric material [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019]. This interface can be considered as an unavoidable byproduct produced during ALD process in the temperature range 250-300 °C and annealing at 1000 °C.

The oxidation of bottom and top electrode is also asymmetrical, which leads to different defect concentrations withinside the material [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019]. Interfaces with electrodes are the responsible of bias field and enable parallel aligned domains to switch at lower field, while antiparallel domains switch at higher field, resulting in I-E and P-E plots noticed for pristine samples. The first imprint in pristine state and tetragonal phase relaxation into orthorhombic phase upon cycling are attributed to the initial charge accumulation at the interface [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019]; [Pešić et al.,2016]. Performing electrical cycling can reduce imprint due to the redistribution of defects across the film, especially at grain boundaries, where the energy is higher [Pešić et al.,2016].

This leads to a migration of O vacancies away from the interface, with t-phase transforming into o-phase, producing thinner dead layer at the interface [Pešić et al.,2016]; [Starschich, Menzel, and UJAPL Böttger,2016]. Figure 2.10 (a) and 2.11 (b) shows the resulted macroscopic effects after cycling, such as: higher P_r value and merging the two peaks in the I-E plot, respectively.



Figure 2.10: Electrical cycling trend of Sr:HfO₂ ferroelectric. (a) P_r as a function of cycles and (b) I-E plot; (c) leakage current measurements upon field at different cycles (reproduced from [Pešić et al.,2016]).

As more electrical cycling applied, the continuous polarization switching starts to generate too many defects in the structure. As a result, P_r decreases, leakage current becomes higher and the device finally shows strong breakdown. This leads to permanent degradation of the structure, which can be recovered only through exposing the film to excessive temperature [F. Huang et al.,2017]. In addition to that, in fatigue process there is a creation of new imperfections [Pešić et al.,2016].

The more O vacancies and other defects created during cycling, the more charge accumulation along the grain boundaries which costs higher energy for grain walls to move [Pešić et al.,2016]; [Tagantsev et al.,2001]. The control of the domain size can affect leakage current in thin films [M. H. Park, Y. H. Lee, Thomas Mikolajick, et al.,2018]. As it is observed in the fatigue, P_r will decrease when a portion of the material does not switch due to domain pinning.

Furthermore, defects' accumulation along the grain boundaries creates conduction paths that are responsible for breakdown the film [Pešić et al.,2016]; [Tagantsev et al.,2001].

Moreover, there is a sudden breakdown in HfO₂-based films that is difficult to avoid, since the ratio between coercive field and breakdown field is kind of high, approximately one order of magnitude compared to that of perovskite ferroelectrics [S. J. Kim, Mohan, Scott R Summerfelt, et al.,2019].

2.3 Structural and electrical characteristics

2.3.1 Structural properties

The x-ray diffraction (XRD) technique was used to investigate deep information about the studied samples. When electrons of high energy impinge on the metallic anode of the x-ray tube, x-rays with continuous energy distribution (known as Bremsstrahlung) are generated. Lines specific to the anode materials, which are called the characteristic x-ray lines with independent energy from the anode voltage, are then superimposed on this continuum. The anode atoms will be ionized through electron effect in any one of the upper shells leaving vacancy or hole, and then an electron from a higher energy level will fill that hole [Birkholz,2006].

The energy transformed into an element-specific x-ray. When x-rays with wavelength (λ) impinge on any studied thin film sample under diffraction angle (θ), a constructive interference after scattering only appears when the path difference of the partial waves that reflected from the lattice planes differs by one or more wavelengths [Birkholz,2006], as shown in Fig.2.12.



Figure 2.11: Bragg scattering on the lattice surface.

This situation is referred to the Bragg equation [Pathania, Kumari, and Gupta,2015]:

$$2d\sin\theta = n\lambda\tag{2.5}$$

Where θ is the diffraction angle, λ is the x-ray wavelength, d is the inter planner spacing and n is an integer number reflects the order of diffraction. When x-rays of wavelength λ strike a lattice plane of a crystal of spacing d at a diffraction angle of θ , then the reflected rays will only be subject to constructive interference when Bragg's condition is fulfilled. Bragg's condition implies that all of the waves scattered at the atom are in phase and so amplify each other, whereas partial waves that are scattered in directions not fulfilling Bragg's conditions are of opposite phase and so extinguish each other [Pathania, Kumari, and Gupta,2015].

By using the modified Scherrer equation [Suryanarayana,2004], more deep structural properties of crystallite size (D) and lattice strain (ε) can be investigated.

$$\beta\cos\theta = \frac{K\lambda}{D} + 4\varepsilon\sin\theta \qquad (2.6)$$

Where β is the full width at half maximum (FWHM) of the diffraction peak and K is the geometric factor (0.94). The dislocation density (δ), which is a measure of the number of dislocations per unit volume in a crystalline material, was estimated using the relation [Khusayfan, Al Garni, and Qasrawi,2017]:

$$\delta = \frac{15\varepsilon}{aD} \tag{2.7}$$

Where a is the lattice constant. Moreover, the stacking factor (SF), which is a type of defect that characterizes the disordering of crystallographic planes, was determined using the following relation [Bouguerra et al.,2015]:

$$SF = \frac{2\pi^2\beta}{45\sqrt{3\tan\theta}}100\% \tag{2.8}$$

2.3.2 Capacitance-voltage characteristics: p-MOS mechanism

The MOS capacitor is a metal-oxide-semiconductor structure as shown in Fig. 2.12, the p-type bulk semiconductor substrate with an oxide layer (ferroelectric), capped with top metallic electrode (gate). Another metallic ohmic contact that touches the back surface of the semiconductor is called bulk contact. There are 3-different bias voltages lead to 3-bias regimes called: accumulation, depletion and inversion modes [Heinzel,2008].



Figure 2.12: Cross sectional view for p-MOS capacitor.

Applying a negative voltage to the metallic gate attract the majority carriers (holes) to semiconductor/oxide interface, where the majority carrier's concentration (holes) near the surface is larger than the equilibrium hole concentration in the substrate; this is called carriers accumulation [Heinzel,2008], see Fig. 2.13 (a). The surface conductivity increases due to holes accumulation at the semiconductor surface. In this regime, the capacitor acts like a conventional capacitor with a capacitance per unit area is given by the following equation:

$$C_0 = \frac{K_0 \varepsilon_0}{X_0} \tag{2.9}$$

Where K_0 is the dielectric constant, ε_0 is the free space permittivity and X_0 is the oxide layer thickness.

Now, suppose that a small positive voltage is applied to the gate contact, the holes (majority) are repelled and back away from the oxide/silicon interface, creating a space charge region involves static negative acceptors ions, as shown in Fig. 2.13 b; this is

called depletion region. The space charge region behaves as another capacitor C_d , that is in series with the oxide capacitor [Heinzel,2008]. The overall capacitance per unit area, C is calculated using:

$$\frac{1}{C} = \frac{1}{C_o} + \frac{1}{C_d}$$
(2.10)

Where C_d equals:

$$C_d = \frac{K_s \varepsilon_0}{X_d} \tag{2.11}$$

Where X_d is the depletion region depth and K_s is the dielectric constant of semiconductor. When more positive voltage is applied to the gate, the width of depletion region increases and the overall capacitance decreases. In depletion mode, the majority carriers (holes) are repelled out while the minority carriers (electrons) are attracted. By applying sufficiently large positive voltage, this effect predominates and the semiconductor layer enters the inversion mode, see Fig. 2.13 (c). In such a case, the number of electrons (minority carriers) becomes higher than holes; the surface becomes like n-type and it is called surface inversion [Heinzel,2008].



Figure 2.13: The charge distribution in (a) accumulation, (b) depletion and (c) inversion modes of p-MOS capacitor.

2.3.3 Polarization versus voltage measurements

The hysteretic nature of polarization is one of the main features of the ferroelectric materials. This makes the polarization vs voltage (P-V) measurements the most important among the electrical methods by revealing the remnant polarization and coercive voltage. The hysteresis loop is a signature of ferroelectricity and the key to more advanced measurements, such as fatigue. It is important to perform the leakage current measurement before carrying out the P-V test, which provides information about the dielectric nature of HfO₂ material [Heinzel,2008].

During the characterizations of the ferroelectric capacitors, we used the Pulse Measurements (PM) mode of polarization measurements, which record the current response of the Capacitor Under Test (CUT) after applying a series of sequence pulse excitation signals. One of the very common measurements is PUND for Positive Up Negative Down, with two positive and two negative consecutive pulses. The software of the PM measures the P-V curve and some characteristic value of the sample [Heinzel,2008].

Figure 2.14 represents the PM parameters that can be determined for each measurement. The initial write pulse is used to set the material's polarization in a specific direction. The read pulse is essential for characterizing the response of the material following the write pulse. The delay time between two subsequent pulses is 1s. The pulse width is the duration of the transmitted signal. The risetime is time taken for the voltage signal to transition from a specified lower voltage threshold to a specified upper voltage threshold.



Figure 2.14: Positive Up Negative Down (PUND) consecutive pulses parameters.

Figure 2.15 illustrates the PUND sketch for the device under test, which contains five trapezoid (or triangle) pulses, with the same amplitude $\pm(V_{max})$ and rise time. The

different colors in the graph refer to the different pulses (P_1 : red, P_2 : green, P_3 : blue, P_4 : cyan, P_5 : magenta).

- Pre-switch pulse: it aligns the domains along specific direction (P_1) .
- First positive pulse (P): to switch domains upward, it includes other contributions due to domain motion and leakage current (P_2).
- Second positive pulse (U): to measure other contributions to the current, which are not due to the domain switching (*P*₃).
- First negative pulse (N): it switches domains downward; it includes other contributions due to the domains motion and leakage current in the opposite direction (*P*₄).
- Second negative pulse (D): it is used to measure other contributions to the current, which are not due to the domain switching (P_5).



Figure 2.15: Schematic of PUND measurements.

This measurement allows to easily quantify significant properties such as the positive $(+P_r)$ and negative $(-P_r)$ remnant polarization values of positive and negative reference read pulse, respectively, and the positive $(+V_c)$ and negative $(-V_c)$ values at which the polarization crosses the x-axis with increasing and decreasing voltage values. It is also possible to determine if the material a full polarization response or contrarily the loop is

pinched or degrading. By integration the recorded current during each pulse of PUND train, the hysteresis loop can be extracted according to the following equation [Hachemi,2022]; [Segantini,2023]:

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} = \varepsilon_0 \varepsilon_r \vec{E} \tag{2.12}$$

Where ε_r is the relative dielectric constant, and \vec{D} is the displacement vector. Thus, the charge Q as a function of displacement vector \vec{D} ,

$$Q = \int I \cdot dt = \int_{S} \vec{D} d\vec{S}$$
 (2.13)

$$Q = \frac{1}{S} \int I \cdot dt \tag{2.14}$$

Where $d\vec{S}$ is the surface crossed by the current I in time δt . For the case of positive (P) and up (U) pulses:

$$\vec{D} = \frac{1}{S} \int_0^{t_{\text{pulse}}} \left[I(P) - I(U) \right] dt$$
 (2.15)

$$\vec{D} = \frac{1}{S} \left[\left[\int_0^{t_{\text{pulse}}} I(P) dt \right] - \left[\int_0^{t_{\text{pulse}}} I(U) dt \right] \right]$$
(2.16)

$$\vec{D} = \vec{D}(P) - \vec{D}(U) \tag{2.17}$$

From equation 2.17, \vec{D} can be expressed in terms of polarization:

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P}(P) - \varepsilon_0 \vec{E} + \vec{P}(U)$$
(2.18)

$$\vec{D} = \vec{P}(P) - \vec{P}(U)$$
 (2.19)

Now, the pulse (P) includes the current due to the switching of ferroelectric domains with other current contributions; leakage current. Whereas, the next pulse (U) records the contribution of leakage current. Thus, the ideal case:

$$D_{PU} = P_{PU,ferreelectric} \tag{2.20}$$

If the same process is repeated for the (N) and (D) pulses, the resulted loop will only correspond to ferroelectric effect.

Chapter Three: Methodology

This chapter is divided into three main sections: the first one will introduce the fabrication process used to create the Metal-Oxide-Semiconductor (MOS) and Metal-Ferroelectric-Metal (MFM) devices that are investigated in this work. In particular, it will mainly explain the deposition technique: Plasma Enhanced Atomic Layer Deposition (PEALD). After that, the photolithography and etching steps to obtain the capacitor structures that were studied. The second and third sections of the chapter will describe, in respective, structural and electrical characterization techniques that were utilized to analyze the ferroelectric properties of HfO₂-based thin films.

3.1 Fabrication process

The characterization of the ferroelectric HfO_2 -based thin films requires a suitable structure for structural and electrical characterization. In this work, the capacitor structure that was used to investigate the ferroelectricity, consisting of sandwiching the ferroelectric layer between either semiconductor and top metal electrode, or two similar conducting electrodes.

The process starts from a SiO₂/Si wafer, which is often cut into $2x2 \ cm^2$ pieces, on top of which the appropriate material layers are deposited by using PEALD technique. The SiO₂/Si substrate is critical for this work due to several key reasons. Firstly, the SiO₂ layer provides electrical insulation, preventing leakage currents from the silicon substrate into the HfO₂ layer, which is vital for accurate characterization of ferroelectric properties [Wenger et al.,2008]. Additionally, the SiO₂/Si substrate ensures compatibility with existing semiconductor processes, allowing the integration into CMOS devices. The SiO₂ layer also acts as a smooth, stable surface for the deposition of TiN and Gd:HfO₂, promoting uniform film growth, which is essential for the consistency of device properties [Chourasia and Chopra,1995]. These attributes make the SiO₂/Si substrate indispensable in the fabrication and performance optimization of the studied structures.

After that, an optimized annealing step is crucial for particular kind of ferroelectrics. Then, the desired structure is created by executing patterning of such materials stack using photolithography and etching. The process flow will be presented qualitatively, paying a special attention to the PEALD technique that was responsible in obtaining the correct ferroelectric properties.

3.1.1 Growth of ferroelectric thin films and annealing

The deposition of HfO_2 -based thin films was achieved by PEALD technique, which was used to deposit HfO_2 in the microelectronic industry due to many advantages such as a great control over thickness, high conformality and strong chemical selectivity. PEALD applies thin films to substrate with atomic scale precision through control chemical reactions by using precursors that are injected to the chamber and reacted chemically with the substrate. It is not possible to inject two precursors simultaneously inside the chamber, and to ensure that they are never in contact, a purging step takes place between them to avoid any contamination.

It is self-limiting mechanism in which a limited amount of film (a few Å normally) can be grown in every cycle. A typical PEALD process involves multiple reactive and purging cycles to deposit the film monolayer by monolayer until achieving the required thickness. In addition, to control the dopant concentration in PEALD, we need to fix the ratio of dopant/Hf precursor cycles.

In this section, a general overview about PEALD mechanism, equipment used, will be presented as well as the growth of HfO₂, Gd-HfO₂ layers and TiN electrode PEALD and finally an annealing process is performed for crystallization films.

3.1.1.1 PEALD: overview and principle

Atomic Layer Deposition (ALD) is a highly precise thin-film deposition technique that enables the controlled growth of materials at the atomic scale. The ALD technique is based on the sequential use of self-limiting gas-solid reactions to deposit thin films one atomic layer at a time. This layer-by-layer growth mechanism enables excellent control over film thickness, composition, and conformality, even on complex 3D structures [Evers and Macco,2017].

ALD is widely utilized in manufacturing microelectronics, optoelectronics, energy storage components, and various advanced materials due to its capability to produce high-quality, uniform thin films with precise atomic-level control. The ALD technique typically involves exposing the substrate to precursor gases in a sequential manner, which react with the surface to form a monolayer of the desired material. By consistently repeating this process, precise control over the film's thickness is achieved [Evers and Macco,2017].

ALD offers considerable benefits, including its self-limiting growth, excellent step coverage, and the ability to deposit conformal films on structures with high aspect ratios. These features make ALD a powerful technique across numerous fields, ranging from semiconductor manufacturing to the development of new functional materials [Evers and Macco,2017].

Plasma-Enhanced Atomic Layer Deposition (PEALD) is an advanced version of traditional Atomic Layer Deposition (ALD) that incorporates plasma into the process. This integration of plasma provides several benefits including faster deposition rates compared to conventional ALD, enhanced film quality and a wider variety of material options. The use of plasma in PEALD enhances the control over surface reactions, allowing the deposition of high-quality films with precise atomic-level accuracy.

The integration of plasma into ALD processes has expanded the possibilities for material synthesis and device fabrication. Incorporating plasma's unique properties allows researchers to customize the characteristics of deposited films to meet specific needs, such as enhanced electrical conductivity, better optical properties, or developed mechanical strength [Evers and Macco,2017].

This section will present the key features of PEALD, the relevant concept and basics of the technique.

Basics of ALD

This part will explain the basics of ALD with several important concepts which helps in the understanding of ALD, based on an ideal ALD process [Evers and Macco,2017].

1. Standard ALD process scheme

Thin films are incrementally constructed in ALD through cycles where the surface undergoes exposure to different vapor or gas-phase substances in distinct, alternating doses. During each cycle, a sub-monolayer of material is precisely deposited. As shown in Figure

35

3.1, a standard cycle involves the following four stages:

(i) Precursor dosing: an inorganic chemical compound is introduced to the reaction chamber. During this step, the precursor gas is injected into the reaction chamber, where it adsorbs onto the surface of the substrate. This self-limiting adsorption is key to the ALD process, as it ensures that only a single monolayer of the precursor reacts with the surface at a time.

(ii) Purge: the chamber is purged to remove the excess precursor and any reaction byproducts by using an inert gas.

(iii) Pulse of co-reactant: a second chemical is introduced with the surface-bound precursor.(iv) Second purge: another pump with inert gas to remove any excess co-reactant and by-products, to prepare the surface for the next cycle.



