Mechanisms of polarization fatigue in ferroelectric $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ epitaxial thin-film capacitors

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Minh Thanh Do

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Cover: The first figure schematically shows the profile of bipolar field cycling in fatigue measurements on ferroelectric capacitors. The second figure shows the polarization hysteresis loops of a capacitor before and after field cycling, indicating a strong fatigue behavior of the capacitor. The cover was designed by M.T. Do.

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DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
Prof. dr. T.T.M. Palstra,
on account of the decision of the graduation committee,
to be publicly defended
on Friday the 25th of September 2020 at 14:45

by
Minh Thanh Do

born on the 19th of November 1990
in Haiduong, Vietnam

This dissertation has been approved by:

Supervisors

Prof. dr. ing. A.J.H.M. Rijnders

Prof. dr. ir. G. Koster

Co-supervisor

Dr. ir. E.P. Houwman

Dedicated to my love, **Nhung Nhung**

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Chapter 1

Introduction

This chapter begins with an introductory description of the physical concepts behind ferroelectricity and practical applications of ferroelectric materials. The crystal lattice structure and the temperature-composition phase diagram of lead zirconium titanate – one of the most typical ferroelectric materials – are briefly introduced. Polarization hysteresis and domain switching, the most characteristic properties of ferroelectric materials, are addressed. Then physical concepts behind some main ferroelectric failures including polarization fatigue, polarization imprint, retention loss, and electrically breakdown are introduced. The chapter closes with a description of the scope and an outline of this thesis.

1.1 Ferroelectric materials

1.1.1 Ferroelectricity

Ferroelectricity is the characteristic behavior of certain materials which have a spontaneous polarization that is switchable under a sufficiently large external electric field (Figure. 1.1). Materials exhibiting ferroelectricity are called ferroelectric materials or ferroelectrics.

Figure 1.1: *Schematic visualization of ferroelectricity. The spontaneous polarization P_{sp} is switchable under the sufficiently large external field E .*

In a simple microscopic picture, the spontaneous polarization of ferroelectrics originates from electric dipoles, which are formed by the imbalanced distributions of the (positively and negatively) charged ions inside the unit cells of the material.

A region in the material crystal in which the unit-cell polarization vectors have the same direction is called a polarization domain. Ferroelectric samples (thin films, bulk single crystals, polycrystalline ceramics) normally contain a large number of polarization domains. The effective polarization of the sample is therefore dependent on the domain structure inside the sample.

Ferroelectricity was first discovered in Rochelle salt in the 1920s [1]. Barium titanate ($BaTiO_3$) was then discovered to be also a ferroelectric material in 1944 [2]. Nowadays, there are hundreds of different ferroelectrics known. The most common ferroelectric material for practical applications are lead-based materials such as lead titanate ($PbTiO_3$), lead zirconate titanate ($PbZr_xTi_{1-x}O_3$, a solid solution of $PbTiO_3$ and $PbZrO_3$), lead lanthanum zirconium titanate ($Pb_{1-x}La_xZr_{1-y}Ti_yO_3$).

1.1.2 Piezoelectricity and pyroelectricity

The polarization of ferroelectric materials can be changed by an application of mechanical stress and vice versa. Therefore, ferroelectric materials exhibit piezoelectricity, i.e. the ability to generate an electric charge in response to an applied mechanical stress (direct effect) or vice versa (converse effect) (Figure. 1.2).

Ferroelectric materials also change their polarizations by being heated or cooled. Therefore, they also exhibit pyroelectricity, i.e. the ability to generate a temporary voltage in response to a change of temperature and vice versa.

Figure 1.2: *Schematic visualization of direct piezoelectricity (internal charges result from external mechanical stresses).*

1.2 Applications of ferroelectric materials

Ferroelectricity, piezoelectricity, and pyroelectricity are interrelated behaviors of ferroelectric materials, making the material potential in various technological applications [3–5] (Figure. 1.3). Ferroelectricity is used in non-volatile ferroelectric random-access memories as the two distinguishable polarization states can represent the binary state “0” and “1” in data storage [6, 7]. Piezoelectricity is the working principle of various piezo-based micro- and nano-electromechanical systems including sensors [8], actuators [8], transducers [9], energy harvesting devices [10], photovoltaic devices [11], [12], field-effect transistors [13, 14]. Pyroelectricity can be used for infrared thermal imaging [15].

Figure 1.3: *Application ranges of ferroelectric, piezoelectric and pyroelectric materials. The figure is after [4].*

1.3 Lead zirconium titanate (PZT)

1.3.1 Microscopic view

$\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) is the most widely used ferroelectric materials. PZT has a perovskite structure with Pb ions sit at the corners, Zr or Ti ions at the body center, and O ions at the face centers of the material unit cell (Figure. 1.4). Below the so-called Curie temperature (T_C), energetically favorable positions of Zr or Ti ions deviate from the unit cell center. The distribution of the positive charges (Zr or Ti ions) and negative charges (O ions) in the unit cell therefore becomes non-centrosymmetric, making the unit cell electrically polarized with a spontaneous polarization $\mathbf{P}$.

Figure 1.4: The crystal structure of PZT (with a "tetragonal" composition) above and below the Curie temperature T_C . In the cubic structure (above T_C), the charged ions are distributed centro-symmetrically, so that the material is paraelectric. In the tetragonal structure (below T_C), imbalanced displacements of the positive and negative ions result in a spontaneous polarization in the unit cell.

1.3.2 Temperature-composition phase diagram

PZT shows a complex temperature-composition phase diagram [16–18] (Figure. 1.5). Above T_C , the material has a cubic structure and is in the paraelectric phase (P_C). Below T_C , the material has either a rhombohedral (F_R) or a tetragonal structure (F_T), depending on the Zr/Ti ratio: rhombohedral for the Zr-rich compositions and tetragonal for the Ti-rich compositions. Both these structures show ferroelectricity. However, it was found that PZT exhibits maximum piezoelectric response and electromechanical coupling properties for Zr/Ti ratios near 52/48 (at room temperature) [19]. This rhombohedral-to-tetragonal transition region is separated by the so-called morphotropic phase boundary (MPB). In PZT with a composition close to MPB ratio, Noheda *et al.* [20, 21] discovered the presence of an additional monoclinic phase (FM), that exists at lower temperatures together with the tetragonal and rhombohedral phases. Therefore, at the MPB the structure of the material is not changing abruptly from one structural phase into another, but rather transiting "smoothly" through a "bridge" monoclinic phase, and the strong piezoelectric properties of these compositions are attributed to the presence of this monoclinic transitional phase [18].

Figure 1.5: The temperature-composition phase diagram of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$. P_C represents the paraelectric cubic phase existing above T_C . F_R , F_T , and F_M are the ferroelectric rhombohedral, tetragonal, and monoclinic phase, respectively. The open circles denotes data points collected by Jaffe et al. [17], whereas the solid circles and squares represent data from Noheda et al. [18]. The nearly horizontal line gives the Curie temperature, whereas the nearly vertical line denotes the MPB. The monoclinic phase exists in a narrow composition range as indicated by the hatched area. The graph is from [18].

1.3.3 Practical advantages and disadvantages of PZT

Lead-based ferroelectric materials (specifically PZT) are widely used in applications because of their high Curie temperatures (300 - 400°C, which is higher than the operation temperature of most devices) and large polarization values (20 - 60 $\mu\text{C}/\text{cm}^2$, depending on Zr/Ti ratio). However, their uses currently becomes regulated because of the presence of Pb, a toxic element. This has pushed the search for discovery and application of lead-free ferroelectric materials such as BiFeO_3 , BaTiO_3 , $\text{K}_{1-x}\text{Na}_x\text{NbO}_3$ [22].

1.4 Polarization hysteresis and domain switching

The most important property of ferroelectric materials is that their polarization switching can be driven by an external electric field. This is usually achieved in a capacitor configuration in which the ferroelectric material is sandwiched between two electrodes.

The macroscopic representation of polarization switching is the polarization hysteresis loop (P-E loop) showing the measured polarized charge density (actually the so-called displacement - time integrated - current from one electrode to the other in response to the changing polarization charge) as a function of the applied electric field (Figure 1.6). When the external field (for example in the positive direction) is switched on to a capacitor and increased, the polarization domains start switching into the direction of the field, leading to a rapid increase of the measured charge density (as seen by the nonlinear route A-B-C-D). When the field is decreased from the saturated state (point D), some domains can switch back (back-switching effect), but the majority of the domains keep their polarization state so the total polarization at zero field has a finite value (point E). This is called remnant polarization P_R . If the field is reversed into the opposite direction and reaches a particular value E_C (point F), the measured polarization is zero. This is called the coercive field E_C . At this point, the total volume of downward-oriented domains is compensated by the total volume of upward-oriented domains. When the field is further increased (in the negative direction), the domains will realign further parallel to the field and the net polarization saturates again (point G). The saturated polarization P_S is normally taken as the intercept of the extrapolated tangent to the loop at high fields with the polarization axis.

Generally, one considers the ferroelectricity of a material in a given device as "well-developed" if the P-E loop has a square shape with steep slopes at both coercive fields and large P_R values (close to P_S). However, the shape of the P-E loop and therefore E_C , P_R , and P_S values are sensitive to multiple factors, including device thickness [24–26], ferroelectric composition [27, 28], ferroelectric microstructure and crystalline orientation [29, 30], electrode material(s) [31, 32], and measurement conditions [33–35].

The switching of ferroelectric polarization domains under external electric field has been experimentally observed [36–40]. A schematic visualization is shown

Figure 1.6: A typical polarization hysteresis loop (measured on (111)-oriented sol-gel derived $\text{Pb}(\text{Zr}_{0.45}\text{Ti}_{0.55})\text{O}_3$ thin film). The inset circles with arrows schematically show the domain structure at the indicated positions along the loop. The figure is Damjanovic [23].

in Figure 1.7*, assuming that the initial domains were in the polarized upward direction and the external electric field pointed downward. Several processes take place in series. First, nano-sized reverse domains nucleate at capacitor interface(s) [36–38, 41]. Then, the needlelike reverse domains quickly grow forward through the ferroelectric layer until reaching the opposite interface. During this stage, the ferroelectric layer contains a pattern of alternating upward and downward oriented domains [36]. Next, the reverse domains slowly expand by sideways motion of the domain walls. The polarization switching is completed as the reverse domains coalesce into a single, downward oriented domain. For PZT thin films, the total characteristic switching time is in the range from micro to milliseconds (depending on the applied field) [42].

One can logically infer that the switching of the polarization can become suppressed if the nucleation of reverse domains is inhibited and/or the motions of domain walls are hindered. The suppression of domain switching in ferroelectric

*This is for a tetragonal-structure materials. Rhombohedral-structure materials have a more complicated picture, but the vertical component of P follows roughly the same picture as sketched here.

Figure 1.7: *Schematic visualization of the domain switching in ferroelectrics with three characteristic stages: domain nucleation at the interfaces, domain forward growth and sideways growth inside the ferroelectric layer.*

devices will be discussed further in the following sections of the thesis.

1.5 Polarization fatigue and other ferroelectric failures

As mentioned above, ferroelectric materials are potential in a wide range of applications. However, ferroelectric devices show some issues and become inefficient because of ferroelectric failures. The major manifestations of ferroelectric failure are polarization fatigue, polarization imprint, retention loss, and electrical breakdown.

Polarization fatigue is defined as the loss of polarization when the ferroelectric device undergoes prolonged field cycling (Figure 1.8a). Polarization fatigue is one of the major issues in practice because many ferroelectric devices operate under an AC drive voltage (or field cycling). If the polarization loop of the device after field cycling is significantly suppressed as compared to the virgin loop, the device shows a strong fatigue effect.

Figure 1.8: *The macroscopic characteristic behavior of polarization fatigue (a), imprint (b), and retention loss (c) of ferroelectric capacitor. The figure is after [43].*

Polarization imprint is macroscopically characterized as the shift of the P-E loop along the field axis with respect to the origin (Figure 1.8b). In practice, polarization imprint can appear if the ferroelectric device experiences a DC voltage for a prolonged period. A direct consequence of the imprint effect is that the remnant polarization of one polarized state will be lost (for example the positive remnant polarization in Figure 1.8b). Therefore, the imprint effect causes failure in “read” and “write” process in memory devices.

