Bachelor's thesis

NTNU
Norwegian University of Science and Technology
Faculty of Natural Sciences
Department of Chemistry

Daniel Muszko

Advantages and challenges of hafnia-zirconia based ferroelectric random-access memories

Bachelor's thesis in Bachelor in Chemistry
Supervisor: Julian Walker
April 2023

Norwegian University of
Science and Technology

Daniel Muszko

Advantages and challenges of hafnia-zirconia based ferroelectric random-access memories

Bachelor’s thesis in Bachelor in Chemistry
Supervisor: Julian Walker
April 2023

Norwegian University of Science and Technology
Faculty of Natural Sciences
Department of Chemistry

Table of contents

1 ABSTRACT 0

2 INTRODUCTION 1

3 THEORY/DEFINITIONS 6

DIELECTRIC PROPERTIES 6
PIEZOELECTRIC AND PYROELECTRIC PROPERTIES 6
FERROELECTRIC PROPERTIES 7
DOMAINS IN FERROELECTRICS 7
DEPOLARIZATION FIELDS IN FERROELECTRICS 10

4 DISCUSSION 11

ADVANTAGES OF HZO 11
Scalability 11
Hydrogen annealing and Electrodes 12
Dielectric constant and depolarization field 13
CHALLENGES WITH HZO 13
Wake-up effect 13
TiN as an electrode 14
Imprint-, Fatigue-, Endurance/Retention and Leakage effects 15

5 CONCLUSION 16

6 REFERENCES 17

1 Abstract

Since the discovery of ferroelectricity in fluorite structure oxides, such as hafnia and zirconia in 2011, they have attracted increased interest. One of the most promising applications for these materials are non-volatile ferroelectric random-access memories (FeRAM). These materials are promising for this application due to their high coercive fields, high remanent polarization, low dielectric constant, small thickness, and excellent complementary metal oxide semiconductor (CMOS) compatibility. Therefore, for this bachelor's project, a closer look is taken at this application, and how hafnia and zirconia solid solutions ($Hf_xZr_{1-x}O_2$), often labeled as HZO, are used in these device. In addition, this bachelor's project will include a quick overview of what FeRAM is and how it works, and the properties of HZO, in comparison to the state-of-the-art FeRAM, lead zirconate titanate ($PbZr_xTi_{1-x}O_3$, PZT), as well as the theory and terms needed to explain this topic. It was found that HZO has a major advantage when it comes to scaling of the application compared to PZT, however in its current state has too many challenges and is unreliable for use in commercial products. This is due to effects such as "wake-up",

fatigue, imprint, and a less than sufficient endurance. Further research and development is necessary before HZO can be commercially viable as a FeRAM material.

2 Introduction

A ferroelectric material is a functional material with a stable, and switchable spontaneous polarization (P_s) (1, 2). The spontaneous polarization is a prerequisite for ferroelectric materials, which originates from a non-centrosymmetric crystal structure (1, 2). Ferroelectric materials exhibit this property below the Curie temperature (T_c), where permanent dipoles are developed in the material (3). The Curie temperature is the temperature above which the crystal structure assumes a high symmetry centrosymmetric structure, and below which the center of inversion is broken, resulting in the formation of a spontaneous polarization (3).

What makes ferroelectrics intriguing, is their essential property, which is the ability of spontaneous polarization to be switched when an external electrical field is applied (2). Ferroelectrics have a significant technological importance as a result of their switchable polarization (2). Because all ferroelectrics are also piezoelectric, the polarization direction in randomly oriented grains can be aligned with an external electric field, in polycrystalline piezoelectric materials (1, 2, 4, 5). This process in referred to as poiling (1, 2, 4). This can be exploited to provide commercially useful and important piezoelectric responses in simple to manufacture ceramic material. In addition, ferroelectrics have become technologically important for many other types of applications, including FeRAM's. (2). FeRAM's, which are nonvolatile random access memory devices (NVRAM), make use of the two or more, reversible spontaneous polarization states of these materials, by an external electric field (1, 2, 5). These reversible spontaneous polarization states, which can be negative and positive, represent the computational "0" and "1" in these devices (6). Memory devices are divided into two groups, based on the requirement of power to retain information (7). Volatile memories need constant power to retain information, whilst nonvolatile memories do not (7). FeRAM stores information within the material, by storing the polarization states (3, 8, 9). For example, the negative remanent polarization ($-P_r$) can be used to store the computational "1", whilst a "0" is encoded using the positive remanent polarization ($+P_r$) (3, 8, 9).

FeRAM's are attractive due to their low power consumption, which is lower than most other nonvolatile technologies, as well as the write and read cycle times being within the sub 100 nanosecond range (7). These devices are usually designed in the so called 1T/1C

architectures, given in Figure 1, which consist of one transistor and one capacitor (10). With this design, the ferroelectric capacitor is used to store data, and transistor are used to control the access to the capacitor (10). If a switching charge pulse is detected from the capacitor, on the bit line, the cell capacitor is in “1” state, outputting the computational “1”, whilst the opposite, if no charge pulse is detected, the capacitor is in “0” state, outputting the computational “0” (10).

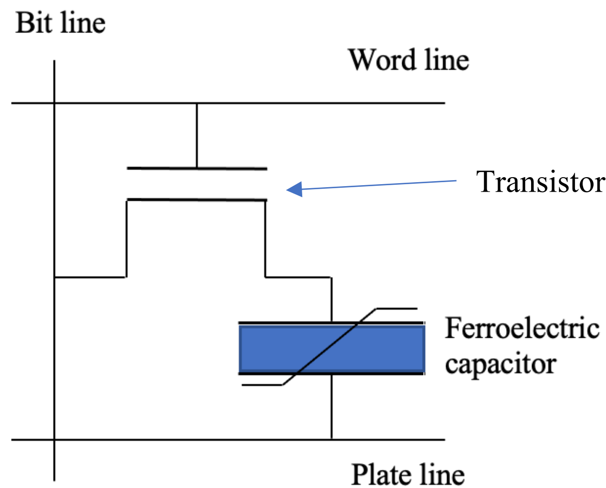

Figure 1: Sketch of a 1T/1C FeRAM cell, inspired by Kohlstedt et al. (5)

The current state of the art FeRAM’s are made of $PbZr_xTi_{1-x}O_3$ (PZT). PZT is a solid solution of $PbTiO_3$ and $PbZrO_3$ and has a perovskite structure (3). The properties of PZT depend on the value of x and temperature (3). Figure 2 shows a phase diagram of PZT, where at high temperature, the structure is cubic, and paraelectric/non-centrosymmetric (3). At lower temperatures, the given phase diagram shows two main regions (3). These regions are the tetragonal titanium-rich region (space group: P4mm) and a rhombohedral zirconium-rich region (3). The rhombohedral region consists of two temperature phases, one high temperature phase (R3m) and the other low temperature phase (space group: R3c) (3).