Figure 3.1: A schematic representation for an ALD process of various steps including the two half-reactions [Evers and Macco,2017].

In ALD, the precursor and co-reactants must undergo self-limiting reactions with the surface, where both can only react with accessible surface sites and/or chemical groups; consequently, the surface eventually becomes saturated and the reactions cease. The precursor molecules and co-reactants react neither with themselves nor with the surface groups that they create.

In the purge and/or pump steps, the gaseous reaction products that may be generated during the surface reactions and any excess precursor or co-reactant molecules, are removed from the ALD reactor. This step plays a vital role for preventing reactions between precursor and co-reactant molecules either in the gas phase or on the surface, otherwise, unwanted components from chemical vapor deposition (CVD) could be produced. During each half cycle, the surface reactions reach coverage saturation at each cycle step. The saturation of both half-cycles results in a characteristic level of growth per cycle, often referred to as the growth per cycle (GPC) [Evers and Macco,2017].

Besides the basic ALD cycle (Fig. 3.2a) with two alternating half-cycles (AB), the ALD cycles for a certain material can be alternated with cycles for other materials (Fig. 3.2a). This allows for the growth doped films with specific elemental mixtures. In a supercycle, the first process is run *m* times, followed by *n* cycles of a second ALD process. This supercycle of m + n cycles is then repeated several times until the desired thickness is achieved.



Figure 3.2: A schematic representation of the various steps in (a) a basic ALD process and (b) a supercycle [Evers and Macco,2017].

2. Temperature window

Each ALD cycle operates under specific chemical and physical conditions for selflimiting growth, resulting in unique growth per cycle (GPC) characteristics. This ALD process occurs within a certain temperature range, illustrated in Fig. 3.3, where the GPC exhibits minimal temperature dependence (relatively stable). Outside this range, the ALD behavior can be affected. Low temperatures may lead to increase the GPC due to precursor and co-reactant condensation, while limited thermal energy can prevent complete reaction saturation and decreasing growth. At high temperatures, precursor decomposition can enhance the growth, leading to increased growth with a CVD component [Evers and Macco,2017]. Additionally, very high temperature, film desorption or surface group etching may occur, causing growth reduction.



Figure 3.3: The growth per cycle as a function of temperature for idealized temperature window of the ALD process [Evers and Macco,2017].

3. Uniformity and Conformality

The self-limiting nature of ALD ensures uniform (2D) and conformal (3D) thin film deposition, even with differences in source flux across the substrate or in a 3D structure, as long as sufficient flux reaches all areas. This is a key advantage over other thin film deposition techniques, such as chemical vapor deposition (CVD) and physical vapor deposition (PVD), which are flux-controlled processes. Careful reactor engineering is required for flux-controlled processes to ensure a constant flux across the whole surface area, which is difficult to achieve.

3.1.1.2 Flexal overview

An ALD processing system called FlexAL®II is used to deposit a wide variety of materials. In this system, the substrates can be loaded without needing for vent the main process chamber. It accommodates substrates up to 8 inches in diameter, while smaller substrates are manually placed on a carrier, which is also manually loaded into the loadlock. After that, the system automatically transfers the carrier to the process chamber to execute the desired deposition process. In FlexAL®II system, there are two types of deposition processes:

1. Plasma process: This approach directs reactive ionic species towards the substrate's front surface by using radio frequency (RF) power to generate a plasma in a source.

2. Thermal process: This method uses high temperatures to facilitate material deposition on the front surface of the substrate.

The FlexAL®II consists of multiple essential components: Base Unit, process Chamber, Pumping Module, RF Generator, Loadlock, Gas Handling System, precursor Delivery Modules, Power and Control Boxes: Services Panel and System Control, see Fig. 3.4. These elements work together to facilitate the ALD process in the FlexAL®II system.



Figure 3.4: Outline of a typical FlexAL®II plasma system.

Principle of operation

The operating steps are simplified as follows:

- A specific recipe is chosen on the attached computer.
- Substrate wafers are manually positioned directly on the sample carrier.
- Wafers are then automatically transferred to the process chamber and placed on the lower electrode (known as the table).
- The chamber is evacuated and the lower electrode is heated to improve the deposition process's efficiency.

- The deposition process is conducted by using either the thermal ALD or the remote plasma ALD processes.
- After the recipe is completed and the process chamber is purged, the processed wafers are moved to the loadlock.
- The processed wafers are then manually unloaded from the carrier within the load-lock.

Remote Plasma ALD

Remote plasma ALD is a process where the deposition involves sequentially exposing the substrate to two precursors, designed to ensure that these precursors do not directly mix. One or both precursors might be created by dissociating a vapor or gas in a plasma chamber, and the substrate can also be heated as needed. The deposition process includes four key steps:

- Introduce the first precursor into the chamber to deposit a monolayer on the substrate.
- Purge the chamber to clear any leftover unreacted precursor.
- Introduce the second precursor into the plasma source to generate reactive species that combines with the initial monolayer to form the final desired compound.
- Finally, again, purge the chamber to eliminate any leftover precursor.

This cycle adds one atomic layer at a time, and repeating the cycle gradually builds up the material's thickness, layer by layer. An ellipsometer system can be used to monitor the growth thickness and refractive index of the layers.

3.1.1.3 HfO₂, Gd:HfO₂ and TiN plasma enhanced atomic layer deposition processes

In this work, a series of the following stacks: HfO_2 , TiN/HfO_2 , $TiN/Gd:HfO_2$, $Gd:HfO_2/TiN$ and $TiN/Gd:HfO_2/TiN$ were deposited using PEALD Flexal chamber, from Oxford Instruments, on $2x2 \ cm^2$ of 100 nm-thick SiO_2 that was grown thermally on Si substrate. The substrate temperature was kept at $250^{\circ}C$ during HfO_2 , TiN and $Gd:HfO_2$

PEALD deposition processes without exposing to air between layers depositions within a stack. Describing the preparation process of HfO_2 layer on SiO_2/Si substrates involves several specific steps. Below, the detailed procedures are shown in order.

- 1. Substrate preparation:
 - a) Cut the SiO₂/Si wafer into $2x2 \ cm^2$ substrates.
 - b) Clean them by a Nitrogen gas gun to remove any surface contaminants.

For starting the process, the user interface should be opened to control the vacuum system and wafer transfers.

- 2. Loading the substrates:
 - a) Use the loadlock control for venting the loadlock.
 - b) Open the door of loadlock and carefully load your substrates on the base holder inside the loadlock.
 - c) Evacuate the loadlock to pump down the loadlock to a base pressure, typically to 10^{-6} Torr.
- 3. Transferring the substrate from the loadlock to the chamber, as shown in Fig. 3.5. The location of the wafer is indicated by a green wafer indicator and the blue, arrowed path shows the destination of the currently available wafer.



Figure 3.5: A schematic representation for transferring the substrate from the loadlock to the process chamber.

4. Deposition process: For starting the deposition process on whatever substrate, there is a scrollable sequential list of steps, called recipe, that will be performed as the list requires. Each step has its own parameters.

HfO₂ PEALD deposition

HfO₂ PEALD represents repeated cycles, the number of cycles was varied to have the desired thickness. One PEALD cycle consist of $Hf[N(CH_3)_2]_4$ liquid precursor injection (Tetrakis(dimethylamido)hafnium(IV) (or $Hf[N(CH_3)_2]_4$,TEMAHf), precursor purge using inert Ar gas, interaction with O_2 plasma, and purge after plasma with Ar.

- a) TEMAHf precursor was injected into the reactor chamber using a bubbler. TEMAHf bubbler was heated up to 70 °C to increase TEMAHf partial pressure (higher number of precursor molecules), Ar was used as carrier gas (Ar flow was 250 sccm, time of TEMAHf injection was 5s).
- b) Purging step includes 250 sccm of Ar flow ending at the chamber, time of purge was 5s.
- c) The flow of O₂ gas, used for plasma, was 60 sccm directly to the chamber, time of injection was 5s, to produce HfO₂ compound.
- d) Purging step includes 250 sccm of Ar flow for 2s.

In the general case, interaction of HfO_2 surface with TEMAHf precursor can be described as [Ding et al.,2020]:

$$\|(OH)_2 + Hf L_4 \to \|O_2Hf L_2 + 2HL$$
 (3.1)

During the O_2 plasma step, some different chemical reactions are possible, for instance:

$$\|\text{HfL L}_2 + 2O^*(\text{ plasma }) \to \|\text{H}f(OH)_2 + 2C_2H_5 \text{ N}$$
 (3.2)

or:

$$\|Hf L_2 + 2O^*(\text{ plasma }) \rightarrow \|Hf(OH)_2 + 2HNO + 2C_2H_4$$
(3.3)

where L (ligand) is $-N(CH_3)_2$.

♦ Gd:HfO₂ PEALD deposition

The PEALD process of HfO₂ doped with Gd (Gd:HfO₂) involved a supercycle approach. One supercycle includes several sequential HfO₂ PEALD cycles (4 cycles in our case), and one Gd doping cycle. The Gd growth cycle within the supercycle included 4 steps. Firstly, the injection of [tris(cyclopentadienyl)gadolinium(III)] solid precursor, $(Gd(C_p)_3)$, purging with Ar, O_2 plasma exposure as an oxidant, and finally reactor purging. The temperature of Gd Bubbler was heated up to 185 °C. Precursor purge with Ar, O_2 plasma injection, and plasma purge.

- a) After 4 HfO₂ cycles, there is one Gd doping cycle, which includes $Gd(C_p)_3$ precursor injection for 40s, Ar was used as carrier gas, Ar flow was 600 sccm in total arriving to the chamber.
- b) Purging step includes 250 sccm of Ar flow ending at the chamber, time of purge was 3s.
- c) The flow of O₂ gas, used for plasma, was 60 sccm directly to the chamber, time of injection was 6s.
- d) Purging step includes 250 sccm of Ar flow, time of purge was 2s.

Similar to HfO₂ chemical reaction, we can assume possible chemical reaction during Gd precursor injection:

$$\|(OH) + Gd(C_6H_6)_3 \to \|OGd(C_6H_6)_2 + 2HC_6H_6$$
(3.4)

And during interaction with O_2 plasma:

$$\|Gd(C_6H_6)_2 + O^* plasma \rightarrow \|Gd(OH)_2 + C_{10}H_8$$
 (3.5)

TiN PEALD deposition

TiN PEALD represents a series of consecutive cycles, one PEALD cycle consist of $Ti[N(CH_3)_2]_4$ metal liquid precursor injection (or Tetrakis(dimethylamido)titanium(IV)), (TDMAT) precursor purge using inert Ar gas, interaction with N_2 and H_2 plasma, and purge after plasma with Ar.

a) TDMAT precursor was injected into the reactor chamber using a bubbler. TDMAT bubbler was heated up to 70 °C to increase TDMAT partial pressure (higher number of precursor molecules), Ar was used as carrier gas (Ar flow was 100 sccm, time of TDMAT injection was 300 ms) ending at the chamber.

- b) The Ar flow during the precursor purge was 300 sccm, time of purge was 5s.
- c) The flow of N_2 and H_2 gases, used for plasma, were 5 sccm and 40 sccm (respectively), time of injection was 15s.
- d) The Ar flow during the plasma purge was 150 sccm, time of purge was 2s.

The possible chemical reaction of TDMAT precursor with TiN surface can be described as:

$$\|2\mathbf{NH} + \mathbf{TiL}_4 \to \|\mathbf{N}_2\mathbf{TiL}_2 + 2\mathbf{HL}$$
(3.6)

After the TDMAT precursor purge, during interaction with H_2 and N_2 plasma, several chemical reactions are possible. Some following reactions are described in the literature for the H_2 [Caubet et al.,2008] plasma and NH_3 [Belahcen et al.,2020]; [Elam et al.,2003] plasma processes:

$$\|\operatorname{Ti}L_2 + 2\operatorname{H}_2 \operatorname{plasma} \to \|\operatorname{Ti}(\operatorname{NH}_2)_2 + 4\operatorname{CH}_4$$
(3.7)

where L (ligand) is $N(CH_3)_2$.

$$\|\mathrm{TiL}_2 + 2\mathrm{H}_2 \text{ plasma} \to \|\mathrm{TiH} + 2\mathrm{HL}$$
(3.8)

$$\|\operatorname{Ti} L_2 + 2\operatorname{NH}_3 \operatorname{plasma} \to \|\operatorname{Ti} (\operatorname{NH}_2)_2 + 2\operatorname{HL}$$
(3.9)

Rapid Thermal Annealing:

The fabrication of all the prepared samples concludes with an annealing step, which is an essential part of the overall process. Rapid Thermal Annealing (RTA) is a heat treatment process primarily used to influence the structural and electrical properties of thin films, enhancing their performance in semiconductor devices.

In this work, the annealing of ALD grown HfO₂ samples was performed by using Rapid Thermal Annealing (RTA) using RTP-100 equipment from UniTemp GmbH with a 50 °C per second temperature increase rate under constant N_2 flow (2 l/min). The samples were annealed at 650 °C under N_2 flow for 10 min. The RTA facilitates the transformation of HfO₂ films into desired crystalline phases, affect the interface and oxide charges, reduce the leakage current and enhance the dielectric properties which makes HfO₂ films suitable for high k-applications [B. Wang et al.,2024].

3.1.1.4 In-situ ellipsometry

Ellipsometer, particularly spectroscopic ellipsometry, hereinafter SE, is a widely used optical technique for thin film thickness measurements. It's common in the semiconductor industry and other areas which needs thin film analysis for research, development, and manufacturing quality control. Ellipsometry measurements are quick, reproducible and non-destructive.

Ellipsometry is a foundational advanced tool in Atomic Layer Deposition (ALD) for non-destructive, in-situ monitoring of thin film growth with sub-nanometer resolution. It is integrated directly into ALD setups to monitor the film thickness during each deposition cycle, to track changes in film thickness, optical properties, compositions, doping concentration, and surface roughness during each deposition cycle associated with a change in optical response.

Measuring principle:

All of the observable properties of light (such as reflection, refraction, and absorption polarization) are described by a set of 4 partial differential equations known as "Maxwell's Equations" [Sharma,2014]. According to Maxwell's Equations, a beam of light contains an electric field component which oscillates perpendicular to the beam's direction of propagation.

The polarization state of the beam is defined by the orientation and phase of the oscillating electric field. When light is reflected obliquely from a sample, a coordinate system can be defined by the plane of reflection: if the electric field vector is oscillating parallel to the plane of incidence, the light is referred to as "p-polarized" light. Conversely, if the electric field vector oscillating perpendicular to the plane of incidence, the light is denoted "s-polarized" light [Sharma,2014].

Figure 3.6 shows a beam of linearly polarized light with known wavelength is incident onto a sample of interest. The polarization state of light is changed to an elliptically polarized light upon reflection or transmission through the sample, and hence the name of the technique "ellipsometry". The enabling principle of ellipsometry is that p-polarized and s-polarized light are reflected differently from a sample. Ellipsometry basically measures the change in polarization state of a light beam reflected from the surface of a sample, which is commonly written as:

$$\frac{R_P}{R_S} = \tan \psi e^{i\Delta} \tag{3.10}$$

Where R_p and R_s are the complex reflection coefficients for p- and s- polarized light, which characterize both the magnitude and phase of the reflected beams. The ellipsometric parameters are defined as: Ψ , which is related to the magnitude of the ratio of p- to sreflected light, and Δ , which is the phase difference between p- and s- reflected light.



Figure 3.6: Schematic illustration of experimental setups used for spectroscopic ellipsometry [Sharma,2014].

In the Film Sense FS-1 EX Multi-Wavelength Ellipsometer, an ellipsometric data at 4 wavelengths in the visible spectrum: 465 nm (blue), 525 nm (green), 590 nm (yellow), and 635 nm (red) are acquired. By analyzing the ellipsometric data, the determination of important sample properties, such as film thickness and index of refraction, become possible [Sharma,2014].

One of the most important parameters for the application of ALD films is the film thickness, which can be precisely controlled by selecting the appropriate number of ALD cycles. Determining the film thickness at any stage during the process is allowed by monitoring the ALD process by in situ SE and growth per cycle during the film growth can be calculated. Moreover, SE helps to control the process such that the film deposition can be stopped when the required film thickness is achieved.

For this study, the film thickness as a function of time is shown in Fig. 3.7 (a) and 3.7 (b) for the ALD processes of HfO_2 and $Gd-HfO_2$. The PEALD cycles and supercycles for undoped and Gd-doped HfO_2 are consequent with time for a specific thickness.



Figure 3.7: The film thickness as a function of time for the PEALD processes of (a) HfO₂ and (b) Gd-HfO₂.

A completely different nucleation behavior is observed for ALD of TiN on a thermally grown SiO₂ surface. A nucleation delay is seen and the growth starts only after 20 ALD cycles (see Fig. 3.8). This is attributed to inability of the $TiCl_4$ precursor molecules to react with the siloxane bridges mainly present on the thermal SiO₂ substrate. The slow nucleation is caused by the limited surface density of defect sites and OH groups on which the $TiCl_4$ can absorb and nucleate to start film growth [Langereis et al.,2010].



Figure 3.8: The film thickness as a function of time for the PEALD processes of TiN.

TiN is preferred electrode in this work as it offers high electrical conductivity, which ensures efficient charge transport, making it suitable for use as a gate electrode in MOS devices [Evangelou et al.,2000]. Additionally, TiN exhibits excellent chemical stability and resistance to oxidation, which allows it to maintain performance even under high temperature conditions, such as those required in semiconductor processing [Wittmer and Melchior,1982]. Furthermore, TiN acts as an effective diffusion barrier, preventing the migration of oxygen or other reactive species into sensitive dielectric layers like HfO₂, which helps maintain the integrity of the device structure and improves its reliability [Calzolari and Catellani,2020].

This study demonstrates the ability of in situ SE to precisely measure the film thickness of the nanometer-thick ALD films. Additionally, data acquisition for cycle-by-cycle enables to monitor the film nucleation and linear growth region in detail. This enables fast optimization of the ALD process, where the influence of deposition parameters on the growth rate can easily be obtained from a single deposition run.