Retention loss is sometimes also called the aging effect. As mentioned above, when the external field is reduced to zero, the ferroelectric devices still possess a certain remnant polarization. However, the remnant polarization value may slowly decrease with time (Figure 1.8c). This effect is called retention loss. Retention loss reduces the efficiency to differentiate the polarization states corresponding to the logical states in memory devices, resulting in less reliable data storage.

Electrical breakdown is also a major concern for ferroelectric devices [44].

Electrical breakdown in ferroelectrics is normally identified with the appearance of interrelated phenomena including a suddenly strong increase of the leakage current, opening of the polarization loop, and structural degradation of the ferroelectric and/or electrode layers.

1.6 Aims and outline of the thesis

The stability of ferroelectric-based devices operating under AC drive voltages directly relates to the polarization fatigue resistance of the ferroelectric capacitor. Although the polarization fatigue can practically be remedied by the use of oxide electrodes, understanding on origin(s) and mechanism(s) of the effect still remain controversial. This thesis therefore aims to identify and clarify the dominant origin(s) and mechanism(s) of polarization fatigue in ferroelectric devices, particularly the capacitors with a single-crystalline PZT layer (Figure 1.9).

Figure 1.9: *The aims of this thesis are to identify origins and mechanisms of polarization fatigue in PZT thin-film capacitors.*

The thesis consists of eight chapters, including the first two introductory chapters for background of ferroelectric materials and literature review of polarization fatigue, the five following research chapters solving different research objectives, and the final chapter for summary.

Chapter 1 provides physical concepts and background of ferroelectricity, PZT material, polarization hysteresis, domain switching, and ferroelectric failures. The main aims of the thesis are presented at the end of the chapter.

Chapter 2 briefly reviews different physical aspects of polarization fatigue in PZT capacitors including experimental data on fatigue dependencies on capacitor structural properties and field cycling conditions, structural and ferroelectric behaviors of fatigued PZT layers, and current models for fatigue origins and

mechanisms. Remaining questions and prospective research objectives are proposed at the end of the chapter.

Chapter 3 aims to identify the dominant origins of polarization fatigue in PZT capacitors with metal top electrodes. We found that an interfacial defective layer of carbon contaminants presents at the capacitor interface with *ex situ* deposited metal electrodes and that this layer is the main origin of polarization fatigue in these capacitors.

Chapter 4 focuses to clarify mechanism(s) of the polarization fatigue in PZT capacitors with *ex situ* deposited metal top electrodes. We showed that inhibition of domain nucleation caused by trapped electrons at the metal/PZT defective interface dominantly suppresses the polarization switching of the cycled capacitors.

Chapter 5 aims to identify mechanism(s) of the polarization fatigue in PZT capacitors with *in situ* deposited metal top electrodes. We found that the metal/PZT interface is structurally degraded into a relatively thick non-structured layer, which subsequently screens the external field and consequently reducing the polarization switching of the cycled capacitors.

Chapter 6 discusses the polarization recovery in the fatigued PZT capacitors with *ex situ* metal top electrodes. Charge compensation between interfacial trapped electrons and oxygen vacancies are proposed to be the dominant mechanism behind the effect. The following fatigue behavior of the recovering capacitors is also discussed.

Chapter 7 presents some investigations into the polarization fatigue of oxide-electrode PZT capacitors with respect to the effect of the Zr/Ti ratio and harsh working conditions on the fatigue onset.

Chapter 8 summarizes the main findings and implications of the thesis as well as suggests some future research objectives for further understanding on polarization fatigue.

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Chapter 2

Literature review on polarization fatigue of PZT capacitors

Polarization fatigue, i.e. the loss of polarization of ferroelectric capacitors under field cycling, is one of the main issues limiting practical application of ferroelectric materials. This issue was intensively investigated in the last decades with a huge amount of data reported. One can easily find an article discussing a particular aspect of polarization fatigue. However, it is a challenging job to obtain a systematic and comprehensive understanding on the fatigue effect because the experimental observations and proposed explanations are chaotic and controversial. In this chapter, we attempt to summarize the major aspects of polarization fatigue, as was found in the existing literature, in an organised order. First, we review experimental data on characteristic features of polarization fatigue. Next, we briefly introduce some widely discussed hypotheses and models on mechanism(s) of fatigue. Finally, we highlight some remaining questions and aspects of fatigue that are unclear and propose some prospective research objectives for further understanding into the effect.

2.1 Introduction

Polarization fatigue in ferroelectric devices attracted much research attention in the 1990s because the interest in using ferroelectrics for potential memory applications started growing rapidly [1, 2]. The use of oxide electrodes such as Y-Ba-Cu-O [3], SrRuO₃ [4], IrO₂ [5], and La_{0.5}Sr_{0.5}CoO₃ [6] was timely found to efficiently avoid the fatigue behavior, which did appear strongly in capacitors with metallic Pt or Au electrodes [3, 4, 7]. However, origin(s) and mechanism(s) of polarization fatigue were still unclear, motivating extensive research in the following years.

Over three decades of research, a large body of data on multiple practical and fundamental aspects of polarization fatigue were reported. The dependence of fatigue on capacitor structures (electrode materials, dopants, compositions, film crystallinity and orientation) and fatigue treatment conditions (field cycling amplitude, field cycling frequency, field cycling profile, external testing parameters) can be found in numerous studies. Structural and ferroelectric properties of fatigued capacitors (after field cycling) were also investigated. This large experimental body of data was used for the development of various physical models on mechanism(s) of the fatigue effect. In spite of different physical points of view, each model attempts to address what structurally and ferroelectrically happens inside ferroelectric devices under field cycling.

A systematic literature review on different aspects of polarization fatigue can provide one with a description and some understanding of the effect. Comprehensive review articles were provided by Tagantsev *et al.* in 2001 [8] and Lou *et al.* in 2009 [9]. However, a large amount of relevant data in various ferroelectric samples was reported since then, providing new insights into the physics of fatigue. Therefore, we give in this chapter an updated review on polarization fatigue of ferroelectric devices, mostly PZT capacitors. The chapter is structured as follows. First, we summarize experimental data on the dependence of fatigue on structural parameters of a ferroelectric capacitor (electrode material, dopant, composition, crystalline orientation, and microstructure) and field cycling conditions (field amplitude, cycling frequency, unipolar modes, ambient temperature and gas, and mechanical load) and reported observations on structural and functional properties of fatigued capacitors. Second, we briefly introduce some widely-used hypotheses and models for the origin(s) and mechanism(s) of fatigue including the

2.2. How to measure polarization fatigue behavior?

oxygen-vacancy accumulation, electron injection, electron trapping, and electrode diffusion and doping. Finally, we propose some research objectives for the work described in this thesis which aim to gain further understanding on polarization fatigue.

2.2 How to measure polarization fatigue behavior?

Considering the physical concept of polarization fatigue, the formal way to show fatigue behavior of a ferroelectric capacitor is to measure the change in the amount of the switchable (or alternatively the non-switchable) polarization during field cycling. The standard way to measure the switchable (and non-switchable) polarization is by the so-called positive-up-negative-down pulse procedure [10, 11]. However, one normally uses the profile of the remnant polarization as function of the field cycle number to show the fatigue behavior. To obtain such data, one just needs to measure the P-E loop of the capacitor at different cycling states. The P-E loop is commonly measured using a triangular, bipolar field cycle. Profiles of remnant polarizations, which are collected conveniently from the P-E loops, show a comparable fatigue behavior as measured in the "formal" way [12].

Without specification, polarization fatigue in ferroelectric capacitors is understood as the fatigue behavior under bipolar, square-wave field cycling (Figure 2.1a). This is because most of ferroelectric based devices work under an AC drive voltage, so investigations into the fatigue behavior under bipolar field cycling are directly useful for practical applications. Sometimes, one also fatigued capacitors by (positive or negative) unipolar field cycling, the result is called unipolar fatigue behavior (Figure 2.1b). To compare fatigue behavior of different capacitors, which might have different pristine remnant polarization, one shows the profile of the remnant polarization which is normalized to the pristine value (Figure 2.1c).

Figure 2.1: Electric field cycling profiles for (a) bipolar fatigue and (b) positive and negative unipolar fatigue testing. (c) Examples of normalized remnant polarization profiles of a fatigued and non-fatigued capacitor.

2.3 Characteristic features of polarization fatigue

2.3.1 Effect of capacitor structural properties

Effect of electrode material

The most common feature of polarization fatigue is its strong dependence on the type of the material (either metallic or conductive oxides) of the capacitor electrodes (Figure 2.2). Capacitors with Pt and Au electrodes often showed strong fatigue already after a low number of field cycles, in the range of 10^2 – 10^4 cycles [10, 12–17]. In contrast, capacitors with conductive-oxide electrodes, such as $\text{YBa}_2\text{Cu}_3\text{O}_x$ [3], SrRuO_3 [4], $(\text{LaSr})\text{CoO}_3$ [6], IrO_2 [5], RuO_2 [18], LaNiO_3 [19, 20], and $(\text{LaSr})\text{MnO}_3$ [21], were generally free of fatigue for at least 10^9 cycles. Capacitors with hybrid electrodes consisting of a metal-oxide layer with a metal on top also showed good fatigue resistance [22–26]. Based on these findings, it is

2.3. Characteristic features of polarization fatigue

generally accepted that polarization fatigue is an interface-related effect. These studies also showed that using proper electrodes is a practical way to efficiently avoid polarization fatigue and improve the stability of ferroelectric devices.

Figure 2.2: Fatigue profiles of PZT capacitors with different electrodes after Ref. [3] (a) and Ref. [26] (b).

Effect of PZT crystal orientation and microstructure

The effects of PZT crystalline orientations and microstructure on fatigue behavior are less significant as compared to the electrode(s) material used. Capacitors with oxide electrodes generally show no fatigue, regardless of the crystal orientation and microstructure of the PZT layer [6, 7]. Capacitors with metal electrodes showed fatigue dependent on the PZT orientation and microstructure. Polycrystalline films showed less fatigue than textured and epitaxial films [7] (Figure 2.3a). For epitaxial films with the same dense microstructure, different crystalline orientations ((001), (111) and (110)) showed only a slight different fatigue behavior [27]. Both polycrystalline PZT films and ceramics with small grains were less fatigued than those with larger grains [28–30].

Effect of PZT composition

Only few studies available investigated the dependence of polarization fatigue on the Zr/Ti ratio in PZT [31, 32] (Figure 2.4). K. Amanuma *et al.* [31] reported that fatigue of Au/PZT/Pt capacitors became more severe if the PZT layer had a higher Ti content. A similar trend was observed in Ir/PZT/Ir capacitors by S. M. Bilodeau *et al.* [32]. In addition, L. Pentilie *et al.* [33] observed that PZT

Figure 2.3: *Fatigue profiles of PZT capacitors with different PZT crystallizations (after Ref. [7]) (a) and grain sizes (after Ref. [29]) (b).*

capacitors with a Zr/Ti ratio of 20/80 showed strong fatigue regardless of the electrode materials used (Pt or SrRuO₃). This is different from the fatigue-free behavior commonly observed in SRO/PZT/SRO capacitors with a Zr/Ti ratio of 52/48 [4]. Hence, it can be concluded that PZT capacitors with a higher Ti content become more fatigued than those with a lower Ti content, but the physical mechanism behind this trend still remains unclear.

In general, both acceptor and donor dopants were found to reduce the fatigue of the host PZT film (Figure 2.5). Some examples of the investigated acceptor dopants are Sc [34], Ce [35], Sb [36], Na, Mg, and Fe [37], Mn [38], and of the donor dopants are La [39, 40], Nb [41], [42–44], W [45], and WO₃ [46, 47]. However, none of these studies provided a satisfactory explanation for the observation.