When the PZT composition is close to the phase boundary between the tetragonal and rhombohedral phases ($x \approx 0.47$), as shown in Figure 2, the crystal structure changes abruptly (3). This results in an enhancement of several important piezoelectric and dielectric properties of the material (3). These properties include a large increase in remanent polarization (P_r), spontaneous polarization (P_s) and dielectric constant (ε_r) (3). In addition, the coercive field (E_c) is reduced (3, 6). This makes the material well suited for FeRAM applications (6). These

interfaces/phase boundaries are referred to as morphotropic phase boundaries (MPB), when they occur as a function of composition, and are approximately independent of temperature (3).

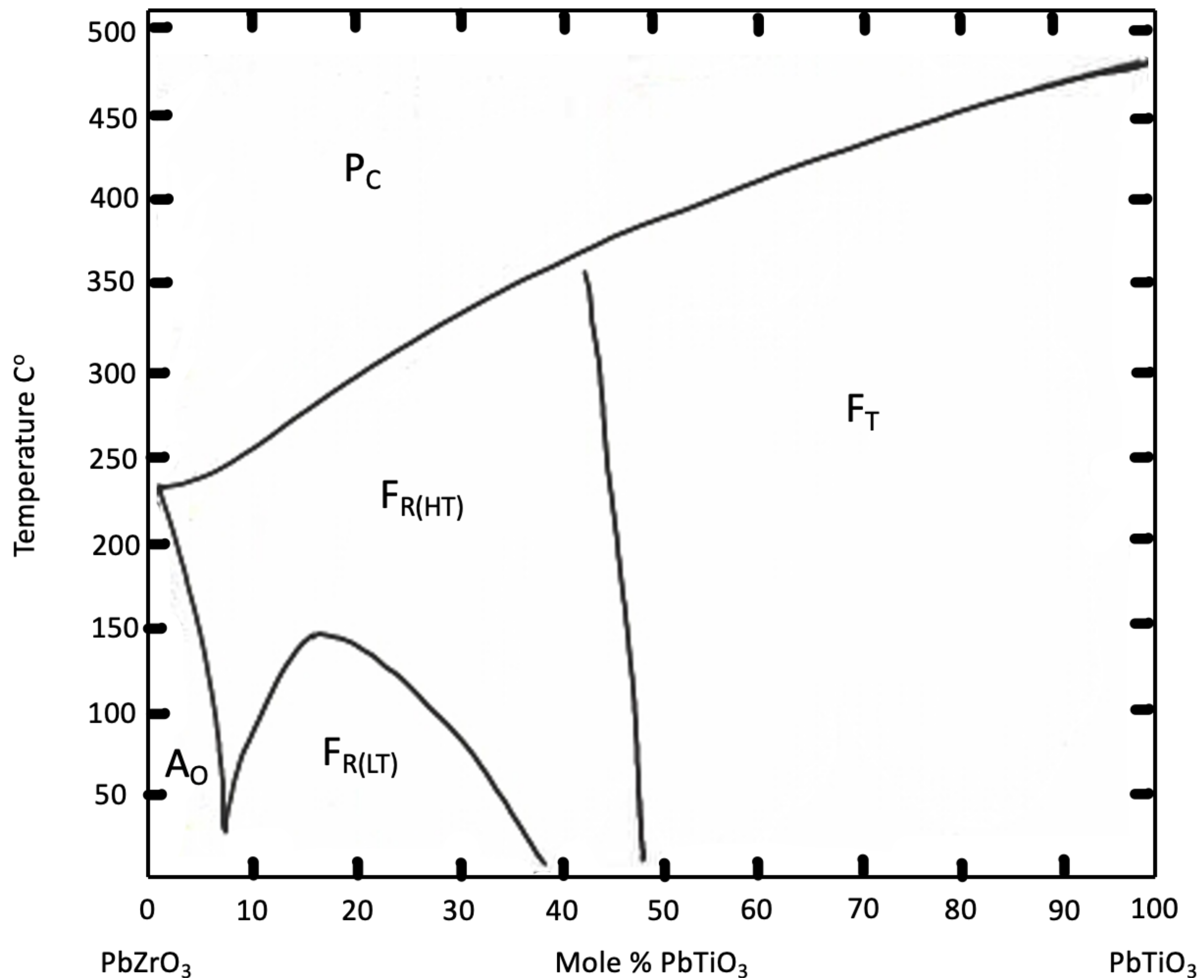

Figure 2: Sketch of the phase diagram for PZT. P_C is the paraelectric cubic phase, F_T, is the ferroelectric tetragonal phase, and the two F_R phases are the rhombohedral phases at high and low temperatures, inspired by Randall et al. (11)

One of the major challenges of PZT FeRAM devices is the issue of scaling. The origin of the scaling issue is the high physical thickness of the ferroelectric thin film (9, 12). The film thickness of PZT is not able to be scaled down further than to 50-70 nm, without compromising the stable ferroelectricity (9, 12). This is because as film thickness decreases, the coercive field increases (5). This results in higher required voltages, which is undesired as NVRAM's are low powered devices (8, 9). Thus, the coercive field to breakdown field (E_B) ratio increases (8, 9). Breakdown field is the field at which the material experiences electrical breakdown (8, 9). By maximizing voltage at a specific operating voltage, maximum speed in a ferroelectric RAM cell is achieved (9). This implies that the thickness of the film should be as thin as possible, without

the material suffering electrical breakdown (9). The cell's capacitance has a reverse linear relationship with the film thickness (9). Hence, to optimize the product, the film thickness should be as small as possible, without the risk of the material breaking down (9). In addition, the complex structure and PZT's poor compatibility with complementary metal-oxide-semiconductor (CMOS) systems, which is the platform for all future NVRAM's, contribute to the issue of scaling (5, 8, 9).

PZT's electrodes is another factor in PZT's scaling challenge. PZT's preferred electrode material is platinum, however, if this electrode material is chosen, PZT is more subject to fatigue with repeated switching (3, 10). Therefore, electrodes such as Ir, IrO_2 and $SrRuO_3$ are utilized instead, which improve the retention, imprint, and fatigue of PZT (5, 9, 13). The use of these electrodes, however, contributes to the scaling issue of PZT, as they increase the complexity of integrating the PZT substrate to CMOS technology (5, 8, 9). In addition, the cost of the product increases with the use of these electrodes (5, 8, 9).