3.1.2 Fabrication of capacitor structures

The last part of the device fabrication after films deposition and annealing step, as mentioned in the introduction of this section, is the patterning of the capacitor structures. After the TiN/Gd:HfO₂/TiN/SiO₂/Si, Gd:HfO₂/TiN/SiO₂/Si and TiN/Gd:HfO₂/SiO₂/Si PEALD stacks deposition and the annealing step, a photolithography/etching process is required, as the last part of the device's fabrication, to create the metallic contacts for electrical measurements.

The mentioned stacks were patterned into circular capacitors of different diameters using optical lithography. Figure 3.9 shows the mask which represents lines with arranged transparent circles. The circles are with the same diameter are arranged in the 7 lines, the diameter of the circles from one line to other changes as 1500, 1000, 800, 600, 400, 200, and 100 μ m. Ultra Violet (UV) lithography is adequately precise to achieve the desired dimensions (100-1500 μ m).



Figure 3.9: The photolithography mask with different diameters circular pads.

Figure 3.9 represents the schematic representation of the photolithography steps for one of the samples of this work, TiN/Gd:HfO₂/TiN/SiO₂/Si, as an example. The first step was the deposition of positive image reversal (negative) resist AZ5214 on the top of the deposited film. The AZ5214 resist, from Micro-chemicals, is polymer sensible to UV light. The spin coating of the reversible photoresist is a required step in a typical photolithography process. For a spinning at 4000 rpm and acceleration 2000 rpm/s in 60s, we obtain a thickness of about 1.4 μ m.

A subsequent evaporation by heating was performed on a hot plate at 100 °C for 120s, in order to prepare the resist for exposure step, as shown in Fig. 3.10 (b). Finally, as shown in Fig. 3.10 (d), the sample with a resist was exposed by UV light, with a wavelength of 365 nm, through the mask in a vacuum contact mode, using a mask aligner (MJB4 Mask Aligner from SUSS MicroTec Group), which exposes the selected region of the chip.

After UV exposure, the sample was annealed for the reversal of photoresist at 120 °C for 120s (Fig. 3.10(e)). Then, the second ultraviolet exposition (365 nm) without mask during 33s was performed. Next, the sample was developed in AZ developer (1 volume of AZ developer and 1 volume deionized water) during 40s and rinsed in the deionized water during 20s (Fig. 3.10(f)) to create a photoresist pattern. The pattern now is on the top polymer layer but not yet on the top TiN electrode at this step.



Figure 3.10: Schematic illustration for photolithography process.

After that, a metallic layers 10 nm of Ti for better adhesion and 100 nm of Pt were deposited (Fig. 3.10(g)) by Metal Evaporator MEB550 from Plassy. The growth rate was controlled in situ by Quartz Crystal Microbalance (QCM) - 0.1 nm/s for Ti evaporation and 0.25/s for Pt evaporation. After that, the sample with photoresist and the layers of metal was placed in acetone to dilute the resist (and remove the pieces of the metal on the top of the resist) and then the sample was rinsed in isopropanol and dried with N_2 gas (Fig. 3.10(h)).

The pattern transfer is accomplished through physical etching, which is stopped upon reaching the ferroelectric film, involving the removal of top TiN electrode outside the patterned capacitors. The patterned structure was protected during the etching by thick Pt(100 nm)/Ti(10 nm) layer. During the etching process, some of Pt(100 nm) layer is also etched. For the etching, we used Ion Beam Etching (IBE) technique by IBE 01 PLASSYS (MU400 FROMPLASSYS). For IBE, Ar plasma was used, Ar flow was 3.0 sccm, the RF plasma power was 300 W, the substrate was rotating during the etching (100 rpm),

the angle between the substrate plane and the Ar flow cross-section plane was 30°. The capacitor devices are ready now for electrical characterization.

MFM and MOS capacitor structures fabrication steps have been realized to conduct electrical characterizations. Figure 3.11 represents the resulting circular pads which obtained after photolithography/etching process. Furthermore, each step of the fabrication flow has been optimized to assure the reproducibility, and no step influences the properties of ferroelectric material in a detrimental way.



Figure 3.11: Optical microscope image after etching [Hachemi,2022].

3.2 Structural Characterizations

Once the samples preparation was presented, the structural characterization techniques will be discussed, together with the setups utilized in this study. HfO₂-based materials are known for their ferroelectric properties because of the stabilization of a non-centrosymmetric orthorhombic phase at room temperature. Consequently, the microstructural characterization offers a crucial information about the crystalline state, i.e., orthorhombic phase which is responsible for the ferroelectricity.

Structural information on the deposited annealed films in this work was primarily examined through Grazing Incidence X-Ray Diffraction (GIXRD), in-plane and out-ofplane Bregg-Brentano X-Ray Diffraction. Additionally, X-Ray Reflectometry (XRR) was also applied to precisely determine the thickness of the films.

3.2.1 X-Ray Refelectometry: XRR

The X-Ray Reflectivity (XRR) is another technique which has been used within this thesis. It is a nondestructive and powerful analytical technique used to characterize thin films and multilayer structures, providing detailed information about thickness, roughness and density of thin films, by analyzing the reflected X-rays from the surface interfaces of the samples [Segantini,2023].

The principle of XRR is based on the reflected X-rays from a flat surface and interfaces of the material. The incidence of X-rays on the material at grazing incidence leads to total reflection at or below the critical angle. Above this critical angle, interference patterns (oscillations) appear, due to rapid decreasing in the reflectivity, as a function of the incident angle.

These oscillations are called Kiessig fringes. From the periodicity of the oscillations, it is possible to calculate the thickness of films (For thinner films, the oscillations are longer). Figure 3.12 reports an example of an oscillation pattern obtained by XRR and the parameters of interest that can be extracted. The following Fresnel equation can be used to calculate the thickness[Segantini,2023]:

$$e = \frac{\lambda}{2} \frac{1}{\theta_{m+1} - \theta_m} \tag{3.11}$$

Where e is the thickness, λ is the wavelength of Cu X-ray beam (1.54 Å) and $\theta_{m+1} - \theta_m$ is the angular distance between two consequent interference maxima.



Figure 3.12: Oscillation pattern sketch obtained by means of XRR of a single layer of HfO₂.

The collected XRR data have been by using on Empyrean Malvern Panalytical X-Ray Diffractometer with CuKa wavelength (1.5406 Angstrom). The operation setup was almost identical to Bragg-Brentano geometry of XRD. The incidence angle is varied from 0 to 6°. The OriginLab software was used for plotting the XRR resulting patterns.

3.2.2 Grazing Incidence X-Ray Diffraction: GIXRD

The significance of the discovered orthorhombic phase was recognized since the initial paper of ferroelectricity in Si:HfO₂ [Böscke et al.,2011]. Accordingly, Grazing Incidence X-Ray Diffraction (GIXRD) was one of the most common methods for the microstructural investigation of ferroelectric HfO₂ thin films.

The structural properties of HfO_2 films are important to determine the crystalline phase, which is responsible for dielectric properties, including ferroelectricity. X-Ray Diffraction (XRD) is the basic characterization technique to obtain such information. XRD provides several operation modes which allow having different information such as the grain size, crystal defects, strain, the present phase and others. Moreover, XRD can be used to determine the amorphous-to-crystalline transition temperature of dielectric materials after annealing processing.

The principle of XRD measurements is based on an X-ray beam directed against the material surface, where the X-rays hit the atomic planes that scatter it, as shown in Fig. 3.13. The wavelength of the incident X-ray beam is comparable to the distance between the crystal planes [Hachemi,2022].

When X-rays are scattered by a periodic lattice with a long-range order, diffraction constructive interference at specific angles occurs. In a periodic crystal lattice, the electrons of the atoms coherently scatter the radiation. The strength of the diffracted beams is directly proportional to the number of electrons involved in the scattering process. Consequently, this strong interaction leads to the formation of a diffraction pattern according to the Bragg's law [Sze, Y. Li, and Ng,2021]:

$$n\lambda = 2d\sin\theta \tag{3.12}$$

where n is the diffraction order, λ the X-ray beam's wavelength, d the distance between two parallel crystalline planes, identified by the Miller indexes hkl, and θ the angle between the incident X-ray beam and the crystal plane. The angle at which the constructive interference from X-rays, scattered by parallel planes, generates the diffraction peaks can be obtained by Bragg's law. This diffraction is collected by a movable detector and plotted as a function of the diffracted angle 2θ , which is the angle formed between the incident beam and the diffracted beam.



Figure 3.13: Illustration of the Bragg's law [Segantini,2023].

To ensure that the diffraction patterns are collected from the topmost layers of the sample, the grazing incidence x-ray diffraction (GIXRD) configuration was used. A very low incident angle is chosen for the incoming beam, usually below 2° , which limits the penetration depth of x-rays inside the material to a few nm only. This technique is based on the fact that, at x-ray energies, most materials can reflect x-rays when the beam strikes the surface at a very small angle of incidence, typically below a critical angle. Under these conditions, the substrate is invisible to x-rays and the beams don't penetrate deeply into the material but instead reflect off the surface.

In this work, all the reported XRD data have been performed after annealing process for all studied stacks, in with GIXRD, ω -2 θ scan with fixed incident angle and moving detecting angle (Fig. 3.14), on Empyrean Malvern Panalytical X-Ray Diffractometer, equipped with a PIXcel-1D detector and using a Cu ($\lambda = 1.54$ Å) X-ray beam. The beam was generated with a voltage of 45 kV and a current of 40 mA.

The incident angle (ω) was always fixed at 1° whereas the 2 θ angle was scanned either from 20 to 80° for wider scans, or for a few degrees around 30, which is related to orthorhombic, tetragonal and monoclinic phase in HfO₂, with a scan length of 10 Å which is enough to cover different phases of HfO₂. The GIXRD result is represented by the number of counts as a function of 2 θ angle. The OriginLab software was used for fitting the plots and for the peak identification.



Sample surface normal

Figure 3.14: Sketch of the GIXRD configuration.

3.2.3 In-plane and Out-of-plane Bragg-Brentano XRD

To investigate the crystallographic structure of HfO_2 thin films and to check the assumption that the appearance of orthorhombic/tetragonal phase in HfO_2 can be related to the stress, the in-plane and out-of-plane XRD measurements were performed in Bragg-Brentano θ -2 θ geometry. The key difference between in-plane and out-of-plane XRD measurements is the direction of the scattering vector relative to the sample surface, as shown in Fig. 3.15 and 3.16.

The scattering vector (q) is a crucial parameter in XRD measurements and identified as the difference between the wavevector of the incident $(\vec{K_i})$ and the diffracted $(\vec{K_f})$ X-ray beams (or change in momentum between the incident and scattered beams). In out-ofplane XRD measurements, the scattering vector is perpendicular to the sample surface. Conversely, the direction of scattering vector in in-plane XRD measurements is parallel to the sample surface.

This provides us an information on the out-of-plane and in-plane lattice parameters and stress in both orientations. The incident X-ray beam makes an angle θ with the sample surface, and the diffracted beam is detected at an angle 2θ . The in-plane and out-of-plane XRD measurements were performed by using Rigacu Smartlab X-Ray Diffractometer and Empyrean Malvern Panalytical X-Ray Diffractometer (2D detector), respectively.



Figure 3.15: Sketch of the in-plane XRD configuration.


Figure 3.16: Sketch of the out-of-plane Bragg-Brentano XRD configuration.

3.3 Electrical characterization

The most significant measurements of ferroelectric materials are electrical; where the hysteretic behavior can be detected. The synthesized MFM capacitors were subjected to electrical characterizations at micro-scale by means of different techniques, that provide information about the electrical properties of the specimens. The most interesting functional properties of ferroelectric materials are leakage current, remnant polarization P_r , coercive voltage V_c and endurance.

The measurements were performed are: current (I) vs voltage (V), polarization (P) vs voltage (V), polarization (P) vs number of cycles and capacitance (C) vs voltage (V). The electrical characterizations were conducted by means of a manual probe station, where the electrical contact was made with two tungsten-tip probes and the samples were kept in a closed environment. The voltage was applied by contacting top electrical contact of each device, which is the Pt layer, with one probe, and the other was kept on the common bottom electrode.

3.3.1 Leakage current measurements

The leakage current is a fundamental parameter for the characterization of ferroelectricbased devices. The largest part of technological applications requires the leakage current to be minimized. Indeed, it is responsible for the quality of ferroelectric materials, which is one of the causes that provoke an early electrical breakdown [Hachemi,2022]. I-V characteristics were carried out by means of KEITHLEY 2612B SYSTEM SourceMeter analyzer, shown in Fig. 3.17.



Figure 3.17: KEITHLEY 2612B SYSTEM SourceMeter analyzer.

In this measurement, two conductive probes are in contact with top and bottom electrodes of the capacitor and are connected by triaxial cables to the FE module which is in turn connected to the computer. A magnifying lens is used to facilitate the operation of the micromanipulators to which the conductive probes are attached. One probe touches the top surface of Pt metallic contact as a top electrode, and the other probe must be in contact with bottom TiN electrode to measure the current flow through the dielectric material.

As we etched down to the ferroelectric layer, which lies just above the bottom TiN electrode, without reaching it. This leaves the area between Pt contacts as dielectric layer. To establish contact with bottom TiN electrode, one specific capacitor is subjected to a high

voltage until it breaks down, effectively creating a pathway to the bottom TiN electrode. The voltage at which the capacitor breaks down is considered the highest voltage that can be safely applied the capacitor.

An externally applied voltage creates a leakage current flow through the dielectric material, which depends on the mobility of free electronic or ionic charges in the dielectric properties. High leakage current can affect the ferroelectricity of HfO₂. Figure 3.18 illustrates an example of the characteristic curve of the leakage current of the ferroelectric capacitor.



Figure 3.18: Logarithm of the current density vs the applied electric field of a ferroelectricbased device.

3.3.2 Polarization vs voltage measurements: Hysteresis cycle

The hysteretic nature of polarization is one of the main features of the ferroelectric materials. The hysteresis loop is a signature of ferroelectricity and the key to more advanced measurements, such as fatigue. This makes the polarization vs voltage (P-V) measurements the most important among the electrical methods by revealing the remnant polarization and coercive voltage.

For extracting the macroscopic ferroelectric properties of HfO₂-based films, the TF 2000 analyzer with FE module by AixACCT was the main tool. In this characterization, two conductive probes touch the bottom and top electrode of the capacitor, which are connected by triaxial cables to the FE module that is in turn connected to the computer. To facilitate the operation of the micromanipulators to which the conductive probes are attached, a magnifying lens is used.

In this work, the voltage was applied in triangular wave, with the ability of defining the amplitude depending on the thickness of the sample under test. The frequencies used in this work range from 200 Hz to 20 KHz. For the optimization of the resulting curve, the current range was 1-100 μ A and 1 mA for 200 Hz and 20 KHz measurements, respectively. The OriginLab software was used to extract the hysteresis loop from the resulted PUND measurement, as early mentioned in chapter two.

3.3.3 Fatigue measurement (FM) test: Endurance test

The ferroelectric tester (TF 2000 analyzer with FE module by AixACCT) allows to cycle the capacitor electrically and test the endurance of the material. Figure 3.19 shows a train of square waves of the applied excitation voltage were used in this experiment, where the amplitude and frequency can be defined and varied according to the thickness of tested samples.

During cycling, it is possible to execute one or more single measurements, such as PUND, in between the fatigue cycles, to see if there was any change in the polarization properties of the material, which might indicate a wakeup or fatigue effect during this evolution. The number of cycles the sample has to undergo and the number of PUNDs are to be performed for every cycle decade are possible to be defined. As a result, the evolution of the polarization response can be closely followed. The typical plot in this case shows the values of P_r versus the number of cycles, with the latter in logarithmic scale.



Figure 3.19: Sketch of train of square waves required for FM measurements.

A typical result of a Fatigue Measurement (FM) is shown in Fig. 3.20. It displays the remnant polarization of the in between recorded hysteresis loops versus the logarithm of the total number of applied cycles.



Figure 3.20: Typical Fatigue Measurement graph.

3.3.4 Capacitance vs voltage measurements: MOS capacitors

To study the performance of MOS devices, C-V measurements were performed on annealed and not-annealed TiN/Gd:HfO₂/SiO₂ capacitors using one electrical probe placed on the Pt (top electrode) and back side was in contact with the metallic base of the tool. The Agilent E4980A 20 Hz – 2 MHz Precision LCR Meter equipment was used , which is shown in Fig. 3.21. The AC bias frequency is 1 MHz and the amplitude is 25 mV in a forward voltage scan range of 1 to -4 volts.



Figure 3.21: The Agilent E4980A 20Hz – 2MHz Precision LCR Meter equipment.

3.4 Summary

This chapter presented the preparation and characterization techniques that were used throughout this study. The first section highlighted the ALD deposition technique and capacitors fabrication process. In the second and third sections, the structural (GIXRD, in-plane XRD, out-of-plane XRD and XRR) and electrical (I-V, PM, FM and CVM) characterization techniques, in respective, for HfO₂-based films were presented.

Chapter Four: Results

This chapter demonstrates the effect of TiN electrodes and Gd doping on crystallization of ferroelectric phase in HfO₂-based thin films. The first part presents a study on undoped and Gd doped HfO₂, which were deposited onto SiO₂/Si substrate, where the mechanical stress inside the HfO₂ material is explored by means of GIXRD, in-plane and out-of-plane XRD. The data is analyzed by using standard mathematical approaches. The second part mainly presents the evolution of ferroelectric properties in TiN/Gd:HfO₂/TiN/SiO₂/Si thin films in thickness range 5-40 nm.

Furthermore, the endurance behavior of such films was explored by analyzing the progress of hysteresis behavior upon electrical cycling. The presented results are taken as a starting point to understand the evolution of switching behavior at the domain level. Overall, the shown outcomes enrich the findings from electrical measurements and provide an alternative look into the transformations that take place at different levels of cycling.