2.3.2 Dependence on field cycling conditions

Field cycling amplitude

The dependence of the fatigue in Pt/PZT/Pt capacitors on the cycling field amplitude were found to be contradictory between the different studies. Numerous studies found that the fatigue became more severe under field cycling with a higher field amplitude [12, 13, 17, 21, 45, 48, 49] (Figure 2.6a). However, a few

2.3. Characteristic features of polarization fatigue

Figure 2.4: Fatigue profiles of Au/PZT/Pt capacitors with different Zr/Ti ratios after Ref.[31] (a) and of Ir/PZT/Ir capacitors after Ref. [32] (b).

Figure 2.5: Fatigue profile of Pt/PZT/Pt capacitors with Nb and Sc doping, after Ref. [34].

other works reported that the fatigue was nearly independent of the cycling field amplitude [14, 15] (Figure 2.6c).

Cycling frequency

The dependence of the fatigue on the field cycling frequency, reported in the previously mentioned studies, are also inconsistent. According to a few papers,

Figure 2.6: *Fatigue profiles of PZT capacitors under field cycling with varying field amplitudes and cycle frequencies after Ref. [13] (a), Ref. [50] (b), and Ref.[15] (c).*

Pt/PZT/Pt capacitors appeared to be fatigued faster under field cycling at a lower frequency [26, 33]. This trend was also observed in PZT capacitors with oxide/Pt electrodes [49–52] (Figure 2.6 b). However, some other works showed that Pt/PZT/Pt capacitors fatigued independently of the field cycling frequency [15, 16, 25] (Figure 2.6 c).

External factors

During prolonged operations of ferroelectric devices under AC voltages, some external factors such as the ambient temperature, ambient humidity, ambient gas composition and pressure, illumination, and mechanical load might change or be applied on purpose. Therefore, one needs to consider the effect of these factors on the fatigue behavior of the integrated ferroelectric capacitors. The effect of the operating temperature was investigated extensively, but the results are widely diverging. When the temperature increased, the fatigue effect was observed to be decreasing in some studies [25, 53–57], but increasing in others

2.3. Characteristic features of polarization fatigue

[13, 58], and unchanged [17]. Only few preliminary investigations into the effects of the other external factors were reported. J. Lee and co-workers [59] found that PZT capacitors showed less fatigue if the field cycling was performed under illumination of deep UV light from a He-Cd laser. M. Brazier *et al.* [60] observed a non-monotonic dependence of the fatigue in polycrystalline PZT capacitors on the oxygen partial pressure of the surrounding medium during the field cycling. Applying a mechanical load was found to enhance the fatigue resistance of PZT ceramic actuators [61]. However, more research needs to be performed to draw definite conclusions on the effects of these external factors on the fatigue of ferroelectric capacitors.

Figure 2.7: (a) Fatigue profiles of PZT capacitors at various test temperatures after Ref.[54]. (b) Fatigue profiles of PZT capacitors under effect of light illumination after Ref.[59].

Unipolar fatigue

It was commonly observed that unipolar fatigue (fatigue behavior under unipolar field cycling) in PZT capacitors is very small compared to the strong bipolar fatigue [62–64]. In a study, Lou *et al.* [12], however, showed that the PZT capacitors used in their experiments, were strongly fatigued under unipolar field cycling, but the effect was still much less than under bipolar field cycling. These data indicate that the mechanism(s) of the strong (bipolar) fatigue is directly related to the polarization switching of the capacitor, which only happens under bipolar field cycles.

Figure 2.8: Bipolar and unipolar fatigue behavior of PZT capacitors annealed in nitrogen or oxygen ambient (after Ref. [63]). Both capacitors show strong bipolar fatigue but no unipolar fatigue.

2.3.3 Structural and ferroelectric behavior of fatigued capacitors

Investigations into the properties such as structure and ferroelectricity of fatigued capacitors (i.e. cycled capacitors) might provide direct indications for the mechanisms behind the development of the fatigue behaviour.

In some studies, the microstructure of PZT capacitors was found to be changed by field cycling [65, 66]. Using scanning electron microscopy (SEM), Balke *et al.* [65] found that a thin layer of crystalline PZT ceramics nearby the Pt/PZT interface became molten after field cycling (Figure 2.9). Recently, using time of flight secondary ion mass spectrometry, levlev *et al.* [66] observed that Cu ions had diffused from the Cu electrode into the cycled PZT layer.

Using piezoresponse force microscopy, one observed that fatigued PZT capacitors contain non-switchable domains, which did not respond to an applied external field [67–70]. The non-switchable domains in fatigued metal/PZT/metal capacitors have a preferred polarization pointing towards the bottom electrode [68, 69].

Fatigued capacitors were observed to recover the polarization after being subjected to a further field cycling [14, 33, 71], a (large) DC bias field [15, 71], a combination of UV-illumination and DC-bias field or a combination of UV-

2.4. General causes of domain switching suppression

Figure 2.9: *SEM cross-sectional images of pristine (a) and fatigued PZT ceramic capacitors (b, c), after Ref. [65]. The PZT layer nearby the interface melted during field cycling.*

illumination and heating [72], [73], or after being annealed at a high temperature [74, 75] (Figure 2.10). These recovery effects are generally called polarization rejuvenation (of fatigued capacitors). Although these rejuvenation effects seem to be a characteristic feature of (most if not all) fatigued capacitors, the behind mechanisms have not been discussed in detail. However, it seems logical to conjecture that the mechanisms and the degree of the rejuvenation effects are strongly related to the mechanisms of how the capacitor became fatigued in advance.

2.4 General causes of domain switching suppression

As discussed in chapter 1, the switching of polarization domains in ferroelectric capacitors under an external electric field develops in three main stages in series: the nucleation of reverse domains at the ferroelectric/electrode interfaces, forward growth of domains over the thickness of the ferroelectric layer, and growth sideways of the domains by lateral motion of the domain walls. This suggests that there are two general causes that can prevent the overall polarization from a complete switching. These are (i) domain nucleation inhibition and (ii) domain wall pinning.

Figure 2.10: (a) Remnant polarization profile of Pt/PZT/SRO capacitors under field cycling after Ref. [33]. Depending on field cycling frequency, the capacitor was first fatigued (first 10^6 cycles) and then rejuvenated under field cycling ($10^6 - 10^8$ cycles). (b) P - E loops of a fatigued Pt/PZT/Pt capacitor after being annealed at different temperatures after Ref. [74], showing the annealing-assisted rejuvenation effect.

2.4.1 Inhibition of domain nucleation

Nucleation of reverse domains occurs at favorable sites at ferroelectric/electrode interfaces [76–79]. If the domain nucleation at these active sites is somehow inhibited, the reverse domains have no chance to form and grow into macroscopic domains, leading to an incomplete domain switching (Figure 2.11). If the nucleation of reverse domains at one interface of a PZT capacitor is inhibited, one expects that polarization domains in this capacitor become frozen (non-switchable) and the polarization vector in these frozen domains directed towards the nucleation-inhibited interface.

What can be the mechanisms for nucleation inhibition of reverse domains at the capacitor interfaces? The nucleation of reverse domains at capacitor interfaces needs a certain activation energy. In general, this activation energy is sensitive to the properties such as material compositions, impurities, asperities, and (charged) defects of the electrode/ferroelectric interface [80]. To provide enough energy to overcome the activation energy barrier so that the reverse domain can nucleate, an external field needs to be applied against the direction of the current polarization domains and the field amplitude needs to be higher than a certain value. If the external field is not high enough, the nucleation

2.4. General causes of domain switching suppression

Figure 2.11: *Schematic visualization of domain non-switching by inhibition of reverse domain nucleation at a capacitor interface.*

of reverse domains at the interface cannot take place. Particularly, if the capacitor interfaces are electronically and/or structurally changed during the use/cycling of the capacitor, the activation energy barrier for domain nucleation at the interfaces also change, consequently affecting the overall switching behavior of the capacitor.

2.4.2 Domain wall pinning

Under external field, domain walls of reverse domains move forward and sideways to complete the polarization switching. If the domain walls are pinned because of any reason (mostly by defects – as discussed later), their motions (i.e. the domain growth) in response to the external field can be hindered (slowed down) or even completely stopped (Figure 2.12). The pinned domain walls are also called immobile walls. If there are no nucleation sites for reverse domain inside a domain with immobile walls, then this domain becomes non-switchable (frozen). However, if there are nucleation sites, the energetically favorable reverse domains can nucleate and can grow inside this immobile-walls domain, leading to further switching.

What can be the cause of the domain wall pinning? Generally, domain walls become pinned by defects inside the ferroelectric capacitors. The first type of defects is charged point defects such as oxygen vacancies. L. He *et al.* [81] showed theoretically that oxygen vacancies tend to accumulate at the domain walls due to a lowered formation energy and subsequently make the domain walls

Figure 2.12: *Schematic visualization of a non-switchable domain (green-hatched) because of domain wall pinning, preventing sideways growth of the switched domains (blue).*

immobile. Also by theoretical studies, C. H. Park *et al.* [82] showed that sheets of oxygen vacancies can also strongly pin the domain walls. Other types of defects can be non-charged structural defects such as dislocations, grain boundaries, and ferroelastic domain walls [83–90]. For example, A. Kontsos *et al.* [83] calculated the pinning strength of domain walls and dislocation arrays and suggested that dislocations can hinder the domain wall motion. Grain boundaries can also act as pinning sites due to the strong interaction between the strain field created by the lattice distortion around the grain boundary (the lattice distortion causes strain gradients, which in turn act as a local electric field through the flexoelectric effect) and the bound charges at domain walls [84–86]. In conclusion, defects can hinder or even completely stop the motion of domain walls, depending on the defect concentration and the wall-defect interaction strength, subsequently reducing the switchable polarization of ferroelectric devices.

2.5 Models for polarization fatigue

In this section, we introduce and discuss some models proposed in literature that describe the mechanism of how ferroelectric capacitors become fatigued under electric field cycling. Basically, polarization fatigue originates from defects, but what are the defects, are they initially existing in the as-grown capacitor or formed

during field cycling, and how do the defects suppress the domain switching in the cycled capacitor? We will discuss the existing models based on these aspects.

2.5.1 Oxygen vacancy hypothesis

Oxygen vacancies are the most common intrinsic defects in perovskite-structure materials [91–93]. They are formed during the material processing and can be controlled to some extent by the fabrication conditions [94]. The typical characteristic feature of oxygen vacancies is that they are very mobile inside the material [95], especially under an external field. This is because oxygen vacancies are doubly positive charges and perovskite structures form heavily interconnected oxygen backbone lattices, which forms an easy pathway for oxygen diffusion.

The so-called oxygen vacancy hypothesis as a model for the development of polarization fatigue in ferroelectric capacitors contains several suggestions as following. First, it is suggested that the charged oxygen vacancies tend to migrate towards capacitor interfaces during field cycling (Figure 2.13). In oxide/ferroelectrics/oxide capacitors, the oxygen vacancies were suggested to be able to freely move through the interfaces and subsequently be incorporated in the electrode, where their charges are compensated by free carriers. Hence the oxide electrode functions as a sink for oxygen vacancies. Thus, in this way nothing happens to the ferroelectric capacitors with oxide electrodes, except that the vacancy concentration decreases in the ferroelectric and increases in the electrode. In contrast, metal electrodes were thought to block the migration of oxygen vacancies, resulting in a significant accumulation of these defects at metal/ferroelectric interfaces. In general, with increasing field cycle number, the accumulation of oxygen vacancies at metal/ferroelectrics interfaces can become significant, forming charged clusters, space charge and passive layer [96]. These kinds of defects are then expected to cause domain wall pinning [97–99] and domain nucleation inhibition [100], which subsequently suppress domain switching in the cycled capacitor.

At first glance, the oxygen vacancy hypothesis is a plausible model. The migration of oxygen vacancies in perovskites under applied electric field has been experimentally observed [101, 102]. Therefore, it is acceptable to expect an accumulation of these defects at capacitor interfaces during field cycling. The domain wall pinning caused by oxygen vacancies has been discussed extensively in

Figure 2.13: *Schematic representation of the oxygen vacancy hypothesis as a fatigue mechanism. Under field cycling, these charged defects are accumulated nearby metal/ferroelectric interfaces, causing the suppression of domain switching. In contrast, oxide electrodes are transparent to oxygen vacancies so that these defects are neutralized in oxide electrodes.*

theoretical studies (as presented in the previous section). As discussed above, the model can reasonably explain the non-fatigue behavior of capacitors with oxide electrodes and the strong fatigue behavior of capacitors with metal electrodes. In addition, as a consequence of the model, donor species would improve the fatigue resistance of the material because they reduce the number of oxygen vacancies. This is consistent with experimental observations (presented in previous section).