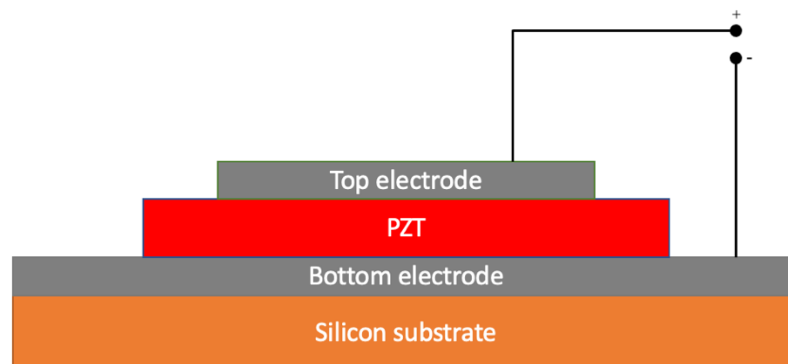

Figure 3: Model of a typical structure of PZT thin film capacitors inspired by (14)

Due to PZT's complex structure and its high thickness, it is not feasible to fabricate 3D capacitors for the 1T/1C architecture, via for example atomic layer deposition (ALD) (12). Due to these challenges, and their small memory array size, the commercialization of perovskite based FeRAM is limited to niche markets (12). Additionally, PZT contains lead, which rises health and environmental concerns for workers involved in the materials production and recycling (5, 9, 15). Therefore, in addition to the challenges with PZT above, other materials are being researched and considered to replace the material.

Hafnia and zirconia are materials that are compatible with existing CMOS technology, which is, as mentioned, the future platform for NVRAM's (5). Thus, the discovery of ferroelectricity in these fluorite structures has led to the materials becoming candidates to replace PZT for FeRAM devices (5). Therefore, this paper will focus on the advantages and challenges for HZO in FeRAM devices and discuss how it can upon improve the application compared to the state-of-the-art of the application.

HZO is a solid solution of HfO_2 and ZrO_2, $Hf_{1-x}Zr_xO_2$. Hf and Zr are both group 4 elements, resulting in similar properties in physical and chemical terms (12). HZO gets its ferroelectric properties from its non-centrosymmetric orthorhombic phase ($Pca2_1$), and recently it has been discovered that the rhombohedral phase also has ferroelectric properties (R3m) (12). In this paper however, the o-phase will be focused on, as this phase has the highest remnant polarization values for this material (5,8). More specifically, the paper will focus on compositions of x=0.5-0.7, where the material exhibits the orthorhombic phase with the highest remanent polarization (5, 8).

HZO aims to improve on the main challenge of PZT, which is its scalability issue (9, 12). HZO has showed excellent CMOS compatibility, making the material promising for future applications, and has strong ferroelectricity with a film thickness of 10 nm or less (5, 8, 12, 16, 17). This results in films being able to be scaled down for simple integration into FeRAM capacitors for technology nodes in the 12 nm size range (12). In 1T/1C FeRAM, HZO enables capacitors with sufficient remnant polarization values for reliable operation (12). In addition, HZO can be deposited with well developed deposition techniques, such as ALD, due to the material's simple composition, which makes it possible to fabricate 3D capacitors, in contrast to PZT (12).

HZO has a low dielectric constant, which results in decreased depolarization field, which is an advantage that will be explained later in this paper (12). In addition, HZO has stronger resistance to hydrogen annealing (12). Hydrogen annealing is a form of heat treatment to increase a materials ductility and reduces the materials hardness, that is crucial for such films (8, 12, 18). The standard metal nitride electrodes in the semiconductor industry can be utilized with HZO, such as TiN, making it more resilient towards hydrogen annealing, and results in improved cost-effectiveness (12). However, HZO has challenges of its own, where the most

impactful ones are the wake-up effect, imprint/fatigue, and limited endurance, due to the material's high coercive field (19).

3 Theory/Definitions

To fully grasp the topic in question, and ferroelectricity in general, it is important to define certain terms. Some of these terms are already introduced above, but a more in-depth definition will be given.

Dielectric properties

Firstly, Dielectric materials are electrical insulators, but application of an electric field causing a temporary electric polarization of the material (1). The dielectric permittivity/dielectric constant (ε_r), which describes a material's resistance to polarization by an external electric field, is often used to characterize dielectric materials (1). Nonferroelectric's, also referred to as paraelectric's, and ferroelectric's, are the two primary categories of dielectric materials (1). There are three other classes of the nonferroelectric's, however these are outside the scope of this article. A material can be piezo-, pyro- or ferroelectric only if it non-centrosymmetric (i.e., it lacks an inversion center) (1). 32 crystal classes can be used to categorize all crystal formations (1). The 32 crystallographic point groups in combination with three-dimensional symmetry elements (glide plane and screw axis) give space groups, which have been given for the structures of HZO and PZT in question (1). However only 21 of the crystallographic groups with have asymmetric properties (1). All the crystals in these 21 classes are piezoelectric (1).

Piezoelectric and Pyroelectric properties

When mechanical stress is applied to a non-centrosymmetric crystal, the ions are displaced asymmetrically from each other, which causes the crystal to become electrically polarized (1). This is referred to as the piezoelectric effect (1). The opposite effect of this has been observed as well, i.e., that an applied electric field induces strain, therefore causing the material to either expand or contract, which depends on the field direction (1). Electrical energy can be transformed into mechanical energy and vice versa via the piezoelectric effect (1). Just 10 of the 12 piezoelectric point groups have a singular polar axis that causes an electric polarization to arise (1). If a piezoelectric material also exhibits a change in spontaneous polarization (P_s) in response to a temperature change, the material can experience the pyroelectric effect, and is

therefore a pyroelectric (1). Thus, the polarization is temperature dependent in pyroelectrics (1).