4.1 X-ray reflectometry study of HfO₂ and Gd:HfO₂ films formed by PEALD

The x-ray reflectometry (XRR) was used to measure the thicknesses of different types of sample stacks: Fig. 4.1 (a) $HfO_2/SiO_2/Si$, (b) $TiN/HfO_2/SiO_2/Si$, (c) TiN/Gd: $HfO_2/SiO_2/Si$, Fig. 4.2 (a) Gd: $HfO_2/TiN/SiO_2/Si$ and (b) TiN/Gd: $HfO_2/TiN/SiO_2$

/*Si*. Figure 4.1 and 4.2 show a series of the XRR curves measured for annealed sample stacks (blue solid lines) and, respectively, their fit lines (red solid lines). For example, Fig.4.1 (a) shows that the curves measured for four $HfO_2/SiO_2(100 \text{ nm})/Si$ samples. HfO_2 thickness was varied by applying different numbers of PEALD cycles for the growth of these stacks: 40 cycles (hereinafter cy), 80 cy, 120 cy, and 160 cy.

Furthermore, Fig.4.2 (a) shows that the curves measured for six Gd:HfO₂/TiN/SiO₂ (100 nm)/Si samples. Gd:HfO₂ thickness was varied by applying different numbers of PEALD supercycles for the growth of these stacks: 10 supercycles (hereinafter scy), 20 scy, 30 scy, 40 scy, 50 scy and 70 scy. One can see that the distance between oscillations decreases by increasing the number of HfO₂ PEALD cycles or Gd:HfO₂ PEALD supercycles, correspondingly, HfO₂ or Gd:HfO₂ thickness increases. HfO₂ thickness obtained

after fit is 5.4 nm (for 40 cy), 10.7 nm (for 80 cy), 16.1 nm (for 120 cy), and 21.3 nm (for 160 cy). Gd:HfO₂ thickness obtained after fit is 5.5 nm (for 10 scy), 11.2 nm (for 20 scy), 17.2 nm (for 30 scy), 23.2 nm (for 40 scy), 29.7 nm (for 50 scy) and 41.8 nm (for 70 scy).

The oscillation period also decreases with increasing the number of HfO₂ cycles or Gd:HfO₂ supercycles as shown for XRR curves measured for other stacks: TiN/HfO₂/SiO₂/Si (Fig. 4.1 (b)), TiN/Gd:HfO₂/SiO₂/Si (Fig. 4.1 (c)) and TiN/Gd:HfO₂/TiN/SiO₂/Si (Fig. 4.2 (b)). The average thickness of the top and bottom TiN electrodes extracted from XRR measurements was found to be 10 and 20 nm for 167 and 334 PEALD cycles, respectively.



Figure 4.1: XRR curves (blue solid lines) and their fits (red) measured after annealing with different number of HfO₂ and Gd:HfO₂ PEALD cycles and supercycles for different types of sample stacks: (a) HfO₂/SiO₂/Si, (b) TiN/HfO₂/SiO₂/Si, and (c) TiN/Gd:HfO₂/SiO₂/Si.



Figure 4.2: XRR curves (blue solid lines) and their fits (red solid lines) measured after annealing with different number of Gd:HfO₂ PEALD supercycles for two types of sample stacks: (a) Gd:HfO₂/TiN/SiO₂/Si and (b) TiN/Gd:HfO₂/TiN/SiO₂/Si.

In this work, the film thickness (measured by XRR) as a function of PEALD HfO₂ cycles and Gd:HfO₂ supercycles are shown in Fig. 4.3 (a) and 4.3 (b) for the PEALD processes of HfO₂ and Gd:HfO₂, respectively. It is evident, that the thickness increases linearly with the number of cycles (or supercycles). The amount of material deposited per cycle, growth per cycle (GPC), can be obtained from linear regression analysis of data. For the data in figure 4.3, the growth rates are 1.3 Å/cycle for HfO₂ cycles or Gd:HfO₂ supercycles.

The linear increase in film thickness during the first deposition cycles reveals that the ALD growth of HfO_2 and $Gd:HfO_2$ proceeds immediately on SiO_2/Si substrate. These two growth curves demonstrate that these metal-organic precursor molecules directly react with the substrates employed.

This study shows good agreement with previous reports regarding the relationship between film thickness and deposition cycles. Skopin et al. [Skopin et al.,2022] and Alrifai et al. [Alrifai et al.,2023] both demonstrated a linear increase in Gd-doped HfO_2 thickness with the number of PEALD cycles, which aligns with my findings over a broader thickness range.



Figure 4.3: HfO₂ and Gd:HfO₂ layer thickness extracted by XRR fit obtained after RTA.

Once the thickness of HfO_2 and $Gd:HfO_2$ layers is presented, a more detailed structural characterization techniques of the thin film are executed. For example, GIXRD, in-plane and out-of-plane Bragg-Brentano XRD are held.

4.2 Impacts of TiN electrodes and Gd doping on ferroelectricity of HfO₂

This section will present the effect of top electrode and doping on the crystallization of HfO_2 thin films, as well as the influence of Gd doping on stabilization of the ferroelectric orthorhombic phase in Gd: HfO_2 thin films. The first subsection will show the observed GIXRD, in-plane and out-of-plane XRD patterns. The second subsection will exhibit the capacitance versus voltage characteristic to check the ferroelectric properties of the studied film.

4.2.1 X-ray diffraction characterization of polycrystalline HfO₂ and Gd:HfO₂ thin films

To study the effect of TiN top electrode on the HfO₂ crystallization after annealing, x-ray diffraction was measured for two different stacks: HfO₂/SiO₂/Si (without top TiN electrode) and TiN/HfO₂/SiO₂/Si (with top TiN electrode). The thickness of TiN top electrode was about 10 nm. The thickness of HfO₂ layer in both stacks was varied up to 20 nm. Figure 4.4 shows measured GIXRD curves for these two stacks: HfO₂/SiO₂/Si (a-b) and TiN/HfO₂/SiO₂/Si (c-d). GIXRD curves were measured in the 2 θ range 20-80° (Fig.4.4 (a) and Fig.4.4 (c)) and also in the more representative area range 27-34° with smaller angle step (Fig. 4.3 (b) and Fig. 4.3 (d)).

It is common that the maximum characteristic peak of ferroelectric non-centrosymmetric orthorhombic phase is observed at $2\theta = 30.2^{\circ}$. It is noted that XRD is limited in this 27-34° range because it is difficult to separate the contributions of ferroelectric orthorhombic phase and non-ferroelectric tetragonal phase.

Figure 4.4 shows that the HfO_2 films reveal a polycrystalline nature. The sharp XRD patterns were analyzed with the help of the "Crystdiff" software package. In the "crystdiff" software package, we inserted the XRD patterns of 21.6 nm-thick HfO_2 film to determine the crystal structure and miller indices for all the diffraction peaks. The structure was solved assuming possible formation of orthorhombic, tetragonal, and monoclinic phases. The peaks are associated to orthorhombic, tetragonal or orthorhombic/tetragonal (mixed) and monoclinic phases with specific orientations.

For XRD patterns shown in Fig.4.4 (b), the peaks in the range of interest are located at 28.5° and 31.6° diffraction angles. These peaks are related to monoclinic $P2_1/c$ (14) space group, with no visible orthorhombic/tetragonal peaks. Whereas for the XRD patterns shown in Fig.4.4 (d), the characteristic peak is located at 30.5° diffraction angle for the thinnest 5.4 nm-thick HfO₂ layer. This peak is related to orthorhombic $Pna2_1$ (30) or/and tetragonal $P4_2/nmc$ (137) space groups.

However, for the thickest 21.6 nm-thick HfO₂ layer, the orthorhombic/tetragonal phase is no longer exist with clear appearance of two peaks located at 28.5° and 31.8° diffraction angles. These peaks are related to monoclinic $P2_1/c$ (14) space group. If we compare our observed XRD patterns to the reference data [Huan et al.,2014], we can see that there is a slight deviation ($\Delta\theta = \frac{\theta_{observed} - \theta_{standard}}{\theta_{standard}}$ 100%) of only 1.5% in the characteristic orthorhombic/tetragonal observed at 30.2° and monoclinic (observed at 28.1° and 31.6°) diffraction angles.

It is observed from Fig. 4.4 that the XRD patterns of the HfO_2 samples exhibit nearly the same crystallization nature with some noticeable differences. Figure 4.4 (b) and 4.4 (d) gives deep information about the effect of varying thicknesses on the structural performance of HfO_2 films.

The intensity of two monoclinic phase peaks in the 2θ range 27-34° (Fig. 4.4 (b)) increases as a function of HfO₂ thickness. Weak peak intensity in the region of orthorhombic and tetragonal phase peaks (about 30.2°) does not increase by increasing HfO₂ layer thickness. In another case of undoped HfO₂ with top TiN electrode (Figs. 4.4 (c-d)), orthorhombic or tetragonal phase peaks are presented for some HfO₂ thickness range (up to 7.6 nm), monoclinic phase peaks are presented for all HfO₂ thicknesses up to 22 nm.



Figure 4.4: GIXRD curves of HfO₂/SiO₂/Si (a-b) and TiN/HfO₂/SiO₂/Si (c-d) samples.

 HfO_2 crystallization in o/t phase (related to ferroelectric properties of HfO_2) probably caused by TiN contact stress or HfO_2 doping. For TiN/HfO_2/SiO_2/Si stack (HfO_2 with top TiN electrode), one can see that o/t peak almost disappeared when HfO_2 thickness increased to 10 nm. Thus, ferroelectric properties of undoped HfO_2 only with the top TiN electrode can be presented in a small HfO_2 thickness range (up to 10 nm).

Boscke et. al. [Böscke et al.,2011] reported that annealing step after capping with top TiN built an in-plane strain which stabilized the unstable orthorhombic phase. The stress induced stabilization reached by annealing after growing the top electrode layer can be better understood if we consider that even undoped HfO_2 exhibited ferroelectric phase. Hence, this intrinsic effect is dependent on Gd doping [D. Ye et al.,2014].

To study the origins of this phenomenon, the XRD patterns for TiN/Gd:HfO₂/SiO₂/Si were measured in thickness range of 5-22 nm and shown in Fig. 4.5. It is clear from Figure 4.5 that the Gd:HfO₂ films reveal a polycrystalline nature. The sharp XRD patterns of 22 nm were analyzed using the "Crystdiff" software package in order to determine the crystal structure and miller indices for all diffraction peaks. The structure was solved as orthorhombic and tetragonal and the calculated lattice parameters were: 5.05, 4.99, 5.08 Å and 3.58, 3.58, 5.00 Å along a-, b- and c- axes, respectively. The peaks are associated to orthorhombic, tetragonal or orthorhombic/tetragonal (mixed) phases with specific orientations. The maximum peak is related to orthorhombic *Pna*2₁ (30) or/and tetragonal *P*4₂/*nmc* (137) space groups.

The main difference between tetragonal and orthorhombic is that the orthorhombic phase is a distorted structure of tetragonal phase; the calculated lattice parameters along a- and b-axes are slightly different. Another further difference between such structures is the space of symmetry (rotational symmetry) [Sze, Y. Li, and Ng,2021]. Comparing our observed XRD patterns to standards [Huan et al.,2014], we can see that there is a slight deviation of only 1.7% in the characteristic o/t peak at 30.2° diffraction angle (the shift between the red line (standard), and both green (thinnest sample) and gray (thickest sample) lines).



Figure 4.5: GIXRD curves of TiN/Gd:HfO₂/SiO₂/Si (a-b) samples with different HfO₂ layer thickness (after RTA): (a) - in the 2θ angle range 20-80° and (b) - in the 2θ angle range 27-34° with higher angular resolution. The upper part represents the GIXRD pattern of the reference HfO₂ structure, corresponding of monoclinic, tetragonal and orthorhombic phases [Huan et al.,2014].

To analyze the behavior of orthorhombic/tetragonal peaks integrated intensity as a function of HfO_2 thickness, measured GIXRD curve functions were deconvoluted using Gauss functions. Figures 4.4 (b,d) and 4.5 (b) show blue area for (111) orthorhombic or (101) tetragonal phase peaks.

Figure 4.6 shows the integrated area of o/t peaks as a function of thickness for $HfO_2/SiO_2/Si$, TiN/HfO_2/SiO_2/Si and TiN/Gd:HfO_2/SiO_2/Si structures (red circles, green rhombohedral and brown squares, respectively). The amount of o/t phase is proportional to the integrated o/t peak. For HfO_2/SiO_2/Si (HfO_2 without top electrode), the integrated peak area (intensity) is almost zero in HfO_2 thickness range 5.4-21.3 nm. HfO_2 crystallization in o/t phase (related to ferroelectric properties of HfO_2) can be caused by TiN contact stress or HfO_2 doping.

For TiN/HfO₂/SiO₂/Si stack (HfO₂ with top TiN electrode), one can see that intensity increases as a function of HfO₂ thickness and reaches the maximum at 4.9 nm. Then,

intensity decreases and almost disappears when HfO_2 thickness reaches 10 nm. Thus, ferroelectric properties of undoped HfO_2 only with the top TiN electrode can be presented in a small HfO_2 thickness range (up to 10 nm).

To study the origin of this phenomenon, the intensity of $TiN/HfO_2/SiO_2/Si$ (green rhombohedral: undoped HfO_2) and $TiN/Gd:HfO_2/SiO_2/Si$ (brown squares: Gd doped HfO_2) stacks were compared. It is clear that the intensity keeps increasing with increasing thickness up to a thickness of 22 nm in Gd:HfO_2 layers. As a result, stabilization of ferroelectric orthorhombic phase can be caused by HfO_2 doping. Related studies offer significant insights into phase transitions in similar systems.

For example, Seya et al. [Seya, Jang, and Ueno,2015] examined the microstructure formation and phase transitions in $Al_2O_3 - HfO_2$ eutectic systems, demonstrating that thermal processing can induce changes in crystal structures, such as the transition from tetragonal to monoclinic HfO₂, driven by stress and solidification dynamics. These results indicate that analogous thermal and mechanical influences may affect phase behavior in undoped and Gd doped TiN/ $HfO_2/SiO_2/Si$ systems.



Figure 4.6: Integrated area of (111) orthorhombic phase as a function of undoped HfO_2 layer thickness (red circles and green rhombohedral) for $HfO_2/SiO_2/Si$ and $TiN/HfO_2/SiO_2/Si$, and integrated area of (111) orthorhombic peak as a function of thickness of Gd doped HfO_2 layers (brown squares).

To get deep information about the effect of the Gd:HfO₂ layer thickness on the structural properties, the interplanar distance (d), the crystallite size (D), the micro-strain (ε), the stacking faults (SF%) and the defect density (δ) along the a, b, and c-axes were calculated, for the thinnest and thickest samples, following equations listed in chapter two. The calculated values of structural parameters for the maximum intensity peaks are tabulated in table 4.1.

Table 4.1:	The structural	parameters	of Gd:HfO ₂	thin films	obtained from	the main]	peak.

HfO ₂ thickness (nm)	d (Å)	D (nm)	ε	δ (line/ <i>cm</i> ⁻²)	SF (%)
undoped 4.90	2.93	6	$2.24 * 10^{-2}$	$1.02 * 10^{13}$	1.18
(Gd) 5.30	2.93	6	$2.16 * 10^{-2}$	$9.42 * 10^{12}$	1.14
(Gd) 22.5	2.91	19	$7.16 * 10^{-3}$	$1.04 * 10^{12}$	0.38

One can observe that the micro-strain value decreases upon increasing thickness, this can be associated with an increase in the grain size of the crystal structure. On the other hand, the thickness of $Gd:HfO_2$ layer has an impact on the deviation of main diffraction peak toward higher diffraction angle. Strain caused by Gd dopants and electrodes play a vital role in lattice distortion and phase transformation.

Our structural study has evidenced that the top TiN layer stabilize the o/t phases up to 5 nm-thick sample. After this thickness, the stabilization is attributed to Gd doping factor. To deeply check the assumption that the appearance of o/t phase in Gd:HfO₂ can be related to the stress, the XRD curves were measured in-plane and out-of-plane in Bragg-Brentano θ -2 θ geometry for undoped and doped HfO₂ layers.

Figures 4.7 (a-b) and 4.7 (c-d) show, respectively, XRD curves measured for TiN/HfO₂/SiO₂ (undoped HfO₂) and TiN/Gd:HfO₂/SiO₂ (Gd doped HfO₂) sample sets. In-plane XRD curves are shown on figs. 4.7 (a) and 4.7 (c); out-of-plane XRD curves are shown on Fig. 4.7 (b) and 4.7 (d).



Figure 4.7: In-plane (a,c) and out-of-plane (b,d) XRD curves measured for the $TiN/HfO_2/SiO_2/Si$ (a-b) and $TiN/Gd:HfO_2/SiO_2/Si$ (c-d) sample stacks as a function of HfO_2 or $Gd:HfO_2$ thickness.

For the case of undoped HfO₂, the o/t peak position is different for in-plane and out-ofplane XRD. In the case of in-plane XRD (Fig. 4.7 (a)), o/t peak position corresponds to the same 2θ as in the reference. In the case of out-of-plane XRD (Fig. 4.7 (b)), o/t peak position shifted to higher θ values compared to the reference. For the case of Gd doped HfO₂, the o/t peak position shift for the cases of in-plane and out-of-plane XRD is more visible than for the case of undoped HfO₂.

In the case of in-plane XRD (Fig. 4.7 (c)), o/t peak position shifted to smaller 2θ values, and in the case of out-of-plane XRD (Fig. 4.7(d)), it is shifted to higher 2θ values. Figure 4.8 (a) and 4.8 (b) simply displays the o/t peak position as a function of HfO₂ or Gd:HfO₂ layer thickness, as extracted from in-plane and out-of-plane XRD data.