Despite the above agreements, the oxygen vacancies hypothesis has some limitations. First, the hypothesis would predict that under the properly poled unipolar cycling (or DC-bias) there would be a significant vacancy accumulation at the interface and thus a comparable fatigue under unipolar cycling as under bipolar cycling. This is completely against the experimental observations showing that unipolar fatigue is always much less than bipolar fatigue. Second, acceptor dopants will enhance the number of oxygen vacancies, then according to this model, they should have a negative effect on the fatigue resistance of PZT capacitors. However, this conflicts with the experimental data showing that acceptor dopants also increase the fatigue resistance of PZT. Last but not least, although oxygen vacancies are expected to accumulate at capacitor interfaces, one observed that there is no any correlation between the defect accumulation and the fatigue degree [103].

Based on the above analysis, it can be concluded that native defects inside

ferroelectric layers such as oxygen vacancies cannot be the main origin of polarization fatigue. These defects might be responsible to some extent for the fatigue, and there must be another major mechanism(s) involving in this degradation phenomenon.

2.5.2 Electronic charge trapping

One popular hypothesis is that trapped electrons are the origin for the development of polarization fatigue in ferroelectric capacitors.

Based on the observation that a fatigued capacitor can recover the polarization under UV-light illumination and/or DC-bias application, Warren *et al.* [72] suggested that, electrons are trapped at the domain walls during field cycling, which subsequently inhibit the motion of domain walls, leading to the domain switching suppression in cycled capacitors. The UV and/or DC-bias application is supposed to generate free carriers inside the PZT layer and drive them to compensate the trapped electrons, thus deactivating the pinning sites and releasing the trapped domain walls.

Some other authors also believed that trapped electrons are the origin of polarization fatigue, but they suggested that the trapped electrons are mostly present at electrode/ferroelectric interfaces [104, 105]. G. I. Rhun *et al.* [104] have built a mathematical model for the development of polarization fatigue caused by interfacial trapped electrons. The resulting modeled fatigue shows some features which are quite consistent with experimental data. However, some physical aspects are still unresolved, for example, what the source is of the electrons and how they become trapped at the interface during field cycling.

Overall, one has not been able to conclusively demonstrate whether or not electron trapping occurs inside ferroelectric capacitors during field cycling. This is because direct experimental observation of electron trapping process is challenging. However, one can look for further experimental data that indirectly infer the trapping process of electrons, similar as was done by Warren *et al.* [72].

2.5.3 Field screening effect

Balke *et al.* [65] suggested that the suppression of polarization switching in their cycled PZT ceramic capacitors is due to the so-called field screening, which

is caused by a non-ferroelectric PZT-degraded layer observed at the capacitor interfaces. The cycled capacitor is simply considered as a series connection of a non-ferroelectric layer (which is formed during the field cycling) and a ferroelectric layer (Figure 2.14).

Figure 2.14: *Schematic representation of a cycled capacitor with a non-ferroelectric formed at one interface. This non-ferroelectric layer is suggested to screen the applied field seen by the ferroelectric layer, consequently might suppress the domain switching of the capacitor.*

One can describe the continuity of the displacement current across the dielectric layer/ferroelectric interface and the voltage drop across the two layers by the following equations, respectively:

$$\varepsilon_0 \varepsilon_i E_i = \varepsilon_0 E_f + P_f \quad (2.1)$$

$$E_i d_i + E_f d_f = E_{appl} L \quad (2.2)$$

with d_i and ε_i are the thickness and dielectric constant of the non-ferroelectric layer; d_f and ε_f are the thickness and dielectric constant of the ferroelectric layer; E_i and E_f are the electric field inside the non-ferroelectric and ferroelectric layer; E_{appl} is the applied field over the capacitor. From Equations 2.1 and 2.2, one can see that, depending on the thickness and dielectric constant of the interfacial non-ferroelectric layer, the electric field inside the ferroelectric layer can be much

smaller than the applied field over the capacitor. Therefore, a particular applied field, which was sufficiently high to switch the pristine capacitor, might be not sufficient to switch the cycled capacitor.

This scenario seems to be plausible in ceramic capacitors because the interfacial degraded layer in the cycled capacitor was observed [65]. However, there are some unclear points related to this scenario. First, formation mechanism(s) of this degraded layer during field cycling was not explained in detail. Second, if the field screening is the reason behind the domain switching suppression in the cycled capacitor, the cycled capacitor must be able to switch under further increased applied field. Third, whether a same scenario takes place in thin-film capacitors is deserved to be discussed.

2.5.4 Electron injection at capacitor interfaces

Another model for fatigue mechanism is that electric field cycling can introduce injected electrons from the electrodes into the ferroelectric layer, which subsequently cause domain switching suppression in the cycled capacitors.

How can electrons be injected into the PZT layer during field cycling? It was quantitatively suggested that the switching of domains under field cycling can initiate an electron injection at capacitor interfaces [13, 14, 106]. A physical model for this process was then mathematically described by Lou *et al.* [74, 107], (Figure 2.15). When a reverse domain nucleates at the capacitor interface, the bound charges on the top of the nucleating domain (with head-to-head polarization vectors) are completely unscreened. These unscreened bound charges produce a strong depolarization field at the capacitor interface, directed from the PZT to the electrode. The electrical force associated with this depolarization field will accelerate electrons (increase their kinetic energy) to move from the electrode towards the ferroelectric layer. Lou *et al.* [107] mathematically showed that the injection of electrons will become exponentially more significant if there is an interfacial dielectric layer at the capacitor interface. This was assumed to be the case of metal/ferroelectrics interface. If the interface is without any dielectric layer, as is expected for oxide/ferroelectric interface, the injection of electrons becomes much reduced because a much weaker depolarization field.

How can injected electron cause domain switching suppression in the cycled capacitors? According to Lou *et al.* [107], there are several steps after the

Figure 2.15: *Schematic representation of electron injection induced by the depolarization field arising from the uncompensated bound charges on the top of the reverse domain (green area). This figure is after Ref. [74].*

injection of electrons at capacitor interfaces. (a) The injected electrons interact with the PZT lattice and release a large amount of their kinetic energy in the form of heat. (b) After each field cycle the local temperature of the PZT nearby the interface increases slightly (as long as the injection is still happening). (c) A high temperature local thermal equilibrium state is reached at the capacitor interface after a certain number of field cycles. (d) If the temperature is high enough the PZT at the interface can become structurally decomposed, forming “dead areas”. (e) The number of dead areas, with degraded PZT crystal structure, will gradually increase during the continued field cycling. At a certain moment the major part or even the entire PZT interface layer may have become decomposed, forming a dead interfacial layer. (f) The dead areas reduce the number of available sites for reverse domain nucleation, leading to switching suppression in the cycled capacitor.

The serial model of electron injection - structure degradation - nucleation cite reduction seems plausible. It can explain why unipolar fatigue is always much less than bipolar fatigue, because electron injection is the direct result of the polarization switching, which is absent under unipolar field cycling. Some specific processes in the proposed model were evaluated and verified experimentally [49,

74, 108–110]. For instance, Lou *et al.* [74] observed delamination in the Pt top electrode, which might be the result of degradation of the PZT underneath. Wu *et al.* [110] observed that fatigued PZT capacitor show a reduced photovoltaic effect as compared to pristine capacitor and this can be an indirect evidence of a PZT-degraded layer at the capacitor interface.

2.6 Discussion

We have briefly summarized different perspectives on polarization fatigue in PZT capacitors. We presented various ways the fatigue manifests itself in remnant polarization - cycle number profiles, that depend on the capacitor structures and the field cycling conditions. We summarized data on structural and functional properties of fatigued capacitors. We have explained domain switching suppression in terms of domain nucleation inhibition and/or domain wall pinning. We described models for the development of fatigue in terms of oxygen vacancy accumulation, electron trapping, and electron injections. Based on this literature review, we are now able to comment on the current knowledge of polarization fatigue and come up with some conjectures and experiments for further understanding into the effect:

a) In general, polarization fatigue is an defect-originated effect. Multiple types of defects such as oxygen vacancies, grain boundaries, dislocations, 90° domains/domain walls, and (as-grown) interfacial, defective or dielectric layers can already exist in the as-grown capacitor. Under field cycling, each type of these defects will "react" with the repeated field cycles in a particular way, forming new "active" defects such as oxygen-vacancy clusters, charged defects (by trapping injected electrons), and structurally degraded layers, which subsequently can suppress domain switching in the cycled capacitor (Figure 2.16). To understand mechanisms behind the development of fatigue, one needs to discuss two main scenarios: (i) the formation of "active defects" during field cycling and (ii) the mechanism of domain switching suppression caused the "active" defects in the cycled capacitor.

b) The origin(s) (the initially existing defects) that contribute most to the fatigue of a particular PZT capacitor is dependent on structural features of the capacitor itself such as the crystalline structure of the ferroelectric layer, the PZT

Figure 2.16: Schematic showing different hypotheses and models for the development of polarization fatigue in ferroelectric capacitors.

composition (Zr/Ti ratio), the microstructure of the interfaces, and the electrode material. These structural features determine how the capacitor reacts with the field cycling and consequently determines the mechanism(s) of the fatigue of that particular capacitor. The dominant origins and mechanisms of fatigue in PZT thin films may be different from those in bulk ceramic devices, which have more bulk defects. For thin-film capacitors, one may expect that epitaxial single-crystalline films have different dominant fatigue origin(s) and mechanism(s) than polycrystalline, sol-gel derived films, which have a more ceramic character. As a consequence, the final fatigue behaviors observed in these devices are also different. This can explain why previous experimental findings on the dependence of fatigue on the field cycling conditions are inconsistent: the investigated ferroelectric structures in these studies differ in many aspects. A meaningful comparison between these data is therefore often not well possible. The model that describes the fatigue of a particular sample therefore cannot satisfactorily explain the features of fatigue observed in other samples with a different structure.

c) However, some of the features of fatigue in different ferroelectric devices have been consistently reported such as the non-fatigue behavior of oxide-electrode capacitors (exclude LaBaSnO_3 as an exception [111]), the strong-fatigue behavior

of metallic-electrode capacitors, the outperformance of bipolar fatigue over unipolar fatigue. These commonalities suggest that there is(are) shared scenario(s) in the development of fatigue of the investigated capacitors. The other reported features including the fatigue dependence on the field cycling conditions and the rejuvenation effect, are inconsistent in literature. This suggests that there are contributions of one or several other (of second order importance) scenarios involved in the development of fatigue of the capacitors, depending on the structural behaviors of the investigated capacitor. Thus, a model with a single origin and mechanism of polarization fatigue is too simple to explain the fatigue in all types of ferroelectric capacitors.

d) Dominant origin(s) and therefore development mechanism(s) of fatigue in thin-film capacitors appears to arise mainly from the interfaces. Electron injection at capacitor interfaces seems to be a plausible model, which, however, needs to be experimentally verified further. First, the assumption of the presence of a low dielectric-constant layer at the metal/ferroelectric interface needs to be proven. Second, it is an open question whether the ferroelectric layer is structurally degraded, inhibiting of the nucleation of reverse domains, or that another mechanism is at play.

e) In previous studies on the dependence of the fatigue on capacitor electrode materials (metal versus oxide), the ferroelectric films often have different crystalline structures because they were grown on different template layers (bottom electrodes and/or substrates) and/or with different deposition techniques (sol-gel, sputtering, pulsed laser deposition). It is therefore hard to evaluate accurately the contribution of bulk versus interfacial origins of the observed fatigue. The investigation on the effect of the electrode (material) would be more conclusive if the investigated capacitors have the same bottom electrode and substrate, and only the top electrode is varied. However, even in that case the top interfaces can be different in multiple (interconnected) ways, such as the material composition, the electrode work function, the crystalline quality and structure of the interface, and the presence of different types of defects. One needs to design experiments that can better classify the effect(s) of each interfacial-related factor (or least number of factor) on fatigue behavior of the capacitor. One possible way is to engineer interfacial defects at capacitor interfaces by varying the fabrication techniques (for example *ex situ* versus *in situ* deposition) of the same top electrode material.

f) The traditional way to interpret the fatigue origins and mechanisms based

on the graphic profile of the remnant polarization as function of the field cycle number may lead to incorrect interpretations. As mentioned before, the fatigued capacitor can recover its polarization under field cycling. Therefore, the observed remnant polarization profile is sometimes due to the combined effects of fatigue and rejuvenation. One needs to experimentally differentiate these two effects in order to accurately determine the origin(s) and mechanism(s) of each of these effects.

g) To create breakthrough new understanding into origins and mechanisms of fatigue, direct investigation into the domain switching behaviors and interface structures of capacitors at different cycling states needs to be performed. Recently, new or improved techniques such as transmission electron microscopy have become more widely available, and have also been used to investigate on the nm-scale domain and lattice structures in (as-grown) ferroelectric devices [Ref [112] and the references cited therein]. Note that the interface structure investigations are particularly challenging if the investigated samples, such as sol-gel fabricated structures, have a large number of void defects and grain boundaries and rough interfaces. Such an investigation can be more straightforward in epitaxial thin-film structures with a dense microstructure and atomically sharp interfaces. Using the appropriate samples in combination with microscopy techniques will allow us to gain more insight into polarization fatigue.