Ferroelectric properties

Ferroelectrics are as mentioned polar materials that possess a minimum of two equilibrium orientations of the spontaneous polarization vector (1, 2, 4). This vector can be switched between these orientations by an external electric field (coercive field, E_c) (1, 2, 4). Most ferroelectric materials undergo a structural phase transition from a higher temperature nonferroelectric, or paraelectric phase, to a lower temperature ferroelectric phase (1, 2, 4). The temperature at which these types of phase transitions occur, is called the Curie point, or Curie temperature, T_C (1, 2, 3, 4). It is important to note that only the transition into the first ferroelectric phase is called the Curie point (1, 2, 3, 4). While ferroelectricity is an effect produced by in a pyroelectric material by the application of an external electric field, piezo- and pyroelectricity are both intrinsic properties (1, 2, 4). Hence, a ferroelectric is by definition a piezo- and pyroelectric material, but the converse is not the case (1, 2, 4). Thus, a piezo- or pyroelectric material is not necessarily a ferroelectric material (1, 2, 4).

Domains in ferroelectrics

To explain the behavior of ferroelectric materials, it is important to have some understanding of domains in these materials. Their behavior can be best described with the hysteresis loop, given in Figure 4.

The electric dipole moment per unit volume of the dielectric substance is used to define polarization intensity (P) (1, 2, 4). A ferroelectric crystal is made up of domains, which are regions of uniform spontaneous polarization (1, 2, 4). A polycrystalline ferroelectric material (crystal, grain in a ferroelectric film, etc.), is always divided into several domains due to the complex set of elastic and electric boundary conditions at each grain (1, 2, 4). If the direction of the spontaneous polarization through the materials is randomly distributed, it will lead to a net zero polarization across the material, and the pyroelectric and piezoelectric effects of individual domains will be cancelled out (1, 2, 4). Such a material is therefore neither pyroelectric nor piezoelectric (1, 2, 4). By applying a strong electric field, typically 10-100kV cm^{-1}, usually at elevated temperatures, polycrystalline ferroelectric materials can be polarized (1, 2, 4). This procedure is referred to as poiling, and it cannot orient grains, but it can reorient

domains within individual grains in the electric field's direction, resulting in a spontaneous polarization vector approximately uniformly aligned throughout the material (1, 2, 4).

There are two types of domain walls, ones who differ in orientation to P_s, and others that differ in orientation to the spontaneous strain tensor (1). They are respectively called ferroelectric domain walls, and ferroelastic domain walls (1). Ferroelectric domain walls are often 180°, as they only differ in the orientation of the polarization vector, whilst non-180° , or ferroelastic domain walls, differ in both the orientation of the polarization vector and the spontaneous strain tensor (1). Both 180° and non-180° domain walls can reduce the effects of the depolarization fields, which will be explained further below, but only the non-180° domain walls can lower the elastic energy (1).

Lattice defects in the material, such as vacancies, interstitials, pairings of positively and negatively charged defects and dislocations, can interact with the domain walls (1, 2, 4). This results in the domain walls experiencing a randomly varying force as the domain walls are displaced by an electric field, due to the random fluctuations in the number and position of the defects (1, 2, 4). A reversible process is characterized by a force that is a linear function of displacement when only minor displacements take place (1, 2, 4). However, large displacements can cause domain walls to migrate over one or more force peaks and prevent the domain walls to return to their initial positions, even when the applied force is zero (1, 2, 4). This causes hysteresis to be observed, showed in Figure 4, and the mechanisms found at large displacements are irreversible (1, 2, 4).

Depending on the symmetry of the ferroelectric phases of the crystal, different types of domain walls can develop in ferroelectric crystals (1). For instance, in the rhombohedral phase of PZT, the paraelectric cubic unit cell's body diagonals, in the (111) direction, are where the direction of the polarization develops (1). This leads to 180°, 71° and 109° domain walls, and eight possible paths for spontaneous polarization (1).

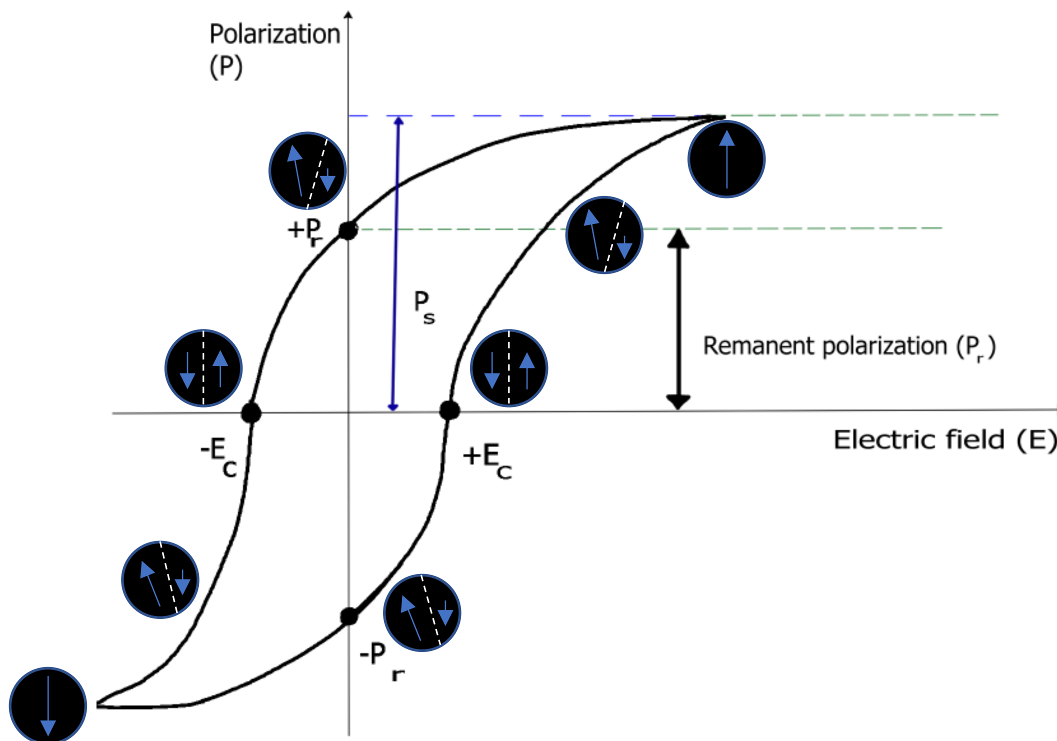

Figure 4: Sketch of a (P-E) hysteresis loop for ferroelectric materials, illustrations of the change of polarization in domains. Characteristic parameters of the hysteresis loop, such as remanent polarization, coercive field, spontaneous polarization, and saturation polarization are indicated, inspired by Damjanovic et al. and Izyumskaya et al. (1, 3)