Figure 4.8: The O/T peak position as a function of (a) HfO_2 and (b) $Gd:HfO_2$ layer thickness, as extracted from in-plane (blue squares) and out-of-plane (red circles) XRD data.

For better understanding of the stress phenomenon, we calculated interplane distance d, grain size and micro-strain corresponding to (111) ferroelectric orthorhombic phase or (101) tetragonal phase XRD planes. Figures 4.9 (a) and 4.9 (b) show calculated d_{o111}/d_{t101} as functions HfO₂ and Gd:HfO₂ layer thickness, correspondingly (TiN/HfO₂/SiO₂/Si and TiN/Gd:HfO₂/SiO₂/Si sample stacks).

Blue squares on the figures show the values of d calculated using in-plane XRD data (diffraction planes are perpendicular to the sample plane). Red circles on the figures show the values of d calculated using out-of-plane XRD data (diffraction planes are parallel to the sample plane).



Figure 4.9: Interplane distances d (calculated for (111) ferroelectric orthorhombic phase or (101) tetragonal phase XRD planes) as functions of HfO₂ and Gd:HfO₂ thickness measured for (a) TiN/HfO₂/SiO₂/Si and (b) TiN/Gd:HfO₂/SiO₂/Si (b) sample stacks. Blue squares / red circles, respectively, correspond to the d of the planes which are perpendicular/parallel to the sample surface.

In the case of undoped HfO_2 in the HfO_2 thickness range 4.9-7.6 nm (Fig. 4.9 (a)), d is the same as the reference d value for the planes perpendicular to the sample surface and smaller for the planes which are parallel to the sample surface. This corresponds to the compressive stress to the planes parallel to the sample surface.

In the case of Gd doped HfO_2 in the HfO_2 thickness range 5.3-22.6 nm (Fig. 4.9 (b)), d is higher than the reference d for the planes perpendicular to the sample surface and increases as a function of HfO_2 thickness. The value of d for the planes parallel to the sample surface is smaller than the reference d, and the d decreases as a function of HfO_2 thickness.

For the thinnest Gd:HfO₂ (5.3 nm), d is 0.5% higher and 0.6% smaller, correspondingly, for the planes perpendicular and parallel to the sample surface. Also for the thickest Gd:HfO₂ (22.6 nm), d is 0.9% higher and 1.6% smaller, correspondingly, for the planes perpendicular and parallel to the sample surface. The difference between d measured by in-plane and out-of-plane XRD increases as a function of Gd:HfO₂ thickness. Thus, the compressive stress to the planes parallel to the sample surface in Gd:HfO₂ is higher when the Gd:HfO₂ thickness is higher (in the studied thickness range).

Figures 4.10 (a) and 4.10 (b) exhibit the grain size progression and strain as a function

of Gd:HfO₂ layer thickness, which were calculated using the in-plane and out-of-plane XRD data. For planes that are parallel to the sample surface, the crystallite size strongly increases as Gd:HfO₂ thickness layer increases, as shown in Fig. 4.10 (a): red circles. This is affected by a strong decrease in the micro-strain values as is seen in Fig.4.10 (b): red circles.

On the other hand, in the planes that are perpendicular to the sample surface, the crystallite size (blue squares) values (Fig. 4.10(a)) are almost the same with varying thickness. This is in good agreement with what can be seen in Fig. 4.10 (b), where the micro-strain values are almost constant. As a result, the stress generated in a direction perpendicular to the surface is less effective than that applied in a direction parallel to the surface, since the grain size in such a direction doesn't change significantly. Thus, a tensile mechanical stress caused by top TiN electrode and Gd dopant stabilizes the orthorhombic ferroelectric phase in Gd:HfO₂ thin films.



Figure 4.10: (a) Grain size and (b) strain calculated from in-plane and out-of-plane XRD data for TiN/Gd:HfO₂/SiO₂/Si samples

4.2.2 Capacitance-Voltage characteristics

Figure 4.11 shows the capacitance-voltage curves for annealed and deposited $TiN/Gd:HfO_2$ (11 nm)/SiO₂ (22 nm)/Si(p) MOS capacitors on p-Si substrates in the positive-negative voltage scan between 1 and -4 volts. The positive to negative voltage scan between 1 and

-4 volts showed well-behaved inversion \rightarrow depletion \rightarrow accumulation typical of a MOS stack on p-type substrate.

The theoretical equivalent accumulation capacitance (C_{eq}) value was calculated to be 189.3 pF using the following equation: $1/C_{eq} = 1/C_{HfO_2} + 1/C_{SiO_2}$, where C is the capacitance measured in Farad (F): $C = \varepsilon \varepsilon_0 A/t$, where ε_0 is the permittivity of free space (8.85 * $10^{-14}F/cm$) and ε is the relative permittivity of HfO₂ ($\varepsilon_{HfO_2} = 25$) [Tony Schenk, Stefan Mueller, et al.,2013] or SiO₂ ($\varepsilon_{SiO_2} = 3.9$) [Men et al.,2020]. A is the area of the capacitor device ($1.3 \times 10^{-3}cm^2$) and t is the layer thickness, 11 and 22 nm for HfO₂ and SiO₂ respectively. The measured accumulation capacitance value for both annealed and not-annealed Gd:HfO₂ capacitors is between 163-170 pF, which is mostly due to SiO₂ layer in the accumulated region.

In addition, the annealed sample C-V characteristic shows a voltage shift towards negative voltages by approximately 1 Volt. This means that the flat band voltage is different in both samples, which can be explained by the presence of remnant dielectric polarization (which causes the ferroelectric behavior of the annealed Gd:HfO₂ film [Kalkur, Jacobs, and Argos,1994]). Indeed, x-ray analysis showed that annealing at 650 °C leads to the crystallization of the otherwise amorphous as deposited Gd-doped HfO₂ layer.

By attributing the observed voltage shift to a ferroelectric behavior, a remnant dielectric polarization 2 $\mu C/cm^2$ was calculated, using the following equation: $P_r = \Delta Q/A$, where $\Delta Q = C_{HfO_2}\Delta V$ and A is the area of the capacitor device $(1.3 * 10^{-3}cm^2)$. For $C_{HfO_2} = \varepsilon_{HfO_2}\varepsilon_0 A/t$, where ε_0 is the permittivity of free space (8.85 * $10^{-14}F/cm$) and ε is the relative permittivity of HfO₂ ($\varepsilon_{HfO_2} = 25$) [Tony Schenk, Stefan Mueller, et al.,2013] and t is the HfO₂ layer thickness (11 nm). This confirms the ferroelectricity of the annealed 11-nm thick Gd:HfO₂ layer.



Figure 4.11: Capacitance-voltage (C-V) curves for annealed and as deposited TiN/Gd: $HfO_2/dry SiO_2$ MOS capacitors on the p-Si substrate.

To understand the mechanism of TiN/Gd:HfO₂/SiO₂/Si MOS capacitor, a schematic representation is presented in Fig. 4.12 (a) and 4.12 (b), for as deposited and annealed capacitors, respectively. In the as deposited case, applying positive gate voltage across the oxide layers results in the accumulation of positive and negative charges (Q: in black) on the surfaces of top TiN electrode and Si interface, leading to the formation of electric field that span between the electrodes.

For annealed sample, the domains inside the ferroelectric material create an opposite electric field due to domains switch results in higher charge density $(Q + Q_r)$ on the surfaces of top TiN and Si interface, where Q_r is the remnant charges accumulated due to ferroelectric polarization effect. The capacitance was measured in positive to negative forward scan bias, thus, applying negative gate voltage to the top TiN electrode leads to compensating the accumulated positive charges until the flat band voltage (VFB) is achieved. In the annealed case, we need higher amount of negative charges to compensate $(Q + Q_r)$ instead of Q in the as deposited case, consequently, the flat band voltage is shifted to negative in the case of annealed sample.



Figure 4.12: A schematic representation of TiN/Gd:HfO₂/SiO₂/Si MOS capacitors in the (a) as deposited and (b) annealed case.

This behavior poses the question of the origin of HfO_2 ferroelectric behavior and the role of doping. Some published reports in literature showed the fundamental role of electrodes and mechanical stress in stabilizing the ferroelectric phase.

Nakamura et. al. [Nakamura and Kamoshida,1974] studied the C-V characteristics of MOS capacitors annealed at various temperatures between 300 and 900 °C for 30 min after implantation of Boron ions through 1500-A gate-oxides of p-channel MOS transistors. The C-V curves showed that the gate voltage of the transition region shifted in the positive direction with increasing the annealing temperature. This result aligns with our finding, where the gate voltage of the transition region of n-channel MOS capacitor is shifted in the negative direction for annealed sample compared to the as deposited sample.

The results shown in figures 4.4 - 4.11 suggest that exposing the HfO₂ layer to mechanical stress leads to its stabilization in the orthorhombic (ferroelectric) crystalline phase. In the case of undoped HfO₂ layers, the analysis of these results shows that mechanical stress is mainly due to the bottom TiN electrode. Indeed, in the without TiN bottom electrode TiN/HfO₂/SiO₂/Si(p) stack, figures 4.4, 4.5 and 4.7(a) show the absence of important HfO₂ non-centrosymmetric o/t crystalline phase and the absence of interplanar distance deformation between in plane and out of plane diffraction geometries, *i.e.* the absence of mechanical stress, respectively.

In contrast, in the case of Gd-doped HfO2, the TiN/Gd:HfO2/SiO2/Si(p) stack shows a

strong o/t diffraction (figure 4.5 and 4.7(c,d)) peak correlated to significant interplanar distance deformation between in-plane and out-of-plane diffraction geometries resulting from internal mechanical stress due to Gd-doping. In addition, the existence of the orthorhombic/ferroelectric phase in Gd-doped HfO₂ is further evidenced by C-V characteristics analysis.

Our conclusion on the role of electrode-applied mechanical stress in stabilizing the HfO₂ non-centrosymmetric orthorhombic/ferroelectric phase is supported by several reports [Alrifai et al.,2023]; [Nishimura et al.,2016]; [Kim et al.,2016]; [P. Fan et al.,2019]; [S.-T. Fan, Y.-W. Chen, and CW Liu,2020].

It was reported that the undoped HfO_2 can be crystallized into the orthorhombic ferroelectric phase by the interface controlling process. Nishimura et al. [Nishimura et al.,2016] reported that TiN interface serves as the nucleation site of the ferroelectric phase in HfO_2 . They found that as the grain size of HfO_2 increases with the thickness of the HfO_2 film, the non-ferroelectric monoclinic phase becomes more stable than the ferroelectric phase. This finding aligns with our work, where the lack of a bottom TiN interface affects the stabilization of the ferroelectric HfO_2 phase in films exceeding thickness 7.6 nm.

Additionally, Kim et. al. [Kim et al.,2016] have been emphasized that the undoped HfO_2 thin films could crystallize in both o- and t-phases when they are sufficiently thin and exhibiting small grain size, where the mechanical stress is more pronounced in thinner films, and it diminishes as the film thickness increases. Moreover, he showed that controlling the substrate temperature during ALD process of undoped-HfO₂ thin films achieves ferroelectricity even without intentional doping of other metallic elements.

As a result, decreasing the deposition temperature down to 220 °C could effectively decrease the average grain size without significant increase in the leakage current. Increasing the impurity concentration by lowering the deposition temperature effectively reduces the lateral grain growth during crystallization annealing at 650 °C via RTA.

Using simulation techniques, Fan et al. [P. Fan et al.,2019]; [S.-T. Fan, Y.-W. Chen, and CW Liu,2020], reported that HfO₂ exhibits antiferroelectric properties under compressive strain conditions. However, when subjected to in-plane tensile strain, the non-ferroelectric HfO₂ could be triggered to transition into an out-of- plane polarized orthorhombic ferroelectric phase after being poled by a small out-of-plane electric field. Moreover, by applying a biaxial tensile strain, the ferroelectric orthorhombic phase becomes further

stabilized under a compressive strain exceeding 3%.

In conclusion, our work enriches the previous findings and provides an additional proof that the undoped HfO_2 thin films, deposited onto SiO_2 substrate, could be ferroelectric for ultrathin layers up to 5.4 nm. Beyond this thickness, the presence of bottom TiN electrode or/and Gd doping is important to stabilize the ferroelectric orthorhombic phase up to higher thicknesses.

4.3 Thickness-dependent evolution of ferroelectricity in Gd:HfO₂ thin films

This section mainly presents the evolution of ferroelectric properties in TiN/Gd:HfO₂ /TiN/SiO₂/Si thin films in thickness range 5-40 nm, as well as the impact of capping layer before and after annealing process; from crystallographic (5-42 nm) and electrical points (selected thicknesses) of view.

In addition, the endurance behavior of such films was explored by analyzing the progress of hysteresis behavior upon electrical cycling. The presented results are taken as a starting point to understand the evolution of remnant polarization value and switching behavior at the domain level. Overall, the shown outcomes enrich the findings from electrical measurements and provide an alternative look into the transformations that take place at different levels of cycling.

4.3.1 Structural Study: Hints of ferroelectric phase

The optical images for the annealed Gd:HfO₂/TiN/SiO₂ and TiN/Gd:HfO₂/TiN/SiO₂ PEALD thin films are shown in inset-1 of Fig.4.13 (b) and inset-2 of Fig.4.14 (c), respectively. Thin Gd:HfO₂ films displayed a dark blue color. The color of this sample is converted to light blue, green and light green as the thickness increased from 5.4 nm to 42.3 nm for TiN/Gd:HfO₂/TiN/SiO₂/Si (capped) thin films, whereas for Gd:HfO₂/TiN/SiO₂/Si (uncapped) films, the color converted from dark blue to light blue and turquoise as the thickness increases from 5.5 nm to 41.8 nm.

In order to explore the effect of annealing before and after capping TiN electrode layer, increasing thickness and Gd doping on the structural performance of HfO₂ thin films, the

GIXRD patterns of HfO₂ films are displayed in Fig. 4.13 in thickness range of 5-42 nm.

Figure 4.13 and 4.14 show measured GIXRD patterns for these two stacks: Gd:HfO₂ /TiN/SiO₂/Si (a-b) and TiN/Gd:HfO₂/TiN/SiO₂/Si (c-d). GIXRD curves were measured in the 2θ range 20-80° (Fig. 4.13 (a) and Fig. 4.14 (c)) and also in the more representative area range 27- 34° with smaller angle step (Fig. 4.13 (b) and Fig. 4.14 (d)). It is clear that the Gd:HfO₂ films reveal a polycrystalline nature.



Figure 4.13: GIXRD curves of Gd:HfO₂

/TiN/SiO₂/Si (a-b with different HfO₂ layer thickness (after RTA): (a) - in the 2 θ angle range 20-80° and (b) - in the 2 θ angle range 27-34° with higher angular resolution.



Figure 4.14: GIXRD curves of TiN/Gd:HfO₂/TiN/SiO₂/Si (c-d) samples with different HfO₂ layer thickness (after RTA): (c) - in the 2θ angle range 20-80° and (d) - in the 2θ angle range 27-34° with higher angular resolution.

It is observed from Figure 4.13 that the XRD patterns of the Gd:HfO₂ samples display almost the same crystallization nature with some noticeable differences. Figure 4.13 (b) and 4.14 (d) give deep information about varying thickness's effect on the structural properties of Gd:HfO₂ films. By increasing the Gd:HfO₂ thickness layer, the maximum peak becomes more intense and sharper and shifted systematically toward higher diffraction angle. This was validated by calculating the degree of orientation, which raised from 30.6 for 5.4 nm

to 30.7 for 42.3 nm-, whereas, 30.7 for 5.5 nm to 30.8 for 41.8 nm-thick Gd:HfO₂ layers in capped and uncapped samples, respectively.

As mentioned before (in section 4.2.1), the maximum peak is related to orthorhombic $Pna2_1$ (30) or/and tetragonal $P4_2/nmc$ (137) space groups. Figures 4.13 (b) and 4.14 (d) show red areas for (-111) and (111) monoclinic phase peaks and blue area for (111) orthorhombic or (101) tetragonal phase peaks. Figure 4.15 shows the integrated area of o/t peaks as a function of thickness for Gd:HfO₂/TiN/SiO₂/Si and TiN/Gd:HfO₂/TiN/SiO₂/Si structures; pink circles and blue stars, respectively.

The integrated peak area (intensity) increases as a function of $Gd:HfO_2$ thickness and reaches the maximum at 42 nm. Thus, ferroelectric properties of $Gd:HfO_2$ with and without the top TiN electrode can be presented in a large $Gd:HfO_2$ thickness range (up to 42 nm). As a result, the top TiN electrode has no significant impact on stabilizing the orthorhombic (or tetragonal) HfO_2 phase.



Figure 4.15: Integrated area of (111) orthorhombic or (101) tetragonal phase as a function of Gd:HfO₂ layer thickness for Gd:HfO₂/TiN/SiO₂/Si (pink circles) and TiN/Gd:HfO₂/TiN/SiO₂/Si (blue stars).

To know how much the orthorhombic or tetragonal phase occupy from the total phase of HfO₂ films, we used "Measure" software to calculate the phase weight of each phase compared to the total phases according to the following equation: $\left(\Delta\% = \frac{\Sigma A_{o/t}}{\Sigma A_{all peaks}} 100\%\right)$, since $\Delta\%$ is the phase weight in HfO₂ films and A is the area of the peak. For TiN/Gd:HfO₂

/TiN/SiO₂/Si thin films; 10.8-thick Gd:HfO₂ layer, the orthorhombic and tetragonal phases HfO₂ occupied 94.6% and 90.1%, respectively, whereas for 42.3 nm, the orthorhombic and tetragonal phases HfO₂ occupied 96.3% and 94.8%, respectively.