Based on the discussion above, we choose to clarify the origin(s) and mechanism(s) of fatigue in PZT epitaxial thin-film capacitors. Working on epitaxial films allows us to ensure that the structure dependent behavior of the ferroelectric layer in different samples are the same and well-controlled, allowing a clean comparison between devices with different top electrodes and ferroelectric/electrode interface structures. In addition, it allows us to minimize the contributions of possible bulk-related origins to the observed fatigue of these capacitors. Moreover, the high crystalline quality of the epitaxial films allows us to obtain reliable characterizations of the structural changes in the capacitors at different cycling states, which may provide useful hints for understanding mechanisms behind the fatigue. Since the fatigue in thin-film devices seems to start from the interfaces, we will first focus on the relation between the capacitor interfaces and the fatigue behavior, as presented in Chapter 3.

2.7 Summary

Polarization fatigue in PZT capacitors has been extensively investigated for decades. A large body of data on different perspectives of the fatigue behavior has been reported as well and various models for the mechanism(s) have been suggested, providing a somewhat complicated and even confusing picture of the effect. From the literature data, we suspect that there must be multiple origins and mechanisms concurrently involved in the polarization fatigue of ferroelectric capacitors. The most dominant origins and mechanisms of fatigue in a particular capacitor are expected to be determined by the (interface and layer) structure of the capacitor. Particularly for thin-film capacitors, the fatigue is widely accepted to arise predominantly from the capacitor interfaces, but there is limited supporting evidence for this. Further investigation directly into the microstructure of the capacitor during field cycling is considered the most reliable way toward a more conclusive insight into the physics of polarization fatigue.

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Chapter 3

Origins of fatigue in $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ capacitors with Pt top-electrode*

Although polarization fatigue of ferroelectric thin-film capacitors is widely accepted as an interface-related effect, its origin(s) still remain unclear. In this chapter, we experimentally identify origin(s) of polarization fatigue by investigating the dependence of the fatigue behaviour on the interface structure of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) thin-film capacitors. The PZT layers are epitaxially grown on SrRuO_3 -buffered SrTiO_3 substrates by a pulsed laser deposition (PLD), and the capacitor top-electrodes are various, including SrRuO_3 (SRO) made by *in situ* PLD, Pt by *in situ* PLD (Pt-inPLD) and *ex situ* sputtering (Pt-sputtered). The fatigue behaviour was found to be directly related to the top-electrode/PZT interface structure. The Pt-sputtered/PZT/SRO capacitor has a thin defective layer at the top interface and shows early fatigue while the Pt-inPLD/PZT/SRO and SRO/PZT/SRO capacitor have clean top-interfaces and show much more fatigue resistance. The defective dielectric layer at the Pt-sputtered/PZT interface mainly contains carbon contaminants, which form during the capacitor *ex situ* fabrication. Removal of this defective layer significantly delays the fatigue onset. Our results clearly indicate that interfacial defective layer is the main origin of polarization fatigue in ferroelectric capacitors with conventional *ex situ* metal electrode.

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3.1 Introduction

The most common feature of polarization fatigue observed in ferroelectric thin-film capacitors is its dependence on the type of the electrode material. Capacitors with conductive oxide electrodes such as SrRuO_3 [1, 2], LaNiO_3 [3, 4], LaSrMnO_3 [5], IrO_2 [6], LaSrCaO_3 [7], $\text{YBa}_2\text{Cu}_3\text{O}_x$ [8, 9], and RuO_2 [10, 11] are generally free of fatigue for more than 10^{12} electric field cycles. In contrast, capacitors with metal electrodes such as Pt and Au are strongly fatigued after only 10^3 field cycles [3, 9]. This indicates that fatigue in thin-film ferroelectric capacitors is an interface-related effect. In other words, origin(s) of the fatigue in such devices mainly come from the capacitor interfaces.

To explain the strong fatigue in metal-electrode capacitors, Lou et al. [12] assumed that there is a thin layer with a low dielectric constant (compared to ferroelectric materials) at the metal-electrode/ferroelectric interface. This interfacial layer is suggested to induce the local depolarization field of the unscreened positive bound charges of nucleating reverse domains to an order of MV's/cm. This depolarization field then causes a significant electron injection from the metal electrode into the ferroelectric layer during each polarization switching under field cycling. The associated electron injection can thermally decompose the ferroelectric layer, subsequently leading to suppression of polarization switching [13–15]. The interfacial dielectric layer was believed not to be present at oxide-electrode/ferroelectric interfaces so such a capacitor is free of fatigue. Thus, the origin of polarization fatigue was theoretically modeled to be the low-dielectric defective layer at the metal/ferroelectric interface. However, this model needs to be experimentally verified. Detailed investigations into the relation between fatigue behaviour and interface structure of ferroelectric capacitors would provide some insights. To the best of our knowledge no such investigation has been reported. Note that these experimental objectives are particularly challenging for sol-gel fabricated structures, which contain voids, grain boundaries, and undefined interfaces. Such study is more straightforward in epitaxial thin-film capacitors with dense microstructures and atomically sharp interfaces.

In this chapter, we aim to experimentally identify the origin(s) of polarization fatigue in ferroelectric thin-film capacitors. To realize this objective, we investigated fatigue behaviour and interface structure of PZT epitaxial thin-film capacitors with different top electrodes, including SRO by PLD, Pt by *in situ* PLD

(Pt-inPLD), *ex situ* PLD (Pt-exPLD), and *ex situ* sputtering (Pt-sputtered). The Pt-sputtered/PZT/SRO and Pt-exPLD/PZT/SRO capacitor have a defective dielectric layer at their top interfaces and become rapidly fatigued under field cycling. The Pt-inPLD/PZT/SRO capacitor has a clean top interface without any defective layer and becomes fatigued much more later, at $10^7 - 10^8$ field cycles. The SRO/PZT/SRO capacitor has atomically sharp epitaxial interfaces and is free of fatigue. The defective dielectric layer at the Pt-sputtered/PZT (and Pt-exPLD/PZT) interface contains carbon contaminants, which arise from the exposure of the PZT surface to ambient atmosphere during the *ex situ* electrode fabrications. *In situ* removal of this defective layer significantly enhances fatigue resistance of the capacitor. Our results clearly indicate that interfacial dielectric defective layer is the major origin of polarization fatigue in ferroelectric capacitors with conventional *ex situ* sputtered metal electrodes.

3.2 Methods

3.2.1 Capacitor fabrications

Epitaxial ferroelectric PZT and bottom-electrode SRO layers were grown by a pulsed layer deposition (PLD) technique [16]. A 100-nm thick SrRuO_3 (SRO) layer was first grown on a TiO_2 -single-terminated SrTiO_3 (STO) (001)-oriented substrate [17]. Substrate temperature and deposition pressure of the SRO layer were 600°C and 0.13 mbar oxygen, respectively. A 250-nm thick $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) layer was subsequently grown on top of the SRO layer at 600°C and 0.10 mbar oxygen. The small lattice mismatch between SRO ($3.93\text{\AA}$) and PZT ($4.10\text{\AA}$) allows the PZT layer to grow epitaxially with only few misfit dislocations. After deposition, the films were cooled down to room temperature in a 1 bar oxygen atmosphere with a ramp rate of $8^\circ/\text{min}$. Various top electrodes were made on top of the PZT layer (Figure 3.1a).

For SRO/PZT/SRO capacitors, the SRO top layer was grown on top of the PZT layer by an *in situ* PLD with the same conditions as the SRO bottom layer. The SRO electrodes were then defined by photolithography combined with Ar ion etching (home-built system, NanoLab, MESA+).

For Pt-inPLD/PZT/SRO capacitors, the PZT/SRO stack was cooled down in the PLD chamber then a 100 nm thick Pt layer was deposited by PLD at room

temperature and a pressure of 0.1 mbar Ar. Subsequent photolithography and Ar ion etching were performed to define the Pt electrodes (Figure 3.1b).

For Pt-sputtered/PZT/SRO capacitors, the PZT/SRO stack was transferred from the PLD chamber to the cleanroom where a standard photolithography was used to make a photoresist pattern on top of the PZT surface. A Pt layer of 100 nm was then deposited on top of the structure by DC-magnetron sputtering at room temperature (home-built T'COathy sputter system, NanoLab, MESA+). The Pt electrodes were obtained by lifting off the photoresist (Figure 3.1c). For comparison, Au-sputtered/PZT/SRO capacitors with sputtered Au electrodes were also made by a similar procedure. Note that sputtered metal electrodes are commonly used in practical devices because of the simple and high throughput fabrication. They also have been used in studies on fatigue of ferroelectric capacitors (see Chapter 2).

For Pt-exPLD/PZT/SRO capacitors, the PZT/SRO stack was taken from the PLD chamber and exposed to ambient atmosphere for 2 hours. The stack was then placed in the PLD chamber again and the Pt layer was deposited by PLD at room temperature and a pressure of 0.1 mbar Ar. Photolithography and Ar ion etching were performed to define the Pt electrodes.

3.2.2 Sample characterizations

Ferroelectric properties were measured with an aixACCT TF-2000 Analyzer. Fatigue behaviour was investigated under bipolar rectangular electric field cycling (Figure 3.2). At fixed cycle number intervals, polarization hysteresis (P-E) loops of the capacitor were measured using a triangular electric field with 200 kV/cm amplitude and 1 kHz frequency. Capacitance-field (C-E) curves of the capacitors were measured with a slow scanning staircase DC bias combined with a low-field (2.6 kV/cm) AC modulation with a frequency of 10 kHz. In all electrical experiments, the capacitor bottom electrode was grounded.

Transmission electron microscopy (TEM) was performed to characterize interfaces between PZT layers and electrodes using the X-Ant-Em instrument at the University of Antwerp. Cross-sectional cuts on the samples along the [001] direction of the STO substrate were prepared by a FEI Helios 650 dual-beam focused ion beam device.

X-ray photoelectron spectroscopy (XPS) measurements were performed to

Figure 3.1: (a) Schematic side-view of top-electrode/PZT/SRO capacitors. Various top electrodes were used. Fabrication procedures of top electrodes by (b) Ar ion etching (c) and lift-off.

Figure 3.2: Profile of bipolar electric field cycling in fatigue measurements. The field amplitude E_{cy} (kV/cm) and cycling frequency f_{cy} (kHz) are variable. P-E loops were measured by using triangular field of 200 kV/cm and 1 kHz.).

characterize the surface of PZT layers. An Omicron XM-1000 monochromated Al-K α source was used with a pass energy to the detector of 20 eV. The angle

between the sample surface normal and the detector was 1° . The recorded core-level spectra of the elements were then analysed by decomposition into Gaussian peak components after subtraction of the background signal.