As described above, the domain wall switching in ferroelectric materials is a factor in the occurrence of the ferroelectric hysteresis loop (1, 2, 4). In so called virgin materials, the domains are as mentioned randomly oriented, netting zero polarization (1, 2, 4). The polarization of domains that are not aligned with the external electric field will start to transition in the direction of the field as the field strength increases, rapidly increasing the observed charge density (1, 2, 4). Once all the domains are aligned, the ferroelectricity approximately behaves linearly, and the polarization is saturated (1, 2, 4). Certain domains will back-switch if the field strength decreases, as indicated by the arrows in Figure 4, but at zero field the polarization is not zero (1, 2, 4). The field must be reversed to achieve zero polarization (1, 2, 4). A new alignment of the dipoles and saturation will result from further rise in the negative field (1, 2, 4). The cycle is then completed by bringing the field strength to zero and reversing it (1, 2, 4). Remanent polarization (P_r) is the value at zero field. The coercive field (E_c) is the electric field required to bring the polarization to zero (1, 2, 4). The spontaneous polarization is often defined as the intercept of the polarization axis with the extrapolated linear segment (1, 2, 4). In polycrystalline materials however, true spontaneous polarization cannot be reached, and it is more correct to use the term saturated polarization (1,

2, 4). An ideal hysteresis loop is symmetrical, meaning $+E_c = -E_c$ and $+P_r = -P_r$ (1, 2, 4). However, the coercive field, remnant polarization and the shape of the hysteresis loop may be affected by multiple factors, such as the thickness of the film, presence of charged defects, mechanical stress, preparation conditions, and thermal treatment (1, 2, 4). In addition, the characteristics of the hysteresis loop will be affected by any process that inhibits the nucleation of new oppositely oriented domains or reduces the movement of domain walls (1, 2, 4). This further affects properties such as the dielectric and piezoelectric properties, as well as the polarization of the material (1, 2, 4).

Depolarization fields in Ferroelectrics

When a ferroelectric material cools during a paraelectric-ferroelectric phase transition, domains form to reduce the electrostatic energy of depolarization fields and the elastic energy associated with mechanical constraints that the ferroelectric material experiences (1). A surface charge emerges when the spontaneous polarization starts to occur at the transition temperature (1). The electric field created by this surface charge, is referred to as a depolarization field (E_d) and is perpendicular to P_s (1). Whenever there is a nonhomogeneous distribution of spontaneous polarization, such as when polarization falls off near the ferroelectric surface, or when polarization changes direction at grain boundaries, the depolarization field will form (1). If the ferroelectric splits into domains with oppositely oriented polarization, the electrostatic energy associated with the depolarizing field may be reduced (1). Conversely, if the depolarizing charge is offset by electrical conduction through the crystal or charges from surrounding materials (e.g., electric circuit which the material is connected to), the depolarization field can be decreased (1). Due to the presence of ferroelectric domains, the depolarizing field is often not completely compensated for, and the piezo- and pyroelectric properties of the formed crystals are often reduced (1). Mechanical pressure can also cause a ferroelectric crystal to split into domains, since the ferroelectric material is also piezoelectric, however, it is more probable that this occurs due to the strain fields associated with the ferroelastic domains (1).

As thinner films are a topic discussed in this paper, with thinner films, the magnitude of the depolarization field generally increases (3, 5, 8, 9, 12, 17, 21, 22). In addition, for long term data retention, a low depolarization field is generally required (3, 5, 8, 9, 12, 17, 21, 22).

The depolarization field is closely linked to leakage in these materials. The spontaneous depolarization of the material is caused by leakage currents through the films of the material

(20). As will be described in the discussion, leakage is increased due to an increase of oxygen vacancies (3, 5, 8, 9, 12, 17, 21, 22). Other effects, such as imprint, fatigue, the wake-up effect, and retention (endurance), are also heavily influenced by the oxygen vacancy concentration (3, 5, 8, 9, 12, 17, 21, 22). Therefore, these effects are explained in more detail, and how they affect the material in the discussion.

4 Discussion

In this paper, the advantages, and challenges with hafnia-zirconia thin films in ferroelectric RAM devices are investigated and compared to the current state-of-the-art technology of this application.

Advantages of HZO

Scalability

Firstly, as mentioned in the introduction, PZT suffers from a scaling issue due to the poor CMOS compatibility (5). The primary scaling problem is the insufficient charge availability for stable sensing, meaning that as the film thickness of PZT gets smaller, maintaining the magnitude of the polarization and stability of the ferroelectric material becomes increasingly more difficult (5, 12). Thus, it becomes increasingly more difficult to obtain a large enough polarization for stable operation of the FeRAM (5, 12). According to Park et al. a stable operation of a 1T/1C FeRAM with a 90nm technology node requires at least double remanent polarization ($2P_r$) of 84 μC/cm^2 (12). The $2P_r$ is limited to under 80 μC/cm^2 for practical polycrystalline PZT thin films (12). Moreover, the negative impact of side wall (domain walls) areas causes the $2P_r$ values of perovskite structure ferroelectrics to often degrade at several tens of nm scale devices (12). This implies that the ferroelectric properties of perovskite oxides become degraded with decreasing thickness below a certain thickness. Therefore, the perovskite-structure ferroelectrics are restricted to 50-70nm film thickness, to retain the robust ferroelectricity (12). To solve this scalability problem, 3D nanoscale capacitor production is crucial (12). A 3D capacitor is necessary below 100 nm thickness because the readout of a ferroelectric capacitor is dependent on the charge that is transferred during switching (13). With the established ALD techniques, it is possible to fabricate 3D ferroelectric capacitors and the techniques provide atomic-scale thickness control. However, there are several critical problems with the manufacturing of 3D capacitors based on the conventional perovskite ferroelectrics (8,

12, 23). The first challenge is to use atomic layered deposition, ALD, to deposit high aspect-ratio perovskite-structure ferroelectrics with two or more cation components (8, 12, 23). It is challenging to obtain sufficient ferroelectric properties for perovskite-structure memory applications with this method. This is due to the volatility and large size of lead (Pb) (23). Scaling of the physical thickness of the thin film is a more critical issue (8, 12). The entire thickness of the capacitor must be less than one third of the technology node to produce 3D capacitors (12), however, the current state-of-the-art technology node is 130 nm (12). As a result, PZT cannot be utilized for a sub-130nm technology node, since to achieve robust ferroelectricity, the thickness of PZT is restricted to 50-70 nm (12).