For Gd:HfO₂/TiN/SiO₂/Si thin films; 11.2-thick Gd:HfO₂ layer, the orthorhombic and tetragonal phases HfO₂ occupied 98.4% and 94.4%, respectively, whereas for 42.3 nm, the orthorhombic and tetragonal phases HfO₂ occupied 97.2% and 95.7%, respectively, for Gd:HfO₂/TiN/SiO₂/Si thin films. There is a gradual increase in orthorhombic and tetragonal phase weight upon increasing thickness. This behavior is in good agreement with the orthorhombic/tetragonal integrated area peaks as a function of Gd:HfO₂ layer thickness, see Fig. 4.15.

To get deep information about the affecting of structural properties by the Gd:HfO₂ layer thickness, the interplanar distance (d), the crystallite size (D), the micro-strain (ε), the stacking faults (SF%) and the defect density (δ) along the a, b, and c-axes were calculated, following equations listed in chapter two, for the thinnest and thickest samples. The estimated values of structural parameters for the maximum intensity peaks are tabulated in table 4.2.

Table 4.2: The structural parameters of Gd:HfO₂ thin films obtained from the main peak in TiN/Gd:HfO₂/TiN/SiO₂/Si and Gd:HfO₂/TiN/SiO₂/Si stacks.

Stack	Gd:HfO ₂ thickness (nm)	d (Å)	D (nm)	ε	d ($line/cm^{-2}$)	SF (%)
Capped	10.8	2.91	11.79	$1.16 * 10^{-2}$	$2.73 * 10^{12}$	0.62
Capped	42.3	2.90	20.99	$6.51 * 10^{-3}$	$8.60 * 10^{11}$	0.34
Uncapped	11.2	2.91	13.44	$1.02 * 10^{-2}$	$2.10 * 10^{12}$	0.54
Uncapped	41.8	2.90	19.12	$7.15 * 10^{-3}$	$1.04 * 10^{12}$	0.38

One can see that the crystalline size increases with thickness, which indicates a decrease in the micro-strain and defects density. In addition, the thickness of $Gd:HfO_2$ layer has an impact on the deviation of main diffraction peak toward higher diffraction angle. This can be attributed to strain and dislocation density in the polycrystalline material which are caused by Gd dopants and electrodes, leading to lattice distortion and phase transformation.

The lattice parameters for the orthorhombic and tetragonal unit cells were calculated from the observed XRD patterns for ~11 nm (thin) and ~42 nm (thick) films, as shown in table 4.3. Whereas the lattice parameters which were reported by Haun et. al. [Huan et al.,2014] for pure HfO₂, as a = 5.29 Å, b = 5.01 Å and c = 5.08 Å and a = 3.58 Å, b =

3.58 Å and c = 5.28 Å, in respective, for orthorhombic and tetragonal unit cells. There is a small difference between what was theoretically reported by Haun et. al. [Huan et al.,2014] and in our work (Gd doped HfO₂ layers with TiN electrodes: polycrystal). This difference is attributed to strain caused by Gd dopants and TiN electrodes. For this work, there is almost no significant difference in unit cell dimensions between thin and thick films for each set of samples.

Stack	Gd:HfO ₂ thickness (nm)	Phase	a (Å)	bÅ)	c (Å)
Capped	10.8	Ortho.	5.10	4.99	5.07
Capped	10.8	Tetra.	3.57	3.57	5.08
Capped	42.3	Ortho.	5.05	4.99	5.08
Capped	42.3	Tetra.	3.58	3.58	5.00
Uncapped	11.2	Ortho.	4.99	5.05	5.08
Uncapped	11.2	Tetra.	3.56	3.56	4.98
Uncapped	41.8	Ortho.	5.00	5.01	5.06
Uncapped	41.8	Tetra.	3.56	3.56	4.98

Table 4.3: The calculated lattice parameters from XRD observed patterns.

4.3.2 PUND measurements: Hysteresis loops

In addition to the structural signatures of the ferroelectric orthorhombic phase in Gd:HfO₂ films, electrical characterization was conducted to investigate whether Gd:HfO₂ PEALD films are truly ferroelectric. PUND measurement procedure was performed on TiN/Gd:HfO₂/TiN/SiO₂/Si capacitor structures, which were capped with top TiN before and after annealing, with triangle signal of 3.5 MV/cm (annealed TiN/Gd:HfO₂/TiN/SiO₂/Si) and 3.5-4.6 MV/cm (TiN/annealed Gd:HfO₂/TiN/SiO₂/Si) amplitudes, respectively, and frequency of 20 KHz.

The selected thicknesses for both capacitor structures are: 24.8, 35.9 and 42.3 nm (capped before annealing) and 17.2, 29.7 and 41.8 nm (capped after annealing). All the studied devices in this work were at pristine state.Figure 4.16 exhibits the extracted hysteresis loops, or polarization as a function of electric field (P-E) characteristic, for annealed TiN/Gd:HfO₂/TiN/SiO₂/Si capacitor structures of 24.8 nm, 35.9 nm and 42.3 nm-thick Gd:HfO₂ layers. The hysteresis response is clear in all thicknesses.

The amplitude of the remnant polarization (P_r) has a maximum at 24.8nm, and then

starts to shrink for thicker Gd:HfO₂ layers. The polarization switching voltage, as expected, increases as a function of Gd:HfO₂ thickness: from 4.5 V for 24.8 nm thick Gd:HfO₂ sample up to 7.0 V for 42.3 nm thick Gd:HfO₂ sample.



Figure 4.16: Polarization as a function electric field, measured for the annealed TiN/Gd:HfO₂/TiN/SiO₂/Si samples with different Gd:HfO₂ thickness.

Figure 4.17 exhibits the polarization as a function of electric field (P-E) characteristic, for TiN/annealed Gd:HfO₂/TiN/SiO₂/Si capacitor structures of 17.2 nm, 29.7 nm and 41.8 nm-thick Gd:HfO₂ films. The hysteresis behavior clearly appears in all samples of different thicknesses. The amplitude of the remnant polarization (P_r) increases as a function of thickness, reaches a maximum at 29.7 nm, and then starts to decrease for thicker Gd:HfO₂ layers. The polarization switching voltage was observed to be 4.2 V for 17.2 nm thick Gd:HfO₂ sample up to 7.1 V for 41.8 nm thick Gd:HfO₂ sample.



Figure 4.17: Polarization as a function electric field, measured for the TiN/annealed Gd:HfO₂/TiN/SiO₂/Si samples of different Gd:HfO₂ thickness.

The extracted total amplitude of remnant polarization $(2P_r)$ values obtained from the hysteresis loops for both capacitor structures are shown in Fig.4.18 (a) as a function of thickness. It was reported [Skopin et al.,2022]; [Alrifai et al.,2023] that the $2P_r$ values, for TiN/Gd:HfO₂/TiN/SiO₂/Si samples of layer thickness lower than 10 nm, exhibit a direct proportionality to Gd:HfO₂ layer thickness. In this work, the maximum $2P_r$ value for annealed TiN/Gd:HfO₂/TiN/SiO₂/Si (blue stars) and TiN/annealed Gd:HfO₂/TiN/SiO₂/Si samples was at 24.8 nm- and 29.7 nm-thick Gd:HfO₂ layer thickness.

However, for thicker samples, the $2P_r$ values experience a significant decrease with increasing thickness. Based on what was mentioned in chapter two, this can be attributed to the large density of oxygen vacancies at high thicknesses. Too many O vacancies favor the development of the t-phase, as well as they are reported to form preferentially at the interface between electrode and ferroelectric material. It migrates to grain boundaries, leading to degradation of ferroelectric properties and progression in non-ferroelectric dead layer [Ihlefeld et al.,2016]; [Lou,2009]; [Genenko et al.,2015]; [F. P. Fengler et al.,2017].



Figure 4.18: Polarization as a function of Gd:HfO₂ thickness for TiN/Gd:HfO₂/TiN/SiO₂/Si (blue stars) and TiN/annealed Gd:HfO₂/TiN/SiO₂/Si (pink circles) capacitors.

This observation, consistent with the findings in Fig.4.15, strongly indicates the presence of two distinct layers of tetragonal and orthorhombic phases within the thickness range of 5-42 nm for Gd:HfO₂ layer. To explain the trend more, the orthorhombic and tetragonal phase weight were calculated using "Measure" software package for the observed XRD patterns and tabulated in table 4.4. It is clear that for samples capped before annealing, the thickness of the orthorhombic (ferroelectric) layer for 24.8 nm layer is larger compared with that of 42.3 nm layer, and the thickness of the tetragonal (non-ferroelectric) layer for 42.3 nm is larger compared with that of 24.8 nm.

Moreover, for samples capped after annealing, the $2P_r$ value has its maximum at 29.7 nm where the phase weight of the orthorhombic phase is larger than that of the tetragonal phase. Beyond that, the $2P_r$ decreases slightly due to the lower thickness of the orthorhombic (ferroelectric) layer at 41.8 nm. This explains the decreasing trend in the $2P_r$ value after 24.8 nm.

It may also be attributed to the decrease in strain upon increasing the crystallite size with thickness, as shown in table 4.2, since the strain plays a vital role in stabilizing the ferroelectric orthorhombic phase. Figure 4.18 (b) show the coercive electric field as a function of thickness for both TiN/Gd:HfO₂/TiN/SiO₂/Si (blue stars) and TiN/annealed Gd:HfO₂/TiN/SiO₂/Si (pink circles) capacitors. The coercive field values are in the range of 1.7-2.45 MV/cm.

Stack	Gd:HfO ₂ thickness (nm)	Ortho. (%)	Tetra. (%)
Capped	24.8	96.7	91.5
Capped	35.9	96.5	94.7
Capped	42.3	96.3	94.8
Uncapped	17.2	97.5	94.8
Uncapped	29.7	98.1	96.4
Uncapped	41.8	97.2	95.7

Table 4.4: The phase weight of orthorhombic and tetragonal phases

To summarize, the best achieved P_r value in this study was about 13 and 16 $\mu C/cm^2$ for 29.7- and 24.8- nm-thick samples annealed before and after capping at 650 °C for 10 min. Comparing our results with relevant reports in the literature, it is noticed that Sharma et. al. [Sharma,2014] reported a remnant polarization value of 12 $\mu C/cm^2$ for 60 nm of Gd doped HfO₂ films deposited by PLD at 650 °C.

In previous reports employing the ALD technique to prepare Gd:HfO₂ films, it was noted that P_r values of 12 $\mu C/cm^2$ and 10 $\mu C/cm^2$ with annealing temperature of 1000 °C and 800 °C, in respective, for Mueller's et. al. [Mueller et al.,2012] and Park's et. al. [M. H. Park, Tony Schenk, et al.,2017] reports, whereas Hoffmann et. al. [Michael Hoffmann, Tony Schenk, et al.,2015] explored a P_r value of 15 $\mu C/cm^2$, with a thermal budget in the range of 450 °C to 800 °C. Moreover, Skopin et. al. [Skopin et al.,2022] and Alrefai et. al. [Alrifai et al.,2023] reported a P_r value of 20 $\mu C/cm^2$ for 8.8 nm-thick Gd:HfO₂ layers at lower thicknesses.

Therefore, while it is evident that the remnant polarization value for the films in this study is less than state of art values reported for ferroelectric HfO₂-based films, it is comparable to that investigated in other studies using PLD or ALD Gd:HfO₂ grown material, which is achieved by a competitive thermal budget. The doping concentration level of Gd in HfO₂ films in this study is possible to slightly different level required to optimize P_r value. In addition, it is easy for TiN to bind with O atoms forming TiO_xN_y or TiO₂, since it is in direct contact with HfO₂ layer during the annealing step [H.-Y. Chen and F.-H. Lu,2005].

The interaction between Ti and O is more probable than between Ti and Hf due to the nature of their chemical bonding and the differences in electronegativity and ionic radius. Titanium (Ti) and oxygen (O) form strong ionic-covalent bonds because of the high charge density of the Ti^{+4} ion and the strong electronegativity of oxygen, leading to Ti-O bonds
that are shorter and stronger, with bond lengths around 1.93 to 2.1 Å in oxides like TiO_2 [Chunyan Liu et al.,2017]. This affinity makes Ti-O interactions energetically favorable, particularly in oxide environments, where oxygen can coordinate with titanium to form stable structures.

In contrast, the interaction between Ti and Hf is less likely due to the similar ionic radii of Ti^{+4} (0.61 Å) and Hf^{+4} (0.71 Å), which results in a preference for both ions to occupy lattice positions rather than form direct bonds with each other. The chemical similarity between Ti and Hf means they do not exhibit a strong tendency to react or bond directly with one another, unlike the strong electrostatic attraction between Ti^{+4} and O^{-2} ions.

Additionally, in mixed oxide systems, oxygen tends to bridge between transition metals, further promoting the formation of Ti-O bonds over Ti-Hf bonds [Oh et al.,2013]. Thus, the stronger chemical affinity of Ti for oxygen compared to hafnium makes Ti-O interactions more probable in mixed material systems.

This creates an interfacial dead layer, rich of O vacancies and majority in the t-phase [Pešić et al.,2016]; [M. H. Park, H. J. Kim, Y. J. Kim, Jeon, et al.,2014]; [Hamouda et al.,2020]. This explains why the ferroelectric phase stabilizes up to higher thickness (29.7 nm) in TiN/Gd:HfO₂/TiN/SiO₂/Si films, which were annealed before capping compared to that annealed after capping at 24.8 nm.

Hoffmann et al. [Hoffmann et al.,2015] emphasized the fundamental role of electrodes and doping in stabilizing the ferroelectric phase. It was reported that TaN electrodes compared to TiN have significantly enhanced the stabilization of the ferroelectric phase in Metal/Gd:HfO₂/Metal stacks, providing a P_r value of up to 35 $\mu C/cm^2$. Moreover, the TaN electrodes in MFM stacks showed lower monoclinic and higher tetragonal/cubic phase contribution compared to TiN, from a crystallinity point of view. Additionally, Hoffmann et al. [Hoffmann et al.,2015] found that the thick MFM films up to 27 nm exhibited increasing monoclinic phase fractions in addition to the orthorhombic phase.

4.3.3 Wakeup and fatigue endurance of Gd:HfO₂ thin films

Endurance is an application-relevant property of ferroelectrics, which presents the resistance of ferroelectric material to voltage cycling. Hence, fatigue measurements (FM) were evaluated for annealed TiN/Gd:HfO₂/TiN/SiO₂/Si samples, by applying a rectangular

wave with an amplitude of 2.6, 2.9 and 2.6 MV/cm for samples of thicknesses of 24.8, 35.9 and 42.3 nm, in respective and frequency of 10 KHz. Fatigue is defined as the decrease in switchable polarization as a function of number of cycles.

The number of endurance cycles was 10^9 . During the fatigue cycles, the samples underwent three PUND measurements every cycle decade with an amplitude of 3.0, 3.5 and 3.1 MV/cm for 24.8, 35.9 and 42.3 nm, in respective, and frequency of 10 KHz. Before discussing the corresponded results, leakage tests were conducted on these devices before the electrical cycling as shown in Fig. 4.19: the current densities in the order range of 10^{-6} to $10^{-3} A/cm^2$ were measured on the devices at a voltage of 2 V, within the range of values which are commonly reported in literature for HfO₂-based ferroelectric films [D. Ye et al.,2014]; [Yoong et al.,2018]; [Mittmann et al.,2019]; [O'Connor et al.,2018]; [Lyu, Fina, Solanas, et al.,2019]; [Y. H. Lee et al.,2017]. It is noted that a higher leakage current is measured for 24.8 nm-thick Gd:HfO₂ layer.



Figure 4.19: Leakage current density versus voltage for 24.8- (red stars), 35.9- (blue triangles) and 42.3- (orange rhombohedral) nm-thick of Gd:HfO₂ layers.

Figures 4.20 (a) and 4.20 (b) show the positive $(+P_r)$ and negative $(-P_r)$ polarization amplitude evolution upon cycling, while Fig.4.20 (c) shows the evolution of corresponding normalized $2P_r$ amplitude. Both 35.9 nm and 42.3 nm samples exhibit a strong "wake up" effect for both polarities up to 10^9 without polarization fatigue, with progressive increase of the +P_r value from 5.5 to 6.5 $\mu C/cm^2$.

However, the 24.8 nm-thick sample shows a clear "wake up" effect up to 10^7 , beyond this fatigue effect occurs gradually, with a progressive reduction of the P_r value from 12.4 to 9.4 $\mu C/cm^2$. This degradation is attributed to the larger leakage current, which was observed on this sample, that leads to electrical breakdown of Gd:HfO₂ layer, quicker than other samples of lower leakage current. One more observation, the negative P_r value at pristine state is lower than positive P_r value, this indicates that polarization was easier in one direction compared to the other. However, upon cycling, both positive and negative P_r values are the same.

Figure 4.20 (c) shows the evolution of normalized $2P_r$ amplitude upon cycling for all three thicknesses. Although the wake-up effect is strong after 10^5 for all three samples, the $2P_r$ values keep increasing up to 10^9 cycles for 35.9 nm and between 10^8 and 10^9 for 42.3 nm. However, for 24.8 nm-thick sample, the polarization improves upon cycling up to 10^7 cycles, then fatigue effect appears clearly up to 10^9 .



Figure 4.20: Endurance of the 24.8-, 35.9- and 42.3 nm-thick Gd:HfO₂ layers: (a) positive remnant polarization +P_r, (b) negative remnant polarization -P_r, and (c) $2P_r/2P_0$ as a function of electrical field cycling.

Figure 4.21 (a-c) illustrates the extracted hysteresis loops which were measured during cycling for 24.8, 35.9 and 42.3 nm samples at pristine state, after 10^7 and after 10^9 cycles. It can be seen that in the case of pristine state, all measured P-E cycles are a bit pinched and not centered for all mentioned thicknesses. It is also worth noting that the remnant polarization amplitude of pristine state is lower than what mentioned in Fig.4.16.