3.3 Results

3.3.1 Crystalline structure and morphology

Structure crystallization and surface morphology of the grown layers were characterized by X-ray diffraction (XRD) and atomic force microscopy (AFM), respectively (Figure 3.3). The XRD θ - 2θ scan shows that the PZT layer and SRO bottom electrode have been grown with a (001) out-of-plane orientation, following the orientation of the SrTiO_3 (STO) substrate. The rocking curve of the PZT (002) reflection has a small FWHM (0.14°), reflecting a high crystalline quality of the PZT layer. The reciprocal space map (RSM) around the PZT ($\bar{1}03$) reflection indicates epitaxial growths of PZT and SRO with a $\text{PZT}[100] \parallel \text{SRO}[100] \parallel \text{STO}[100]$ in-plane relationship. AFM images show that the SRO bottom electrode is atomically flat with unit-cell stepped terraces following the STO substrate surface, indicating a step-flow growth of the SRO layer. Step bunching appears on the PZT surface, indicating a layer-by-layer growth of the PZT layer.

Figure 3.3: (a) XRD θ - 2θ scan and rocking curve of PZT (002) reflection (inset). (b) Reciprocal space map around the PZT $(\bar{1}03)$ reflection (TE and BE represent for top and bottom electrode, respectively). (c-d) AFM images of the SRO bottom electrode and the PZT layer, respectively.

3.3.2 Ferroelectric behavior

Ferroelectric responses of the PZT capacitors with different top electrodes (SRO, Pt-inPLD, Pt-sputtered, and Pt-exPLD) were characterized by their hysteresis (P-E) loops and capacitance-field (C-E) loops (Figure 3.4). In general, all capacitors show square-shaped P-E loops, indicating well-developed ferroelectric behaviours. On the basis of the shape of the loops, one can divide the capacitors into two groups: (i) capacitors with SRO (S1) and Pt-inPLD (S2) top electrode, (ii) capacitors with Pt-sputtered (S3) and Pt-exPLD (S4) top electrode. There are

three main differences in the P-E loop between these two groups. First, the capacitors in group (i) show a lower (average) coercive field $E_C = (E_C^+ + E_C^-)/2$, (26.2 kV/cm for capacitor S1 and 31.2 kV/cm for capacitor S2) than those in the group (ii) (48.2 kV/cm for capacitor S3 and 48.0 kV/cm for capacitor S4). Second, the first group shows a maximum polarization $P_S = 52.8 \mu\text{C}/\text{cm}^2$, slightly higher than that of the second group $P_S = 48.5 \mu\text{C}/\text{cm}^2$ (all measured at 200 kV/cm). Third, the P-E loops of the second group are more slanted and rounded than those of the first group. We suspect that these different features are consequences of a presence of a non-ferroelectric layer at the interface of capacitor S3 (Pt-sputtered) and S4 (Pt-exPLD), which is absent in capacitor S1 (SRO) and S2 (Pt-inPLD).

The C-E curves of the capacitors are also sensitive to the top electrode. For capacitor S1 (SRO) and S2 (Pt-inPLD), the static capacitances at ± 200 kV/cm (where contribution from polarization switching are negligible) are almost similar, and determined by the intrinsic capacitance of the PZT layer only, $C_{PZT} \approx 100\text{pF}$. For capacitor S3 (Pt-sputtered) and S4 (Pt-exPLD), the static capacitances are lower, $C_{tot} \approx 85\text{pF}$. The capacitances of capacitor S3 and S4 can be attributed to the serial connection of the capacitance C_{PZT} of the PZT layer and capacitance C_{int} of the non-ferroelectric interfacial layer, $C_{int} = (\varepsilon_0 \varepsilon_{int} A)/d_{int}$, with ε_{int} and d_{int} are the relative dielectric constant and thickness of the interfacial layer, and A is the area of the capacitor (10^{-8}m^2). Hence, one can have

$$\frac{1}{C_{tot}} = \frac{1}{C_{PZT}} + \frac{1}{C_{int}} = \frac{1}{C_{PZT}} + \frac{d_{int}}{\varepsilon_{int} \varepsilon_0 A} \quad (3.1)$$

$$\frac{\varepsilon_{int}}{d_{int}} = \frac{1}{\varepsilon_0 A} \left(\frac{1}{C_{tot}} - \frac{1}{C_{PZT}} \right)^{-1} \approx 6.4(\text{nm}^{-1}) \quad (3.2)$$

The numerical result holds for the capacitor S3 and S4, which has the Pt-sputtered and Pt-exPLD top electrode, respectively. Thus, if one can observe the (non-ferroelectric) interfacial layer in these capacitors, one can estimate dielectric constant of this layer from Equation 3.2.

Figure 3.4: (a) P - E loops and (b) C - E curves of the PZT capacitors with different top electrodes. (c) Average coercive fields (E_C), maximum polarizations (P_S), and static capacitances (C) of the capacitors.

3.3.3 Fatigue behavior

Fatigue behaviour of the PZT capacitors under field cycling (with field amplitude of 200 kV/cm and cycling frequency of 1 kHz) is strongly dependent on the top electrode (Figure 3.5). Capacitor S1 with both SRO electrodes is free of fatigue for over at least 10^9 field cycles (further tests show that this type of capacitor is still non-fatigued up to 10^{12} cycles). Noted that capacitors with SRO top electrode made by in-situ PLD and ex-situ PLD show exactly similar ferroelectric and fatigue behaviours. Capacitor S2 with Pt-inPLD top electrode is free of fatigue up to 10^7 cycles, but beyond this number of cycles it slowly fatigues (about 80% polarization loss within about 10^8 cycles). We could not make capacitors with in-situ sputtered Pt (or Au) electrodes, but we believe that these capacitors show a similar fatigue as capacitor S2. Capacitor S3 (Pt-sputtered), S4

(Pt-exPLD), and S5 (Au-sputtered) show similar rapid fatigues with more than 80% polarization loss in about $10^3 - 10^4$ cycles. The free fatigue of capacitor S1 with both SRO electrodes and the strong, rapid fatigue of capacitor S3 (and S4, S5) with conventional sputtered Pt (or Au) electrodes are well consistent with a large body of data in literature [18]. The additional information provided in this study, which is to our knowledge not available in literature, is that capacitor S2 with an *in situ* fabricated metal electrode can be free of fatigue for $10^4 - 10^5$ times more cycles than those with an *ex situ* fabricated metal electrode.

Figure 3.5: Fatigue behaviours of the PZT capacitors with different top electrodes under bipolar field cycling. The field cycling is at 200 kV/cm and 100 kHz for capacitor S1 and S2, at 200 kV/cm and 1 kHz for capacitor S3, S4, and S5.

3.3.4 Electrode/PZT interface structures

To characterize the capacitor interface structures, we performed cross-sectional transmission electron microscopy (TEM) on the pristine (before field cycling) capacitor S1 (SRO/PZT/SRO), S2 (Pt-inPLD/PZT/SRO), and S3 (Pt-sputtered/PZT/SRO) (Figure 3.6). The PZT and SRO layers are of high crystalline quality, and the SRO/PZT interfaces are atomically sharp due to the epitaxial growth of these materials. Both the Pt-sputtered and the Pt-inPLD layer show clear (111) lattice planes, in accordance with XRD diffraction of these layers (not shown here). Most importantly, a clear defective layer is observed at the Pt-sputtered/PZT interface and not at the Pt-inPLD/PZT interface. This layer has a poor crystalline

structure with an average thickness of about 1.5 nm. In the Pt-sputtered/PZT sample, the Pt lattice planes start from the top surface of the defective layer, whereas in the Pt-inPLD/PZT sample, the Pt lattice planes start directly from the top PZT atomic layer. We did not characterize the Pt-exPLD/PZT and the Au-sputtered/PZT interface; however, since their fatigue behaviours are similar to that of the Pt-sputtered/PZT capacitor, we expect that these interfaces have a similar defective interfacial layer. For all samples, the PZT/SRO bottom interfaces are atomically sharp with presence of misfit dislocations at regular spacings (marked by arrows), caused the in-plane lattice mismatch between PZT and STO (note that the bottom SRO layer is fully strained to the STO substrate).

With $d_{int} = 1.5nm$ in equation (1), one finds $\varepsilon_{int} \approx 9.6$. This relative dielectric constant value of the interfacial layer is much smaller than the estimated value (from C_{PZT}) of PZT, $\varepsilon_{int} \approx 280$.

3.3.5 Compositions of the interfacial defective layer

As shown above, the fatigue behaviour and the top interface structure of capacitor S2 (Pt-inPLD/PZT/SRO) and capacitor S3 (Pt-sputtered/PZT/SRO) are significantly different. These differences originate from the fabrication procedure of these capacitors. In the capacitor S3, the PZT surface has been exposed to ambient atmosphere before the Pt layer is deposited by a sputtering. In contrast, in the capacitor S2, the PZT surface remains in vacuum before the Pt layer is deposited by an in-situ PLD. We conducted X-ray photoelectron spectroscopy (XPS) measurements to characterize differences in the elemental compositions of a fresh PZT surface remaining in the vacuum (simulating the fabrication of capacitor S2) and an air-exposed PZT surface (simulating the fabrication of the capacitor S3) (Figure 3.7). The survey spectra of the two PZT surfaces show clear characteristic peaks of Pb 4f, Zr 3d, Ti 2p, and O 1s core levels. Most importantly, we can observe a clear peak around 283.8 eV in the spectrum of the air-exposed PZT surface, and not in the spectrum of the fresh PZT surface. This peak corresponds to the C 1s edge, indicating that, when the PZT layer has been exposed to air, carbon contaminants will be present on its surface. As seen from the high-resolution spectra, the air-exposed PZT surface shows an additional shoulder on the left side of the O 1s main peak as compared to the one of the fresh PZT surface (Figure 3.7a inset at arrow). For the other elements, there are

Figure 3.6: TEM investigations on the interfaces of the capacitors with different top electrodes: (a) SRO/PZT, (b) Pt-sputtered/PZT, (c) Pt-inPLD/PZT top interface, and (d) PZT/SRO bottom interface. The Pt-sputtered/PZT interface has a defective layer, which is absent at the Pt-inPLD/PZT interface. The SRO/PZT and PZT/SRO interfaces are atomically sharp because of epitaxial growth. The arrows point to misfit dislocations.

no significant differences between the two samples. The O 1s spectrum of the fresh PZT surface was decomposed into two component peaks at 528.3 eV (O 1s-I) and 528.9 eV (O 1s-II), which are attributed to lattice oxygens and surface adsorbed oxygens, respectively [19, 20]. Apart from these two components, the O 1s spectrum of the air-exposed PZT surface shows an additional left-side shoulder peak at 530.3 eV (O 1s-III), which is attributed to carbon surface contaminants [19]. The C 1s spectrum was decomposed into three components at 283.8 (C 1s-I), 284.5 (C 1s-II), and 287.5 eV (C 1s-III), which are attributed to C-C, C-O, and C=O bonds, respectively [20].

We therefore conclude that a carbon contamination layer is present at the Pt-sputtered/PZT interface in capacitor S3, which was previously shown in the

Figure 3.7: XPS on the fresh and air-exposed PZT surface. (a) Survey spectra with all characteristic core levels (the inset shows high-resolution spectra of O 1s). (b) High-resolution spectra of O 1s and C 1s with component peaks.

TEM image as the non-crystalline defective layer. In contrast, there is no such contamination layer at the Pt-inPLD/PZT interface in the capacitor S2, which is also consistent with the TEM data. The defective layer at the Pt-sputtered/PZT interface consists of carbon contaminants, which have relative dielectric constant values of the order of 10 or less, which is consistent with the value $\epsilon_{int} \approx 9.6$ estimated from the C-E measurements above.