In contrast, as described in the introduction, fluorite ferroelectrics like HZO have excellent CMOS compatibility and can have strong ferroelectricity for sub-10 nm thin films (12). As a result, films can be scaled down to technology nodes in the 12 nm range enabling simple integration into the FeRAM capacitor applications (12). Fluorite-structure ferroelectrics provide 3D capacitors with P_r values sufficient for reliable operation with a cutting-edge sense amplifier for a 1T/1C FeRAM application. This is due to the simple structure of the material, enabling the use of ALD techniques for fabrication of these capacitors (12). The sub-10 nm thickness is another key benefit of the 3D capacitor structure (12). Another important aspect of HZO's simple composition, is that it makes the material suitable for integration in 3D nanostructures (12). This is therefore HZO's greatest advantage, due to the CMOS compatibility which, as mentioned, is the platform for all future NVRAM applications (5). In addition, a generally a smaller technology node means greater performance, the application is faster, and is more power efficient.

Hydrogen annealing and Electrodes

Another advantage that HZO has over PZT, is as mentioned in the introduction, the hydrogen annealing resistance (8, 12). The fluorite-structure ferroelectrics can make use of metal nitride electrodes, which are the common electrode materials in the semiconductor industry (12). A consequence of this is the increased cost effectiveness of these ferroelectrics increases the CMOS compatibility (12). In addition, dissociated hydrogen, had little to no effect on the ferroelectric HZO film, in contrast to the perovskite oxides, where the ferroelectric properties were significantly impaired (8, 12). TiN is significantly more resistant to the hydrogen effect because it lacks the catalytic activity of dissociating the hydrogen molecules (8, 12). In contrast, platinum, the preferred electrode material for PZT, which increases the Pr value of PZT, has

this catalytic activity, and makes PZT more susceptible to fatigue (8, 12). Therefore, special electrode materials such as Ir, IrO_2 and $SrRuO_3$ are necessary for perovskite materials like PZT to demonstrate reliable ferroelectric properties (8, 12). As mentioned, the use of these electrodes complicates the integration of PZT into CMOS technology further, and increases the cost of the product (5, 8, 9, 13, 24). However, the upside of these electrodes, is that they significantly improve the imprint, fatigue, and retention effects in PZT (3, 5, 8, 9, 12, 17, 21, 22).

Hydrogen annealing is a form of heat treatment to increase a materials ductility and reduces the materials hardness (8, 12). Hydrogen annealing is a crucial procedure for improving the oxide/semiconductor interfaces and decreasing the trap density (18). The trap density, or charge trapping will be clarified afterwards. Hydrogen impurities can be incorporated at interstitial positions in a ferroelectric material, which results in the ions' inner unit cell motion to be severely restrained, which decreases P_r (18).

Dielectric constant and depolarization field

Fluorite structured ferroelectrics have another advantage, and that is the low dielectric constant, in contrast to PZT, that has a high dielectric constant. Taking the definition of the dielectric constant, given in the theory section, into consideration, this results in a decreased depolarization field (4, 5, 25, 26). The depolarization field is important because it tends to eliminate the spontaneous polarization (25). Therefore, the depolarization field causes PZT to lose polarization in nanometer-scale thin films (4, 5, 25, 26). In addition, HZO has a high E_c compared to PZT, which suggest that it can withstand a higher depolarization field.

Challenges with HZO

Wake-up effect

HZO, however, has, some critical issues that need to be improved before the material is used in the given application, as these issues reduces the reliability of the product. The first of these issues is the so called "wake-up effect". The wake-up effect is a process of "opening" the initially constricted hysteresis with a low P_r value and this P_r value will progressively rise to saturation with cycling (8, 13, 12, 26). The wake-up effect is believed to result from a phase transition (tetragonal to orthorhombic in HZO's case) during electric field cycling and/or the non-uniformly high oxygen vacancy concentration near the interface adjacent to the electrodes (8, 13, 12, 26). A high oxygen vacancy concentration is expected close to the electrodes as the

TiN electrodes can reduce the HZO layer (8, 13, 12, 26). From experiments, it has been observed that the electrode TaN led to longer wake-up phase time, in contrast to TiN (8, 13, 12, 26). However, the effect of the electrode material is challenging to understand and requires more research (8, 13, 12, 26).

The wake-up effect is attributed to the diffusion and redistribution of the oxygen vacancies by repetitive electric field cycling (8, 13, 12, 26). The degree of the wake-up effect is thus a thermally activated process whose degree is proportional to the time and temperature of the process (8, 13, 12, 26). For example, higher annealing temperature results in a more uniform distribution of the oxygen vacancies in the film (8, 13, 12, 26). The field cycles to a hard breakdown does, however, also decrease as a result (8, 13, 12, 26). The temperature and time dependent charging of the films can also cause imprint effects, which will be discussed later in this part of the article (8, 13, 12, 26).

On the other hand, it is technically challenging to induce ferroelectric behavior in thin films of the orthorhombic phase of HZO without performing an initial wake-up pre-cycling (26). Due to the need for stable polarization hysteresis cycles, it can be difficult to incorporate HZO into reliable memory systems (8, 13, 12, 26).

Another significant aspect that affects the degree of wake-up effect is the doping concentration (8, 13, 12, 26). Optimizing the HZO thin film doping concentration could reduce the wake-up effect (8, 13, 12, 26). The wake-up effect was best optimized at a Zr doping concentration slightly below that of the maximum P_r value ($x<0.5$) (8, 13, 12, 26). This however does not resolve the issue completely and reduces the overall performance of the material. This effect can also be seen in perovskite-structure ferroelectrics (8, 13, 12, 26). If the initial P_r is high enough, the number of cycles required to reach the awakened state, which is of 10^3 order, is insignificant in comparison to the overall cycling stability of the order of 10^{12}–10^{15} (8, 13, 12, 26). In comparison, the highest film cycling endurance found for HZO is $4 * 10^{10}$ which is substantially lower than that of PZT. Therefore, unlike HZO, optimized PZT films using oxide electrodes (e.g., IrO_2) have a negligible wake-up effect (8, 13, 12, 26).

TiN as an electrode

As described in the first part of the discussion, TiN is an advantageous electrode to use for HZO. However, the electrode has an inherent challenge. The use of TiN electrodes can result

in a so-called oxygen scavenging effect, where TiN “steals” oxygen atoms from HZO and is oxidized (8, 12). This results in a lower fraction of the orthorhombic phase, which is responsible for the materials ferroelectric properties (13, 27). In addition, this leads to formation of tetragonal regions in the material, and these regions are considered non-switching, which is detrimental to the performance of the ferroelectric capacitor (13, 27).