This is due to different polarization measurements frequencies: 20 and 10 KHz in Fig.4.16 and 4.21, respectively. Whereas for hysteresis loops at 10^7 and 10^9 cycles, loops

become sharper with higher spontaneous polarization without breakdown. The first imprint in pristine state and tetragonal phase relaxation into orthorhombic phase upon cycling are attributed to the initial charge accumulation at the interface [Schroeder, C. S. Hwang, and Hiroshi Funakubo,2019]; [Pešić et al.,2016].

Performing electrical cycling can reduce imprint due to the redistribution of defects across the film, especially at grain boundaries, where the energy is higher [Pešić et al.,2016]. This leads to a migration of O vacancies away from the interface, with t-phase transforming into o-phase, producing thinner dead layer at the interface.



Figure 4.21: Polarization as a function electric field, measured for the TiN/annealed Gd:HfO₂/TiN/SiO₂/Si samples of different Gd:HfO₂ thickness during cycling.

Figure 4.22 (a) gives a clearer picture of the gradual improvement and degradation in the total remnant polarization values as a function of cycles for all mentioned thicknesses. For example, 24.8nm-thick layer undergoes an increase in $2P_r$ value from 6.6 to 18.5 $\mu C/cm^2$ (180% improvement) at 10⁷ cycles, followed by a decrease from 18.5 to 14.5 $\mu C/cm^2$ (21.6% degradation) at 10⁹ cycles. For 35.9 and 42.3 nm-thick layers, they almost have the same improvement of 208% and 229% at 10⁷ cycles; 300% and 278% at 10⁹ cycles, respectively.

Figure 4.22 (b) presents the change in coercive field values as a function of cycles for all three mentioned thicknesses. An evident gradual decrease in E_c values upon cycling was registered, i.e., from 1.75 to 1.4 MV/cm, from 2.1 to 1.3 MV/cm and 1.8 to 1.25 MV/cm for 24.8-,35.9- and 42.3 nm-thick layers, respectively. This is attributed to the improvement in $2P_r$ values upon cycling which in turns can offset the required voltage for polarization switching [T. Jung, J. Shin, and C. Shin,2020].



Figure 4.22: (a) Total remnant polarization and (b) coercive electric field as a function of cycles for TiN/Gd:HfO₂/TiN/SiO₂/Si capacitors of different Gd:HfO₂ thicknesses.

The observed ferroelectricity in the Gd:HfO₂ layer, with the observed remnant polarization values, indicates its potential for use in ferroelectric random access memory (FeRAM) devices. In FeRAM, the remnant polarization of the ferroelectric material enables binary states to be defined by the polarization direction: a positive polarization corresponds to a binary "1," while a negative polarization corresponds to a binary "0". These states are nonvolatile, meaning they retain their information even after power is turned off, making them ideal for memory applications. The cycling endurance of over 10⁹ cycles demonstrates the durability of the Gd:HfO₂ layer in withstanding repeated switching without significant degradation. This high endurance is critical for practical memory applications, as it ensures that the FeRAM devices can maintain performance and reliability over extended periods of use, thus meeting industry requirements for long-term data storage and frequent read-write operations [S. J. Kim, Narayan, et al.,2017]; [Bondurant and Gnadinger,1989]; [Onishi et al.,1994]; [Kinam Kim and S. Lee,2006]; [Thomas Mikolajick et al.,2001].

Chapter Five: Discussion

In this thesis, we have discussed the formation of metal/ferroelectric/metal and metal/ oxide (ferroelectric)/semiconductor capacitor structures as a non-volatile memory with high-speed switching and low power consumption. The preparation of these thin film capacitors was achieved by using Plasma Enhanced Atomic Layer Deposition (PEALD) technique.

A valuable technique for advanced nanotechnology applications due to its several advantages including: low temperature processing, precise thickness control and enhanced step coverage. The probable formation of these thin film capacitors is characterized by means of structural and electrical measurements and tools. The design was actualized through using the SiO₂/Si substrate to deposit undoped and Gd doped TiN (top electrode)/HfO₂ directly onto the substrate or TiN bottom electrode. The HfO₂-based ferroelectric films were intensely investigated in may previous published work as a promising candidate in non-volatile memory applications.

Having characterized the materials and interfaces, we curve to the result of ability of crystalizing the undoped HfO_2 into ferroelectric non-centrosymmetric orthorhombic/tetragonal phase for ultrathin layers (up to 5 nm) when it is annealed with top TiN electrode (the bottom TiN electrode is absent), see Fig. 4.4 (d). The annealing step after capping with top TiN was built an in-plane strain which stabilize the o/t phase for ultrathin layers. Adding Gd doping factor helps (with other factors) in stabilizing the o/t phase up to higher thicknesses, see Fig. 4.5 (b).

The in-plane and out-of-plane XRD results evidenced the presence of tensile mechanical stress caused by top TiN electrode and Gd dopant stabilizes the orthorhombic ferroelectric phase in Gd:HfO₂ thin films. The Subjecting the as deposited and annealed TiN/Gd:HfO₂/SiO₂/Si capacitor devices to combined alternating AC (1 MHz and 25 mV) and DC signal bias (1 to -4 V) and measuring the capacitance for propagating signals has shown the ferroelectric effect after annealing process indicating the ability of this device to integrate into FeRAM structures.

The second main part of this work investigated the thickness-dependent evolution of ferroelectric properties in Gd:HfO₂ layers, in TiN/Gd:HfO₂/TiN/SiO₂/Si and Gd:HfO₂/TiN/SiO₂/Si structures. From structural point of view, ferroelectric properties

of Gd:HfO₂ with and without the top TiN electrode can be presented in a large Gd:HfO₂ thickness range (up to 42 nm). As a result, the top TiN electrode has no significant impact on stabilizing the orthorhombic (or tetragonal) HfO₂ phase.

PUND measurement procedure was performed on TiN/Gd:HfO₂/TiN/SiO₂/Si capacitor structures, which were capped with top TiN before and after annealing, with triangle signal of 3.5 MV/cm (annealed TiN/Gd:HfO₂/TiN/SiO₂/Si) and 3.5-4.6 MV/cm (TiN/annealed Gd:HfO₂/TiN/SiO₂/Si) amplitudes, respectively, and frequency of 20 KHz. The best achievedP_rvalue in this study was about 13 and 16 μ C/cm² for 29.7- and 24.8- nm-thick samples annealed before and after capping.

However, for thicker samples, the $2P_r$ values experience a significant decrease with increasing thickness (see Fig. 4.17). This is attributed to large density of oxygen vacancies at high thicknesses. Too many O vacancies favor the development of t-phase, as well as they reported to form preferentially at the interface between electrode and ferroelectric material. The coercive field values are in the range of 1.7-2.45 MV/cm (see Fig. 4.17).

Moreover, fatigue measurements were evaluated for annealed TiN/Gd:HfO₂/TiN/SiO₂/Si samples, by applying a rectangular wave with an amplitude of 2.6, 2.9 and 2.6 MV/cm for 24.8, 35.9 and 42.3 nm, in respective and frequency of 10 KHz. Both 35.9 nm and 42.3 nm samples exhibit a strong "wake up" effect without polarization fatigue, up to 10⁹ cycles.

The absence of P_r tfatigue can be attributed to the optimal chemical-composition of TiN/Gd:HfO₂ interface, which is the origin of O vacancies defect generation that usually invoked to explain the ferroelectric polarization fatigue. However, the 24.8 nm-thick sample shows a clear "wake up" effect up to 10^7 , beyond this fatigue effect occurs gradually.

Performing electrical cycling can reduce imprint due to the redistribution of defects across the film, especially at grain boundaries, where the energy is higher. This leads to a migration of O vacancies away from the interface, with t-phase transforming into o-phase, producing thinner dead layer at the interface. An evident gradual decrease in E_c values upon cycling is registered, i.e., from 1.75 to 1.4 MV/cm, from 2.1 to 1.3 MV/cm and 1.8 to 1.25 MV/cm for 24.8-,35.9- and 42.3 nm-thick layers, respectively.

This is attributed to the improvement in $2P_r$ values upon cycling which in turns can offset the required voltage for polarization switching. These properties are promising for employing the MFM capacitors as non-volatile memories. This opens the way to use such MFM stacks in low power applications. In outlook, it is important to notice that, even though the MFM stacks displayed good features that nominate it for low power and non-volatile memories applications, the problem of high leakage current and defects density must be overcome through finding advanced preparation technique to reduce the O vacancies as much as possible to avoid the remnant polarization fatigue effect and quick electrical breakdown.

References

Kim, Si Joon, Dushyant Narayan, et al. (2017). "Large ferroelectric polarization of TiN/Hf0. 5Zr0. 5O2/TiN capacitors due to stress-induced crystallization at low thermal budget". In: *Applied Physics Letters* 111.24.

Bondurant, DW and FP Gnadinger (1989). "Ferroelectrics for nonvolatile RAMs". In: *IEEE spectrum* 26.7, pp. 30–33.

Onishi, Shigeo et al. (1994). "A half-micron ferroelectric memory cell technology with stacked capacitor structure". In: *Proceedings of 1994 IEEE International Electron Devices Meeting*. IEEE, pp. 843–846.

Kim, Kinam and Sungyung Lee (2006). "Integration of lead zirconium titanate thin films for high density ferroelectric random access memory". In: *Journal of applied physics* 100.5.

Mikolajick, Thomas et al. (2001). "FeRAM technology for high density applications". In: *Microelectronics Reliability* 41.7, pp. 947–950.

Böscke, TS et al. (2011). "Ferroelectricity in hafnium oxide thin films". In: *Applied Physics Letters* 99.10.

Kim, Si Joon, Jaidah Mohan, Harrison Sejoon Kim, et al. (2020). "A comprehensive study on the effect of tin top and bottom electrodes on atomic layer deposited ferroelectric Hf0. 5Zr0. 5O2 thin films". In: *Materials* 13.13, p. 2968.

Park, Min Hyuk, Young Hwan Lee, Han Joon Kim, Yu Jin Kim, et al. (2015). "Ferroelectricity and antiferroelectricity of doped thin HfO2-based films". In: *Advanced Materials* 27.11, pp. 1811–1831.

Kim, Si Joon, Jaidah Mohan, Scott R Summerfelt, et al. (2019). "Ferroelectric Hf 0.5 Zr 0.5 O 2 thin films: A review of recent advances". In: *Jom* 71, pp. 246–255.

Materlik, Robin, Christopher Künneth, and Alfred Kersch (2015). "The origin of ferroelectricity in Hf1- xZrxO2: A computational investigation and a surface energy model". In: *Journal of Applied Physics* 117.13.

Mueller, Stefan et al. (2012). "Incipient ferroelectricity in Al-doped HfO2 thin films". In: *Advanced Functional Materials* 22.11, pp. 2412–2417.

Müller, J, U Schröder, et al. (2011). "Ferroelectricity in yttrium-doped hafnium oxide". In: *Journal of Applied Physics* 110.11.

Schenk, Tony, Stefan Mueller, et al. (2013). "Strontium doped hafnium oxide thin films: Wide process window for ferroelectric memories". In: 2013 Proceedings of the European Solid-State Device Research Conference (ESS-DERC). IEEE, pp. 260–263. Mueller, S et al. (2012). "Ferroelectricity in Gd-doped HfO2 thin films". In: *ECS Journal of Solid State Science and Technology* 1.6, N123.

Adelmann, Christoph et al. (2010). "Atomic layer deposition of Gd-doped HfO2 thin films". In: *Journal of The Electrochemical Society* 157.4, G105.

Reinke, Michael, Yury Kuzminykh, and Patrik Hoffmann (2015). "Low temperature chemical vapor deposition using atomic layer deposition chemistry". In: *Chemistry of Materials* 27.5, pp. 1604–1611.

Hoffmann, M et al. (2015). "Stabilizing the ferroelectric phase in doped hafnium oxide". In: *Journal of Applied Physics* 118.7.

Belahcen, S et al. (2020). "TiN/Gd: HfO2/TiN capacitors grown by PEALD showing high endurance ferroelectric switching". In: *Applied Physics Letters* 117.25.

Skopin, EV et al. (2022). "Sub-10-nm ferroelectric Gd-doped HfO2 layers". In: *Applied Physics Letters* 120.17.

Alrifai, L et al. (2023). "Doped and undoped ferroelectric HfO2: Role of Gd-doping in stabilizing the ferroelectric phase". In: *Applied Physics Letters* 123.3.

Park, Min Hyuk, Han Joon Kim, Yu Jin Kim, Young Hwan Lee, Taehwan Moon, Keum Do Kim, Seung Dam Hyun, Franz Fengler, et al. (2016). "Effect of Zr content on the wake-up effect in Hf1–x Zr x O2 films". In: *ACS applied materials & interfaces* 8.24, pp. 15466–15475.

Chernikova, AG et al. (2016). "Ferroelectric properties of full plasma-enhanced ALD TiN/La: HfO2/TiN stacks". In: *Applied Physics Letters* 108.24.

Nishimura, Tomonori et al. (2016). "Ferroelectricity of nondoped thin HfO2 films in TiN/HfO2/TiN stacks". In: *Japanese journal of applied physics* 55.8S2, 08PB01.

Chen, An (2016). "A review of emerging non-volatile memory (NVM) technologies and applications". In: *Solid-State Electronics* 125, pp. 25–38.

Park, Min Hyuk, Young Hwan Lee, Thomas Mikolajick, et al. (2018). "Review and perspective on ferroelectric HfO2-based thin films for memory applications". In: *Mrs Communications* 8.3, pp. 795–808.

Li, Zhinan and Zygmunt J Haas (2016). "On residual path lifetime in mobile networks". In: *IEEE Communications Letters* 20.3, pp. 582–585.

Bohr, Mark T et al. (2007). "The high-k solution". In: *IEEE spectrum* 44.10, pp. 29–35.

Guha, Supratik and Vijay Narayanan (2009). "High- κ /metal gate science and technology". In: *Annual Review of Materials Research* 39.1, pp. 181–202.

Park, Min Hyuk, Dong Hyun Lee, et al. (2020). "Review of defect chemistry in fluorite-structure ferroelectrics for future electronic devices". In: *Journal of Materials Chemistry C* 8.31, pp. 10526–10550.

Valasek, Joseph (1921). "Piezo-electric and allied phenomena in Rochelle salt". In: *Physical review* 17.4, p. 475.

Sze, Simon M, Yiming Li, and Kwok K Ng (2021). *Physics of semiconductor devices*. John wiley & sons.

Damjanovic, Dragan (1998). "Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics". In: *Reports on progress in physics* 61.9, p. 1267.

— (2006). "Hysteresis in piezoelectric and ferroelectric materials". In: *Science of hysteresis*, pp. 337–465.

Kalinin, Sergei V et al. (2018). "Surface-screening mechanisms in ferroelectric thin films and their effect on polarization dynamics and domain structures". In: *Reports on Progress in Physics* 81.3, p. 036502.

Schroeder, Uwe, Cheol Seong Hwang, and Hiroshi Funakubo (2019). *Ferro-electricity in doped hafnium oxide: materials, properties and devices.* Woodhead Publishing.

Pešić, Milan et al. (2016). "Physical mechanisms behind the field-cycling behavior of HfO2-based ferroelectric capacitors". In: *Advanced Functional Materials* 26.25, pp. 4601–4612.

Hyuk Park, Min, Han Joon Kim, Yu Jin Kim, Taehwan Moon, et al. (2014). "The effects of crystallographic orientation and strain of thin Hf0. 5Zr0. 5O2 film on its ferroelectricity". In: *Applied Physics Letters* 104.7.

Ye, Dong et al. (2014). "Patterned graphene functionalization via mask-free scanning of micro-plasma jet under ambient condition". In: *Applied Physics Letters* 104.10.

Ihlefeld, Jon F et al. (2016). "Scaling effects in perovskite ferroelectrics: fundamental limits and process-structure-property relations". In: *Journal of the American Ceramic Society* 99.8, pp. 2537–2557.

Shiraishi, Takahisa et al. (2016). "Impact of mechanical stress on ferroelectricity in (Hf0. 5Zr0. 5) O2 thin films". In: *Applied Physics Letters* 108.26.

Schenk, Tony, Michael Hoffmann, et al. (2015). "Complex internal bias fields in ferroelectric hafnium oxide". In: *ACS applied materials & interfaces* 7.36, pp. 20224–20233.

Hoffmann, Michael, Franz PG Fengler, et al. (2019). "Unveiling the doublewell energy landscape in a ferroelectric layer". In: *Nature* 565.7740, pp. 464– 467. Tagantsev, Alexander K et al. (2001). "Polarization fatigue in ferroelectric films: Basic experimental findings, phenomenological scenarios, and microscopic features". In: *Journal of Applied Physics* 90.3, pp. 1387–1402.

Johnson, Brienne and Jacob L Jones (2019). "Structures, phase equilibria, and properties of HfO2". In: *Ferroelectricity in Doped Hafnium Oxide: Materials, Properties and Devices*, pp. 25–45.

Shin, Dongwon, Raymundo Arróyave, and Zi-Kui Liu (2006). "Thermodynamic modeling of the Hf–Si–O system". In: *Calphad* 30.4, pp. 375–386.

Hanwell, Marcus D et al. (2012). "Avogadro: an advanced semantic chemical editor, visualization, and analysis platform". In: *Journal of cheminformatics* 4, pp. 1–17.

Summerfelt, SR et al. (2007). "High-density 8Mb 1T-1C ferroelectric random access memory embedded within a low-power 130nm logic process". In: 2007 *Sixteenth IEEE International Symposium on the Applications of Ferroelectrics*. IEEE, pp. 9–10.

Müller, J, TS Böscke, S Müller, et al. (2013). "Ferroelectric hafnium oxide: A CMOS-compatible and highly scalable approach to future ferroelectric memories". In: *2013 IEEE International Electron Devices Meeting*. IEEE, pp. 10–8.

Olsen, T et al. (2012). "Co-sputtering yttrium into hafnium oxide thin films to produce ferroelectric properties". In: *Applied Physics Letters* 101.8.