3.3.6 Removal of the interfacial defective layer

The better fatigue resistance of capacitor S2 (Pt-inPLD/PZT/SRO) as compared to capacitor S3 (Pt-sputtered/PZT/SRO), S4 (Pt-exPLD/PZT/SRO), and S5 (Au-sputtered/PZT/SRO) indicates that a clean PZT top surface, which is in

contact with the top electrode, is crucial to the fatigue behaviour of the capacitor. To further prove this argument, we tested fatigue behaviour of capacitors in which the air-exposed PZT surfaces were *in situ* cleaned before deposition of metal top electrodes. In one sample, an *in situ* O₂ plasma was applied to the exposed PZT surface before sputtering an Pt top electrode, named as capacitor S6. In another sample, the air-exposed PZT/SRO stack was annealed at 400°C for 30 minutes in O₂ atmosphere in the PLD chamber before deposition of the Pt top electrode by PLD, named as capacitor S7. Ferroelectric and fatigue behaviour of these capacitors are shown in Figure 3.8. The capacitors at the pristine state show a good ferroelectric response, as indicated by their square-shaped P-E loops. Noted that the capacitor S6 (O₂ plasma) shows a larger coercive field than the other capacitors, indicating that ferroelectric behaviour is sensitive to the PZT surface treatment. The capacitors with treated PZT surfaces show higher capacitances than capacitor S3 (Pt-sputtered/PZT/SRO) and they are closed to capacitor S1 (SRO/PZT/SRO). More importantly, the capacitors show a fatigue resistance similarly to that of capacitor S2 (Pt-inPLD), no significant polarization loss is observed until 10⁷ cycles. These data indicate that the O₂ plasma and oxygen annealing can remove the carbon contamination layer on the air-exposed PZT surface [21], leading to a clean Pt/PZT interfaces. This also explains why both SRO top-electrodes by *in situ* and *ex situ* PLD (not shown here), which were grown at 600°C, provide exactly similar behaviours. These data indicate again that the interface between the electrode and ferroelectric layer is crucial to fatigue resistance of the device.

Figure 3.8: (a) P - E loops, (b) C - E curves, and (c) fatigue behaviours of the capacitors with the (air-exposed) PZT surface treated by O_2 plasma and annealing.

3.4 Discussion

We have shown that the top-electrode/PZT interface directly determines the fatigue behaviour of the PZT capacitor (Table 3.1). A defective, low dielectric constant layer at the Pt-sputtered/PZT (Au-sputtered/PZT and Pt-exPLD/PZT) interface makes a such capacitor strongly fatigued upon only $10^2 - 10^3$ field cycles. The Pt-inPLD/PZT interface is clean without defective layer, consequently this capacitor is fatigue resistant until 10^7 field cycles, which is a factor $10^4 - 10^5$ times longer than the capacitors with ex-situ metal electrodes. In the ideal case

of SRO/PZT/SRO capacitor, the atomically sharp SRO/PZT interfaces due to epitaxial growth make the capacitor perfectly free of fatigue for over 10^9 field cycles. The strong dependence of fatigue behaviour of our PZT capacitors on the interface structure directly confirms that polarization fatigue is an interface-related effect [18].

Sample	TE	Deposition	PZT-surface treatment	Top-interface structure	Fatigue onset (cycles)
S1	SRO	In-situ PLD	No	Epitaxial	$\gg 10^9$
S2	Pt	In-situ PLD	No	Clean	$10^7 - 10^8$
S3	Pt	Ex-situ sputter	No	Defective layer	$10^2 - 10^3$
S4	Pt	Ex-situ PLD	No	Defective layer	$10^2 - 10^3$
S5	Au	Ex-situ sputter	No	Defective layer	$10^2 - 10^3$
S6	Pt	Ex-situ sputter	O ₂ plasma	Clean (expected)	$10^7 - 10^8$
S7	Pt	Ex-situ PLD	Annealing	Clean (expected)	$10^7 - 10^8$

Table 3.1: Investigated PZT capacitors with various top electrodes and their fatigue behaviours

Our data experimentally support the theoretical model of Lou *et al.* [12], which proposed that a thin dielectric layer presents at metal-electrode/ferroelectrics interfaces and that this interfacial layer is the primary cause of polarization fatigue in the capacitor. It is challenging to observe such a thin layer in a frame of crystalline nano-grains and corrugated interfaces in sol-gel fabricated samples. Here, by working on the PZT epitaxially grown layers, we can directly observe a defective layer of 1.5 nm at the Pt-sputtered/PZT/SRO interface. We also determined that the defective interfacial layer consists of carbon contaminants, which have an average dielectric constant $\varepsilon_i \approx 9.6$, much lower than that of bulk PZT ($\varepsilon_{PZT} \approx 280$). Without this defective layer, the capacitor will exhibit much more fatigue resistance, as observed in the Pt-inPLD/PZT/SRO and SRO/PZT/SRO capacitors.

How does the interfacial defective layer accelerate fatigue behavior?

At the Pt-sputtered/PZT interface, a net local transient depolarization field E_{bc} produced by the positive bound charges ($\delta = P_{PZT} \approx 0.4C/m^2$) in the reverse domains can be estimated through Lou's model [12].

$$E_{bc/Pt-sp} \approx \frac{\sigma}{\varepsilon_i \varepsilon_0} \approx \frac{P_{PZT}}{\varepsilon_i \varepsilon_0} \quad (3.3)$$

With the presence of a dielectric layer with $\varepsilon_i \approx 9.6$, one gets an extremely large depolarization field at the Pt-sputtered/PZT interface, $E_{bc/Pt-sp} \approx 50 \text{ MV/cm}$. At the SRO/PZT interface without a dielectric layer, replaced ε_i by $\varepsilon_{PZT} \approx 280$, the depolarization field then $E_{bc/SRO} \approx 1.2 \text{ MV/cm}$, much lower than the former case. The depolarization field can accelerate injection of electrons at the interface following Fowler-Nordheim tunneling mechanism

$$J = \frac{e^3 E_{bc}^2}{8\pi\hbar\varphi_B} \exp\left(\frac{8\pi(2m^*)^{1/2}}{3eh} \frac{(e\varphi_B)^{3/2}}{E_{bc}}\right) \quad (3.4)$$

With φ_B and m^* are the barrier height and electron effective mass at the interface, respectively. Assuming that these parameters are the same for the Pt-sputtered/PZT and SRO/PZT interface and considering that $e\varphi_B = 1 \text{ eV}$ and $m^* = m_e$, the free electron mass, then one obtains $J_{Pt-sp}/J_{SRO} \approx 10^{20}$. Thus, electron injection at the defective Pt-sputtered/PZT interface is significantly larger than that at the epitaxial SRO/PZT interface.

How do the injected electrons involve into the polarization fatigue of Pt-sputtered/PZT/SRO capacitors? Lou *et al.* [12] proposed that the injected electrons can thermally decompose the ferroelectric structure nearby the interfaces, reducing domain nucleation sites and consequently leading to the polarization switching loss. This mechanism likely happens in sol-gel PZT capacitors [13], ceramic structures [22, 23], and organic layers [24] as the presence of structure degradation was observed in the fatigued devices. However, we did not observe any structure degradation in the cycled Pt-sputtered/PZT/SRO capacitors. Also note that the fatigue onset in our Pt-sputtered/PZT/SRO capacitor is $10^3 - 10^4$ cycles, several orders smaller than the field cycles over the fatigued capacitor in Lou's work [13]. Therefore, although our data support the model of electron injection at the metal/ferroelectric interface, we currently cannot draw a definitive conclusion on the subsequent mechanism of the fatigue. Together with structure degradation induced by the charge injection (if it happens), we suspect that injected electrons may be trapped at the defective Pt-sputtered/PZT interface, which then inhibit the polarization domain switching of the PZT layer [25–27]. Further investigations into characteristics of the fatigue (its dependence on field

cycling conditions) and the interface structure of the cycled capacitor need to be performed [28]. These are presented later in chapter 4.

As shown above, *in-situ* fabrications of metal electrodes (by PLD or sputtering) and *in situ* cleanings of the ferroelectric surface (by O₂ plasma or annealing) improve the quality of the capacitor interfaces and consequently enhance the fatigue resistance of the capacitor. However, these capacitors are still much less fatigue resistant than capacitors with both SRO electrodes. This can be understood by some possible reasons. First, the deposition of metal electrodes by either sputtering or PLD may cause some modifications on the top atomic layers of the ferroelectric surface. By *in situ* XPS measurements, McIntyre and co-workers [29, 30] reported on the formation of metallic Pb on PbTiO₃ surfaces during the deposition of sputtered Pt. Similar observations were also reported by Chen *et al.* [31, 32]. The decomposition of Pb²⁺ into Pb⁰ metal was explained due to the heat of the Pt atom condensation on the PZT surface. Therefore, the metal/ferroelectric interfaces always contain lattice defects and elemental vacancies, which can subsequently contribute to polarization fatigue of the capacitor. Second, we conjecture that the chemical bonding between the ferroelectric layer and the electrode is crucial to the fatigue resistance of the capacitor. Indeed, a strong chemical bonding is formed in the continuous oxygen lattice across oxide-electrode/ferroelectric interfaces, which is contrast with a weak bonding at metal/ferroelectric interfaces. A strong chemical bonding not only enhances the adhesion between the layers, but also reduces the number of lattice defects at the interface, both lately might help to reduce the fatigue. Detailed mechanisms of fatigue in the Pt-inPLD/PZT/SRO capacitor are discussed in chapter 5.

Practically, this work provides a way to improve fatigue resistance of metal-electrode ferroelectric capacitors, by using *in situ* fabricated metal electrodes (or *ex situ* electrodes but accompanied with a prior ferroelectric-surface cleaning). Metal such as Pt and Au are still the most common electrodes in technical devices because of their high conductivity and chemical inertness. Moreover, metal electrodes provide better mechanical contacts with metal wiring. Therefore, although the fatigue resistance of these devices (10⁷ cycles) is less than that of the devices with SRO (or other conductive oxides) electrodes (at least 10⁹ cycles), the results are very promising for applications.

3.5 Conclusion

We have experimentally investigated fatigue behaviour and interface structure of PZT thin-film capacitors with various top electrodes. Our data showed that a defective dielectric layer at the metal/ferroelectric interface is the major origin of polarization fatigue in ferroelectric capacitors. This finding directly supports the charge injection model, which suggests that electron injection is significantly induced at the defective interface, giving rise to fatigue of the capacitor. Fatigue resistance of ferroelectric capacitors will be enhanced if the electrode/ferroelectric interface is clean without defective layer. In practice, *in situ* processing of metal electrodes and/or *in situ* cleaning of ferroelectric-layer surface before electrode deposition can be employed to improve the interface purity, which subsequently enhances the fatigue resistance of metal-electrode ferroelectric devices.

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Chapter 4

Mechanisms of fatigue in $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ capacitors with *ex situ* Pt top-electrodes

Interfacial defective layer was previously shown as the major origin of polarization fatigue in capacitors with *ex situ* metal electrodes. However, detail mechanisms of the fatigue in such devices still remain unclear. In this chapter, we aim to identify the mechanism(s) of how these devices, for example Pt-sputtered/ $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ /SrRuO₃ capacitors, become rapidly fatigued. First, we electrically cycled the capacitor under different cycling conditions and found that the fatigue is practically independent of the cycling conditions. Second, we ferroelectrically characterized the fatigued capacitors and observed that they can switch the polarization again if the external field is sufficiently high, but the switching is asymmetric for the two polarization directions. Third, we structurally characterized the capacitor interfaces and observed that their microstructures are unchanged after field cycling. Based on these findings, we propose that electrons are injected and trapped at the metal/PZT defective interface during field cycling, subsequently inhibit domain nucleation at this interface, leading to the observed polarization fatigue.

4.1 Introduction

Previously in chapter 3, we have experimentally shown that the group of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) capacitors with *ex situ* fabricated metal top electrodes becomes fatigued a much earlier compared to the group of capacitors with SrRuO_3 (SRO) or *in situ* fabricated metal top electrodes. The main difference in the capacitor structure between these two groups is the defective layer mainly of carbon contaminants at the *ex situ* metal/PZT interface and not at the *in situ* metal/PZT and SRO/PZT interface. *In situ* removals of this interfacial defective layer can significantly enhance the fatigue resistance of the capacitor. These findings lead to a conclusion that the interfacial defective layer is the main origin of the early, strong fatigue in ferroelectric capacitors with conventional *ex situ* metal electrodes.