Imprint-, Fatigue-, Endurance/Retention and Leakage effects

Imprint, which is a ferroelectric’s tendency/preference to stabilize the state it is stored in and results in a loss of retention of the opposite state, is another significant issue with ferroelectric memories (3, 5, 8, 9, 12, 17, 21, 22). Imprint is also described as a horizontal shift of the hysteresis loop, given in Figure 5, and coercive field (E_c) (3, 5, 8, 9, 12, 17, 21, 22). Charge trapping at the defect sites related to oxygen vacancies is typically associated to the imprint effect (3, 5, 8, 9, 12, 17, 21, 22). Charge trapping is the localization of an electron or hole at a crystal structure’s lattice defect or at an atom’s unsaturated bond on the surface of a nanocrystal (3, 5, 8, 9, 12, 17, 21, 22). Charge mobility is reduced by trapping because the charge can become stable in these sites (3, 5, 8, 9, 12, 17, 21, 22). Fatigue is also an issue within ferroelectric memories, and generally has a similar origin to imprint (3, 5, 8, 9, 12, 17, 21, 22). Fatigue is the degradation of the ferroelectric material, such as remanent polarization and polarization reversals becomes small, with load cycles (3, 5, 8, 9, 12, 17, 21, 22).

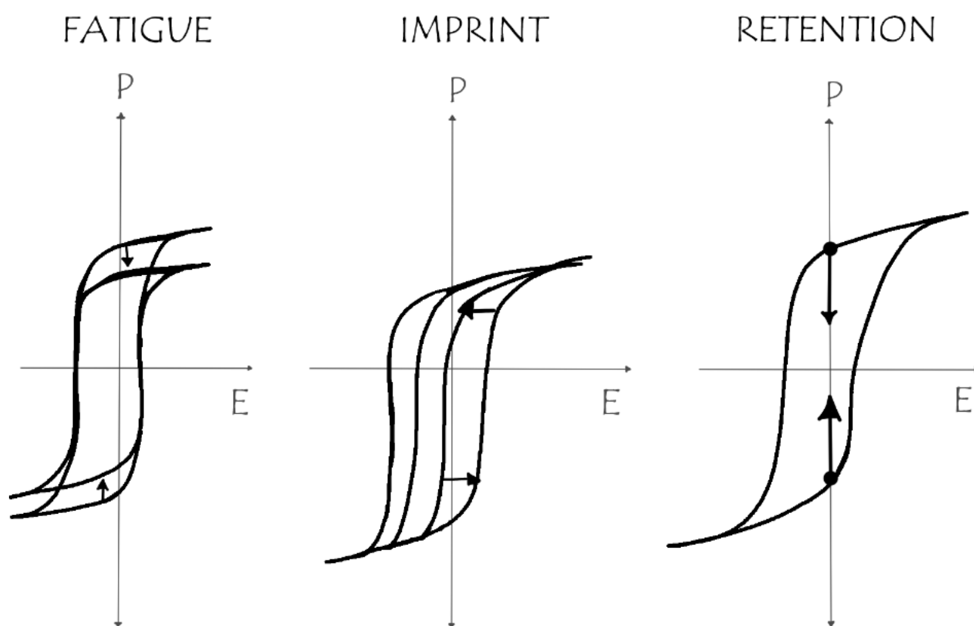

Figure 5: Sketches of the effects of fatigue, imprint, and loss of retention on hysteresis loops in FeRAM 1T/1C cells, inspired by Scott et al. (9)

Ferroelectric memory devices are known to be significantly affected by the imprint effect, which can result in an increase in operating voltage, issues with retention loss, and issues with the read and write operations (3, 5, 8, 9, 12, 17, 21, 22). A ferroelectric capacitor cell's retention, as opposed to fatigue, is its capacity to hold onto its stored charge, and hence its "1" or "0" of stored information (3, 5, 8, 9, 12, 17, 21, 22). This implies that it becomes challenging for the system to distinguish between a "1" signal and a "0" signal. As with the wake-up effect, the concentration of oxygen vacancies has an important role to play in the imprint effect (3, 5, 8, 9, 12, 17, 21, 22). Thus, the imprint effect and fatigue contribute to the issue of insufficient endurance in ferroelectrics (3, 5, 8, 9, 12, 17, 21, 22). Shin et al. found that hafnium-rich films ($Hf_{0.83}Zr_{0.17}O_2$) had a high imprint field because the film had more oxygen vacancies (17). Conversely, in zirconium-rich films ($Hf_{0.17}Zr_{0.87}O_2$) Shin et al. found that the imprint field was lower (17). Similar to changing the concentration to reduce the wake-up effect, the same consequences are true in the case of imprint and fatigue, the materials performance is traded off for higher stability.

Fluorite-structured ferroelectrics have a relatively high coercive field to breakdown field strength ratio (3, 5, 8, 9, 12, 17, 21, 22). As a result, HZO has an insufficient lifetime compared to PZT. The typical failure mode is a hard breakdown after a significant increase in leakage current, which is known to be caused by the formation of a permanent conducting route, because of the accumulation of oxygen vacancies at the grain boundaries (3, 5, 8, 9, 12, 17, 21, 22). Leakage is the gradual transfer of the conducted electrical energy across a boundary, which viewed as insulating (3, 9) Leakage, however, is not a significant issue for PZT, in comparison to HZO (3, 5, 8, 9, 12, 17, 21, 22). Further, the material experiences polarization fatigue, a mechanism that is observed in both fluorite- and perovskite-structure ferroelectrics (3, 5, 8, 9, 12, 17, 21, 22).

5 Conclusion

In this study, the advantages, and challenges of hafnia-zirconia, HZO in ferroelectric RAM were discussed, and compared to the state-of-the-art ferroelectric RAM material lead zirconate titanate, PZT. To conclude, the application of ferroelectric materials in ferroelectric memory applications has its challenges. Imprint, fatigue, and retention are important issues, which often result in limited lifetime. For PZT however, the use of oxide electrodes such as IrO_2 has improved the product, whilst for HZO the endurance is insufficient in comparison. Another

challenge for HZO is the wake-up effect. The origin of this effect is similar to the origins of the previous issues. The wake-up effect makes the application of HZO in ferroelectric RAM challenging, and the product unreliable to some degree, due to the need for a stable polarization hysteresis cycles. However, HZO's greatest advantage over PZT, is its CMOS compatibility, and is able to be scaled down to sub-10nm films, due to the use of matured deposition techniques. The future of NVRAM's is based on the CMOS platform, therefore this is truly a huge advantage, in addition to the physical scaling, as the industry is constantly moving into smaller systems. This also results in the use of typical electrodes in the semiconductor industry, reducing the cost of the product. Therefore, in conclusion, currently, HZO has too many challenges for it to be viable in commercially available products, over PZT. However, the material is promising for future applications, as it is more researched, and its challenges are improved upon.