Müller, J, TS Böscke, D Bräuhaus, et al. (2011). "Ferroelectric Zr0. 5Hf0. 5O2 thin films for nonvolatile memory applications". In: *Applied Physics Letters* 99.11.

Park, Min Hyuk, Young Hwan Lee, Han Joon Kim, Tony Schenk, et al. (2017). "Surface and grain boundary energy as the key enabler of ferroelectricity in nanoscale hafnia-zirconia: A comparison of model and experiment". In: *Nanoscale* 9.28, pp. 9973–9986.

Lehninger, David et al. (2020). "Back-end-of-line compatible low-temperature furnace anneal for ferroelectric hafnium zirconium oxide formation". In: *physica status solidi (a)* 217.8, p. 1900840.

Yurchuk, Ekaterina et al. (2013). "Impact of layer thickness on the ferroelectric behaviour of silicon doped hafnium oxide thin films". In: *Thin Solid Films* 533, pp. 88–92.

Kim, Han Joon, Min Hyuk Park, Yu Jin Kim, Young Hwan Lee, Woojin Jeon, et al. (2014). "Grain size engineering for ferroelectric Hf0. 5Zr0. 5O2 films by an insertion of Al2O3 interlayer". In: *Applied Physics Letters* 105.19.

Lou, XJ (2009). "Polarization fatigue in ferroelectric thin films and related materials". In: *Journal of Applied Physics* 105.2.

Genenko, Yuri A et al. (2015). "Mechanisms of aging and fatigue in ferroelectrics". In: *Materials Science and Engineering: B* 192, pp. 52–82.

Fengler, Franz PG et al. (2017). "Domain pinning: Comparison of hafnia and PZT based ferroelectrics". In: *Advanced Electronic Materials* 3.4, p. 1600505.

Chen, Hong-Ying and Fu-Hsing Lu (2005). "Oxidation behavior of titanium nitride films". In: *Journal of Vacuum Science & Technology A* 23.4, pp. 1006–1009.

Park, Min Hyuk, Han Joon Kim, Yu Jin Kim, Woojin Jeon, et al. (2014). "Ferroelectric properties and switching endurance of Hf0. 5Zr0. 5O2 films on TiN bottom and TiN or RuO2 top electrodes". In: *physica status solidi* (*RRL*)–*Rapid Research Letters* 8.6, pp. 532–535.

Hamouda, W et al. (2020). "Physical chemistry of the TiN/Hf0. 5Zr0. 5O2 interface". In: *Journal of Applied Physics* 127.6.

Hyuk Park, Min, Han Joon Kim, Yu Jin Kim, Woongkyu Lee, et al. (2013). "Evolution of phases and ferroelectric properties of thin Hf0. 5Zr0. 5O2 films according to the thickness and annealing temperature". In: *Applied Physics Letters* 102.24.

Lomenzo, Patrick D et al. (2016). "Annealing behavior of ferroelectric Sidoped HfO2 thin films". In: *Thin Solid Films* 615, pp. 139–144.

Park, Min Hyuk, Ching-Chang Chung, et al. (2018). "Effect of Annealing Ferroelectric HfO2 Thin Films: In Situ, High Temperature X-Ray Diffraction". In: *Advanced Electronic Materials* 4.7, p. 1800091.

Goh, Youngin et al. (2020). "Oxygen vacancy control as a strategy to achieve highly reliable hafnia ferroelectrics using oxide electrode". In: *Nanoscale* 12.16, pp. 9024–9031.

Polakowski, Patrick and Johannes Müller (2015). "Ferroelectricity in undoped hafnium oxide". In: *Applied Physics Letters* 106.23.

Shimizu, Takao et al. (2016). "The demonstration of significant ferroelectricity in epitaxial Y-doped HfO2 film". In: *Scientific reports* 6.1, p. 32931.

Li, Tao et al. (2018). "Epitaxial ferroelectric Hf 0.5 Zr 0.5 O 2 thin film on a buffered YSZ substrate through interface reaction". In: *Journal of Materials Chemistry C* 6.34, pp. 9224–9231.

Yoong, Herng Yau et al. (2018). "Epitaxial ferroelectric Hf0. 5Zr0. 5O2 thin films and their implementations in memristors for brain-inspired computing". In: *Advanced Functional Materials* 28.50, p. 1806037.

Lyu, Jike, Ignasi Fina, Josep Fontcuberta, et al. (2019). "Epitaxial integration on Si (001) of ferroelectric Hf0. 5Zr0. 5O2 capacitors with high retention and endurance". In: *ACS Applied Materials & Interfaces* 11.6, pp. 6224–6229.

Fengler, FPG et al. (2018). "On the relationship between field cycling and imprint in ferroelectric Hf0. 5Zr0. 5O2". In: *Journal of Applied Physics* 123.20.

Zhou, Dayu et al. (2013). "Wake-up effects in Si-doped hafnium oxide ferroelectric thin films". In: *Applied Physics Letters* 103.19.

Park, Min Hyuk, Han Joon Kim, Yu Jin Kim, Young Hwan Lee, Taehwan Moon, Keum Do Kim, Seung Dam Hyun, and Cheol Seong Hwang (2015). "Study on the size effect in Hf0. 5Zr0. 5O2 films thinner than 8 nm before and after wake-up field cycling". In: *Applied Physics Letters* 107.19.

Kim, Han Joon, Min Hyuk Park, Yu Jin Kim, Young Hwan Lee, Taehwan Moon, et al. (2016). "A study on the wake-up effect of ferroelectric Hf 0.5 Zr 0.5 O 2 films by pulse-switching measurement". In: *Nanoscale* 8.3, pp. 1383–1389.

Lee, Tae Yoon et al. (2018). "Ferroelectric polarization-switching dynamics and wake-up effect in Si-doped HfO2". In: *ACS applied materials & interfaces* 11.3, pp. 3142–3149.

Starschich, S, S Menzel, and UJAPL Böttger (2016). "Evidence for oxygen vacancies movement during wake-up in ferroelectric hafnium oxide". In: *Applied Physics Letters* 108.3.

Huang, Fei et al. (2017). "Fatigue mechanism of yttrium-doped hafnium oxide ferroelectric thin films fabricated by pulsed laser deposition". In: *Physical Chemistry Chemical Physics* 19.5, pp. 3486–3497.

Birkholz, M (2006). *Thin Film Analysis by X-Ray Scattering*. Vol. 252. Wiley-VCH Verlag GmbH & Co. KGaA.

Pathania, Deepak, Mamta Kumari, and Vinod Kumar Gupta (2015). "Fabrication of ZnS–cellulose nanocomposite for drug delivery, antibacterial and photocatalytic activity". In: *Materials & Design* 87, pp. 1056–1064.

Suryanarayana, C (2004). "Mechanical alloying and milling. Marcel Dekker Inc". In.

Khusayfan, Najla M, Sabah E Al Garni, and AF Qasrawi (2017). "Design and performance of Yb/ZnS/C Schottky barriers". In: *Current Applied Physics* 17.1, pp. 115–119.

Bouguerra, Wided et al. (2015). "Optimization of the electrocoagulation process for the removal of lead from water using aluminium as electrode material". In: *Desalination and Water Treatment* 56.10, pp. 2672–2681.

Heinzel, Thomas (2008). *Mesoscopic electronics in solid state nanostructures*. John Wiley & Sons.

Hachemi, Mohammed Bilal (2022). "Contribution to the study of structural and ferroelectric properties of HZO thin films". PhD thesis. Université Grenoble Alpes [2020-....]

Segantini, Greta (2023). "Fabrication of ferroelectric tunnel junctions for the implementation of artificial synapses". PhD thesis. Ecully, Ecole centrale de Lyon.

Wenger, Ch et al. (2008). "Investigation of atomic vapour deposited TiN/HfO2/SiO2 gate stacks for MOSFET devices". In: *Microelectronic Engineering* 85.8, pp. 1762–1765.

Chourasia, AR and DR Chopra (1995). "X-ray photoelectron study of TiN/SiO2 and TiN/Si interfaces". In: *Thin Solid Films* 266.2, pp. 298–301.

Evers, VHM and B Macco (2017). "Atomic layer deposited MoOx as a passivating contact in c-Si heterojunction solar cells". In: *Journal of Applied Physics*.

Ding, Yangyao et al. (2020). "Microscopic modeling and optimal operation of plasma enhanced atomic layer deposition". In: *Chemical Engineering Research and Design* 159, pp. 439–454.

Caubet, Pierre et al. (2008). "Low-temperature low-resistivity PEALD TiN using TDMAT under hydrogen reducing ambient". In: *Journal of The Electro-chemical Society* 155.8, H625.

Elam, JW et al. (2003). "Surface chemistry and film growth during TiN atomic layer deposition using TDMAT and NH3". In: *Thin Solid Films* 436.2, pp. 145–156.

Wang, Boxun et al. (2024). "Annealing modulated microstructural and electrical properties of plasma-enhanced atomic layer deposition-derived HfO2/SiO2 nanolaminates on AlGaN/GaN". In: *Journal of Vacuum Science & Technology A* 42.1.

Sharma, Varun (2014). "Spectroscopic ellipsometry for the in-situ investigation of atomic layer depositions". In: *Journal of Vacuum Science Technology A*.

Langereis, Erik et al. (2010). "In situ spectroscopic ellipsometry for atomic layer deposition". In: *Society of Vacuum Coaters Bulletin* 2010.spring, pp. 36–41.

Evangelou, Evangelos K et al. (2000). "Characterization of magnetron sputtering deposited thin films of TiN for use as a metal electrode on TiN/SiO 2/Si metal–oxide–semiconductor devices". In: *Journal of Applied Physics* 88.12, pp. 7192–7196.

Wittmer, M and H Melchior (1982). "Applications of TiN thin films in silicon device technology". In: *Thin Solid Films* 93.3-4, pp. 397–405.

Calzolari, Arrigo and Alessandra Catellani (2020). "Controlling the TiN electrode work function at the atomistic level: a first principles investigation". In: *IEEE Access* 8, pp. 156308–156313.

Huan, Tran Doan et al. (2014). "Pathways towards ferroelectricity in hafnia". In: *Physical Review B* 90.6, p. 064111.

Seya, Kyosuke, Byung-Koog Jang, and Shunkichi Ueno (2015). "Microstructure formation of Al2O3–HfO2 eutectic". In: *Journal of the Ceramic Society of Japan* 123.1437, pp. 433–436.

Men, Rujia et al. (2020). "Dielectric Spectrum of Random Copolymerization Polypropylene Nanocomposites Doped with Nano Silica at Different Temperatures". In: 2020 IEEE International Conference on High Voltage Engineering and Application (ICHVE). IEEE, pp. 1–4.

Kalkur, TS, Brad Jacobs, and George Argos (1994). "Characteristics of ferroelectric gate mos and mosfets". In: *Integrated Ferroelectrics* 5.3, pp. 177– 184.

Nakamura, Kunio and Mototaka Kamoshida (1974). "Annealing characteristics of ion-implanted p-channel MOS transistors". In: *Journal of Applied Physics* 45.10, pp. 4262–4267.

Kim, KD et al. (2016). "Ferroelectricity in undoped-HfO 2 thin films induced by deposition temperature control during atomic layer deposition". In: *Journal of Materials Chemistry C* 4.28, pp. 6864–6872.

Fan, P et al. (2019). "Origin of the intrinsic ferroelectricity of HfO2 from ab initio molecular dynamics". In: *The Journal of Physical Chemistry C* 123.35, pp. 21743–21750.

Fan, Sheng-Ting, Yun-Wen Chen, and CW Liu (2020). "Strain effect on the stability in ferroelectric HfO2 simulated by first-principles calculations". In: *Journal of Physics D: Applied Physics* 53.23, 23LT01.

Park, Min Hyuk, Tony Schenk, et al. (2017). "A comprehensive study on the structural evolution of HfO 2 thin films doped with various dopants". In: *Journal of Materials Chemistry C* 5.19, pp. 4677–4690.

Hoffmann, Michael, Tony Schenk, et al. (2015). "Low temperature compatible hafnium oxide based ferroelectrics". In: *Ferroelectrics* 480.1, pp. 16–23.

Liu, Chunyan et al. (2017). "First-principles calculations on the electronic structure and bonding nature of TaN (111)/TiN (111) interface". In: *Journal of Alloys and Compounds* 717, pp. 326–332.

Oh, Young Jun et al. (2013). "Hybrid functional versus quasiparticle calculations for the Schottky barrier and effective work function at TiN/HfO 2 interface". In: *Physical Review B—Condensed Matter and Materials Physics* 87.7, p. 075325.

Mittmann, Terence et al. (2019). "Origin of ferroelectric phase in undoped HfO2 films deposited by sputtering". In: *Advanced Materials Interfaces* 6.11, p. 1900042.

O'Connor, Éamon et al. (2018). "Stabilization of ferroelectric HfxZr1- xO2 films using a millisecond flash lamp annealing technique". In: *Apl Materials* 6.12.

Lyu, Jike, Ignasi Fina, Raul Solanas, et al. (2019). "Growth window of ferroelectric epitaxial Hf0. 5Zr0. 5O2 thin films". In: *ACS Applied Electronic Materials* 1.2, pp. 220–228.

Lee, Young Hwan et al. (2017). "Preparation and characterization of ferroelectric Hf0. 5Zr0. 5O2 thin films grown by reactive sputtering". In: *Nanotechnology* 28.30, p. 305703.

Jung, Taehwan, Jaemin Shin, and Changhwan Shin (2020). "Impact of depolarization electric-field and charge trapping on the coercive voltage of an Si: HfO2-based ferroelectric capacitor". In: *Semiconductor Science and Technology* 36.1, p. 015005.

آثار الأقطاب الكهربانية والمنشطات على خصائص الاستقطاب الكهرباني لأفلام الهافنيا الرقيقة

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ملخص

تتمتع المواد الفروكهروبائية بمجموعة واسعة من الخصائص ذات الصلة بالتطبيقات، مثل الاستقطاب التلقائي الذي يمكن تبديله عن طريق تطبيق المجال الكهربائي. يتم تمثيل هذه الفئة من المواد بالفيروفسكيت، والتي تستخدم في أجهزة الاستشعار والمحركات والذاكرات غير المتطايرة. يواجه تطبيق الذاكرة غير المتطايرة تحديات تكنولوجية حاسمة؛ نظرًا لأنه ليس من السهل دمج اله البيروفسكيت في تصنيع أشباه الموصلات ذات الأكاسيد المعدنية المتتامة. تعد ميز انية التلدين العالية وعدم استقرار المرحلة الفروكهربائية على نطاق فائق الدقة مسألتين رئيسيتين تمنعان تحقيق الخصائص الكهروضوئية على مستوى الأفلام الرقيقة.

في هذه الدراسة، أدى اكتشاف الطاقة الفروكهربائية في الأفلام المعتمدة على الهافنيا قبل ثلاثة عشر عامًا إلى إعادة ذاكرات الوصول العشوائي الكهروضوئية إلى السباق. يتم استخدامها في تكنولوجيا أشباه الموصلات ذات الأكاسيد المعدنية المتتامة وقد ثبت أنها تحتفظ بخصائصها الكهروضوئية حتى بضعة نانومترات (خمسة نانومتر أو أقل)، مما يتحكم في قيود فئة البيروفسكيت ويجعلها المرشح المثالي للتطبيقات الكهروضوئية منخفضة الطاقة. بعد ذلك، ركز البحث على الفيزياء وراء استجابة الاستقطاب، مما أدى إلى تحسين عملية التصنيع الموثوقة للتكامل في أجهزة الذاكرة. يتناول هذا العمل نقاطًا مثيرة للاهتمام ومثيرة للجدل جزئيًا ويساهم في المعالجة المتوافقة مع أشباه الموصلات ذات الأكاسيد المعدنية المتنامة للهافنا الفروكهربائي.

في هذه الأطروحة، تمت زراعة أغشية الهافنيا بواسطة ترسيب الطبقة الذرية المعززة بالبلازما. يتم النظر في تصنيع وتوصيف. تحتاج الطبقات إلى ميزانية حرارية عالية للحصول على خصائص متعلق بالعازل الكهربائي الشفاف. تتم دراسة الطبقات والواجهات الثلاثة المودعة عن طريق قياس انعكاس الأشعة السينية ، وحيود الأشعة السينية، وحيود الأشعة السينية للمستويات الذرية العمودية والموازية لسطح الفلم الرقيق، وتيار التسرب، التدوير الكهربائي.

وقد لوحظ أن طبقة الأغشية الرقيقة الوحيدة التي تظهر كثافة ذروة الطور الفركهربائي تبلغ سماكة خمسة نانومتر من طبقة الهافنيا. أدى وجود قطب كهربائي علوي أثناء عملية التلدين إلى حدوث إجهاد ميكانيكي يؤدي إلى تبلور الطور الفروكهربائي في طبقة رقيقة جدًا من الهافنيا غير المنشط. تظهر طبقات الهافنيا الأخرى غير المنشورة ذروة أحادية الميل مع زيادة تدريجية في الشدة عند السماكة. بالنسبة لجميع الأفلام المخدرة الأخرى، يمكن رؤية ذروة مرحلة الفروكهربائي في نطاق سمك يتراوح بين 5-42 نانومتر.

كهربائيًا، لوحظ أن قيمة الاستقطاب المتبقي تتقلص عبر ما يزيد عن 24.8 و29.7 نانومتر من طبقات الهافنيا المخدرة بسبب استرخاء الطور المعيني إلى الطور الرباعي، بالنسبة للأفلام المغلفة بقطب علوي قبل وبعد التلدين، على التوالي. علاوة على ذلك، تم تسجيل زيادة وانخفاض تدريجي واضح في قيم الاستقطاب المتبقي و المجال الكهربائي، على التوالي، عند التدوير الكهربائي. وبالتالي، يمكن استخدام الأجهزة كتطبيقات ذاكرة غير متطايرة.

الكلمات المفتاحية: الفروكهربائي، أفلام الهافنيا،الاستقطاب المتبقى، ذاكرة غير متطايرة.