6 References

1. Dragan D. Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics. Reports on Progress in Physics. 1998;61(9):1267.
2. Yuan Z-l, Sun Y, Wang D, Chen K-Q, Tang L-M. A review of ultra-thin ferroelectric films. Journal of Physics: Condensed Matter. 2021;33(40):403003.
3. Izyumskaya N, Alivov YI, Cho SJ, Morkoç H, Lee H, Kang YS. Processing, Structure, Properties, and Applications of PZT Thin Films. Critical Reviews in Solid State and Materials Sciences. 2007;32(3-4):111-202.
4. Boser O. Statistical theory of hysteresis in ferroelectric materials. Journal of applied physics. 1987;62(4):1344-8.
5. Kohlstedt H, Mustafa Y, Gerber A, Petraru A, Fitsilis M, Meyer R, et al. Current status and challenges of ferroelectric memory devices. Microelectronic Engineering. 2005;80:296-304.
6. Mukundan V, Beckmann K, Tapily K, Consiglio S, Clark R, Leusink G, et al. Structural Correlation of Ferroelectric Behavior in Mixed Hafnia-Zirconia High-k Dielectrics for FeRAM and NCFET Applications. MRS Advances. 2019;4(9):545-51.
7. Banerjee W. Challenges and Applications of Emerging Nonvolatile Memory Devices. Electronics. 2020;9(6):1029.

8. Park MH, Lee DH, Yang K, Park J-Y, Yu GT, Park HW, et al. Review of defect chemistry in fluorite-structure ferroelectrics for future electronic devices. Journal of Materials Chemistry C. 2020;8(31):10526-50.

9. Scott JF. Ferroelectric memories [eBook]: Springer Berlin, Heidelberg; 2000. Available from: https://link.springer.com/book/10.1007/978-3-662-04307-3.

10. N. Setter DD. Ferroelectric thin films: Review of materials, properties, and applications. Journal of Applied Physics. 2006;100(5).

11. Randall CA, Kim N, Kucera J-P, Cao W, Shrout TR. Intrinsic and Extrinsic Size Effects in Fine-Grained Morphotropic-Phase-Boundary Lead Zirconate Titanate Ceramics. Journal of the American Ceramic Society. 1998;81(3):677-88.

12. Park MH, Lee YH, Mikolajick T, Schroeder U, Hwang CS. Review and perspective on ferroelectric HfO2-based thin films for memory applications. MRS Communications. 2018;8(3):795-808.

13. Pešić M, Künneth C, Hoffmann M, Mulaosmanovic H, Müller S, Breyer ET, et al. A computational study of hafnia-based ferroelectric memories: from ab initio via physical modeling to circuit models of ferroelectric device. Journal of Computational Electronics. 2017;16(4):1236-56.

14. Yu H, Shin C. Impact of Rapid-Thermal-Annealing Temperature on the Polarization Characteristics of a PZT-Based Ferroelectric Capacitor. Electronics. 2021;10(11):1324.

15. Lin B-T, Lu Y-W, Shieh J, Chen M-J. Induction of ferroelectricity in nanoscale ZrO2 thin films on Pt electrode without post-annealing. Journal of the European Ceramic Society. 2017;37(3):1135-9.

16. Park MH, Lee YH, Kim HJ, Kim YJ, Moon T, Kim KD, et al. Understanding the formation of the metastable ferroelectric phase in hafnia–zirconia solid solution thin films. Nanoscale. 2018;10(2):716-25.

17. Hunbeom Shin VG, Youngin Goh, Yeongseok Jeong, Giuk Kim, Yixin Qin, Sanghun Jeona. A method of controlling the imprint effect in hafnia ferroelectric device. Applied Physics Letters. 2022;122(2).

18. Okuno J, Kunihiro T, Konishi K, Materano M, Ali T, Kuehnel K, et al. 1T1C FeRAM Memory Array Based on Ferroelectric HZO With Capacitor Under Bitline. IEEE Journal of the Electron Devices Society. 2022;10:29-34.

19. Jiang Y-S, Huang K-W, Yi S-H, Wang C-I, Chang T-J, Kao W-C, et al. Ferroelectric ZrO2 ultrathin films on silicon for metal-ferroelectric-semiconductor capacitors and transistors. Journal of the European Ceramic Society. 2022;42(15):6997-7003.

20. Islamov DR, Chernikova AG, Kozodaev MG, Markeev AM, Perevalov TV, Gritsenko VA, et al. Leakage currents mechanism in thin films of ferroelectric Hf0.5Zr0.5O2. Journal of Physics: Conference Series. 2017;864(1):012002.
21. Cordones AA, Leone SR. Mechanisms for charge trapping in single semiconductor nanocrystals probed by fluorescence blinking. Chemical Society Reviews. 2013;42(8):3209-
22. Genenko YA, Glaum J, Hoffmann MJ, Albe K. Mechanisms of aging and fatigue in ferroelectrics. Materials Science and Engineering: B. 2015;192:52-82.
23. Kim SJ, Mohan J, Summerfelt SR, Kim J. Ferroelectric Hf0.5Zr0.5O2 Thin Films: A Review of Recent Advances. JOM. 2019;71(1):246-55.
24. Scott JF. Applications of Modern Ferroelectrics. Science. 2007;315(5814):954-9.
25. Glinchuk MD, Eliseev EA, Stephanovich VA. The depolarization field effect on the thin ferroelectric films properties. Physica B: Condensed Matter. 2002;322(3):356-70.
26. Silva JPB, Sekhar KC, Negrea RF, MacManus-Driscoll JL, Pintilie L. Progress and perspective on different strategies to achieve wake-up-free ferroelectric hafnia and zirconia-based thin films. Applied Materials Today. 2022;26:101394.
27. Schroeder U, Materano M, Mittmann T, Lomenzo PD, Mikolajick T, Toriumi A. Recent progress for obtaining the ferroelectric phase in hafnium oxide based films: impact of oxygen and zirconium. Japanese Journal of Applied Physics. 2019;58(SL):SL0801.

Norwegian University of
Science and Technology