A subsequent question can be posed: how does the interfacial defective layer cause polarization fatigue? According to Lou et al. [1], a low dielectric-constant layer at metal/ferroelectrics interfaces can significantly induce a local depolarization field produced by positive bound charges upon nucleating reverse domains to an extremely high value. This high local field then causes a strong injection of electrons from the metal electrode through the interfacial layer into the ferroelectric layer. During field cycling, the current of injected electrons can thermally decompose the surrounding ferroelectric lattice, leading to damaged, non-functional areas in the structure [2]. The damaged areas then reduce the number of nucleation sites for reverse domains, consequently suppressing the polarization switching, leading to the polarization fatigue. In short, the proposed mechanism for fatigue is the sequence of (1) injection of electrons, (2) thermal degradation of ferroelectric lattice and (3) reduction of domain nucleation sites [2–4]. However, experimental evidence is needed to verify these scenarios. It is challenging to directly observe the injection of electrons into the ferroelectric layer during field cycling. However, based on the characteristic dependence of the resulting fatigue on the field cycling conditions, we can infer whether or not electron injection is involved in the development of fatigue behaviour. Furthermore, it is still an open question whether the ferroelectric layer is structurally degraded by the current of injected electrons, reducing the available nucleation sites for reverse domains, or that another mechanism could be at play. More detailed characterizations on the ferroelectric behaviour and interface structure of fatigued

capacitors at different cycling states would provide some important clues to answer this question.

In this chapter, we aim to identify the mechanism(s) of how the Pt-sputtered/PZT/SRO capacitors (with Pt top electrodes made by *ex situ* sputtering) become early fatigued under field cycling. First, we observed that the polarization fatigue of the capacitor is practically independent of the field cycling conditions, suggesting that electron injection playing an initial role in the fatigue mechanism of the capacitor. Second, we found that fatigued capacitors becomes switchable again under sufficiently high external field, but the switching is asymmetric between the two polarization directions. The polarization switching initiating from the Pt-sputtered/PZT top interface was severely hindered after field cycling while the switching initiating from the PZT/SRO bottom interface was almost unaffected. However, we observed that both capacitor interfaces stay structurally unmodified under field cycling, indicating that there is no degradation of the PZT lattice in our devices. Guided by these findings, we propose that injected electrons are trapped in the defective layer at the Pt-sputtered/PZT interface, subsequently inhibit the nucleation of domains at this interface, leading to the polarization fatigue in the device.

4.2 Methods

4.2.1 Capacitor fabrications

Pt-sputtered/PbZr_{0.52}Ti_{0.48}O₃/SrRuO₃ capacitors (Pt-sputtered/PZT/SRO) grown on (001)-oriented SrTiO₃ (STO) substrates were chosen as the benchmark for investigation.

A standard fabrication process of the Pt-sputtered/PZT/SRO capacitor has following steps: First, the PZT layer was grown on an SRO-buffered STO substrate by pulsed layer deposition (in home-built system, NanoLab, MESA+). More details on the growth conditions and sample features can be found in Chapter 3 (Method section). Second, the PZT/SRO/STO stack was transferred from the PLD chamber to a cleanroom for patterning a photoresist (OPD 6242) structure on top of the PZT surface. Next, a Pt layer was deposited on top of the structure by DC-magnetron sputtering at room temperature (home-built T'COathy sputter system, NanoLab, MESA+). Finally, the Pt electrodes were obtained by lifting

off the photoresist residuals.

4.2.2 Sample characterizations

Ferroelectric behaviour of the capacitors was measured using the aixACCT TF-2000 tool. The fatigue behaviour was investigated under various field cycling parameters, including field profiles (bipolar and unipolar), field amplitudes, pulse durations, and cycling frequencies. Polarization hysteresis (P-E) loops of the capacitors were measured using a bipolar triangular field with a frequency of 1 kHz and a field amplitude chosen depending on the measurement purposes. Capacitance-field (C-E) curves of the capacitors were measured with a slow scanning staircase DC bias combined with a low-field (2.6 kV/cm) AC modulation with a frequency of 10 kHz. In all electrical measurements, the capacitor bottom-electrode is always grounded.

Piezoresponse force microscopy (PFM) mode was used to characterize the domain switching of the PZT film, using Cr/Pt coated tips with spring constant of 42 N/m (Nanosensors). For the writing mode, an AC modulation at 1.5 V and 35 kHz was applied to the tip. For the reading mode, the DC bias was applied to the SRO bottom electrode during the scanning of the tip.

Transmission electron microscopy (TEM) was performed to characterize the interfaces of the capacitors, using the X-Ant-Em instrument at the University of Antwerp. Cross-sectional cuts on the samples along the [001] direction of the STO substrate were prepared by a FEI Helios 650 dual-beam focused ion beam device.

4.3 Results

4.3.1 Ferroelectric behavior

We tested the ferroelectric behavior of the Pt-sputtered/PZT/SRO capacitors by measuring their P-E loops with a bipolar triangular AC field at a fixed frequency of 1 kHz and at various field amplitudes (Figure 4.1). The field frequency of 1 kHz ensures that the field duration (10^{-3} second) is sufficiently longer than the characteristic switching time (order of 10^{-6} - 10^{-4} second) of thin-film PZT domains [5]. For fields above 120 kV/cm, the P-E loops have a square

shape with the saturated polarization value, indicating a complete polarization switching. For fields less than 120 kV/cm, the P-E loops have a rounded-end shape with unsaturated polarization, indicating an incomplete polarization switching. Therefore, to evaluate accurately the fatigue behavior of the capacitor under field cycling, the P-E loop of the capacitor at different cycling states need to be measured with a maximum field above 120 kV/cm (and at 1 kHz).

Figure 4.1: The P-E loops of the pristine Pt-sputtered/PZT/SRO capacitor measured with a triangular AC field at a frequency of 1 kHz, but with different field amplitudes.

4.3.2 Fatigue-profile dependence on P-E loop measurements

We fatigued two identical capacitors (named as capacitor 1 and capacitor 2) using the same bipolar, square-pulse field cycling of 160 kV/cm and 1 kHz. For capacitor 1, the P-E loops at different cycling states were measured with a triangular field of 200 kV/cm and for capacitor 2, the P-E loops were measured with a triangular field of 600 kV/cm (Figure 4.2a). The resulting profiles of remnant polarizations of these two capacitors as functions of field cycle number are significantly different (Figure 4.2b). Capacitor 1 (P-E loops measured at 200 kV/cm) loses its remnant polarization rapidly by an amount of 80% of the initial polarization after 10^4 cycles. This is consistent with a strong fatigue behavior commonly observed in metal-electrode capacitors [6]. One can clearly identify three stages in the fatigue profile of this capacitor: (i) an initial fatiguing stage

with little polarization loss under 10^3 cycles, (ii) a intermediate fatiguing stage with strong polarization loss under $10^3 - 10^4$ cycles, and (iii) a final completely fatiguing stage after more than 10^4 cycles. Differently from capacitor 1, capacitor 2 (P-E loops measured at 600 kV/cm) loses its remnant polarization slowly by only 20% after 10^6 cycles. Note that the two investigated capacitors, which are from the same wafer, have an identical crystal structure. We therefore concluded that the remnant polarization profile under field cycling, which is commonly used to evaluate the fatigue behavior of ferroelectric capacitors, is strongly dependent on which conditions one measures the P-E loops of the cycled capacitors. To the best of our knowledge, this has not been discussed in literature.

Figure 4.2: (a) Field cycling profiles of two identical capacitors fatigued with the same bipolar field cycling of 160 kV/cm and 1 kHz. The P-E loops were measured with a maximum field of 200 kV/cm for the first capacitor and 600 kV/cm for the second capacitor. (b) The fatigue profiles of the two capacitors.

4.3.3 Domain switching of fatigued capacitors

The P-E and I-E loops of the two capacitors at different cycling states presented above (Figure 4.2) will provide more insight into the switching behavior of the fatigued PZT layer. For capacitor 1, the P-E loops (measured at 200 kV/cm) become suppressed and slanted, corresponding to the depression of the switching

peaks in the I-E loops, with increasing field cycle number (Figure 4.3a,b). These data lead to a common conclusion that the polarization of cycled (fatigued) ferroelectric capacitors becomes non-switchable. However, for capacitor 2, the P-E loops and I-E loops (measured at 600 kV/cm) show that the polarization of the cycled capacitors is still largely switchable (Figure 4.3c-e) and that the polarization switching of the cycled capacitors is asymmetric for under negative and positive field:

(1) Under the negative field (when the applied field directs towards the Pt top electrode), the polarization switches from the downward state (P_{down}) into the upward state (P_{up}). In fatigued capacitors, this process happens at one specific applied field (or within a narrow range of field) as shown by the steep P-E loop at E_C^- and the sharp peak in the I-E loops (Figure 4.3c,d). The switching field for the fatigued capacitors (at around -110 kV/cm) is higher in magnitude than that for the pristine capacitor (at around -70 kV/cm), but practically unchanged with increasing field cycle number from 3×10^3 cycles to 10^6 cycles.

(2) In contrast, under the positive field (when the applied field directs towards the SRO bottom electrode), the polarization switches from the upward state (P_{up}) into the downward state (P_{down}). In fatigued capacitors, this process happens over a wide range of applied fields, as indicated by the slanting P-E loop at E_C^+ and the broad peak extending from +50 to +600 kV/cm in the I-E loops (Figure 4.3c-e). The switching peak in the pristine capacitor (the black curve), which is sharply at +50 kV/cm, becomes more depressed in the fatigued capacitor with increasing field cycle. Concurrently, additional switching peaks appear at higher field position (as marked by the arrows).

The polarization switching from the upward state into the downward state starts by the nucleation of downward-oriented domains at the top interface. In the opposite case, the polarization switching starts by nucleation of upward-oriented domains at the bottom interface. Therefore, it is qualitatively concluded that the energy required for domain nucleation at the top interface significantly increases and becomes inhomogeneous after field cycling. On the other side, the domain nucleation energy at the bottom interface just slightly increases and still homogeneous after field cycling.

Capacitor 1

Capacitor 2

Figure 4.3: (a-b) P - E and I - E loops of capacitor 1 at different cycling states, measured up to $\pm 200 \text{ kV}/\text{cm}$. (c-d) P - E and I - E loops of capacitor 2 at different cycling states, measured up to $\pm 600 \text{ kV}/\text{cm}$ (c-e). (e) is a zoom on the positive-field switching currents of capacitor 2. The arrows mark the additional switching peaks in the cycled capacitors.

To further characterize the polarization switching in the fatigued PZT layer, we performed piezoelectric force microscopy (PFM) on the PZT layer which had undergone 10^6 field cycles in a similar treatment as for capacitor 1. To get a high lateral resolution, the Pt top electrode of the fatigued capacitor was removed with a high adhesion tape so that the PFM tip can contact directly the PZT surface. Scanning was performed on the areas nearby the edge and the center of the capacitor (Figure 4.4). First, the tip was run in an AC reading mode to detect the domain states of the unfatigued and fatigued PZT layer (the outer areas in the images). It is seen that the unfatigued PZT shows two different polarized domain states while the fatigued PZT shows only one polarized domain state (see the phase images). Next, we performed writing modes to electrically polarize the PZT areas by applying a DC bias of respectively +5V (for upward poling) and -5V (for downward poling) to the SRO bottom electrode during the scanning of the tip. The domain states of the written areas were then determined by the AC reading mode, marked by outward arrows (dark contrast = upward poling = P_{up}) and inward arrows (bright contrast = downward poling = P_{down}). From the write/read data, several observations are made. First, the fatigued PZT appears with mainly downward polarized domains (P_{down}). Second, some domains in the fatigued PZT are switchable and some are non-switchable (frozen) under the writing bias. These data are consistent with previously reported PFM data for fatigued Pt/PZT/Pt sol-gel layers, which also show the presence of frozen domains [7–9].

Figure 4.4: PFM investigation on pristine and fatigued PZT areas: topology, phase, and amplitude signal of the scanning areas. The left panels are signals from the edge and the right the center of the capacitor. The outward and inward arrows respectively represent for two polarized domain states, P_{up} and P_{down} .

4.3.4 Capacitance behavior

The capacitance - field (C-E) loop of the fatigued capacitor (capacitor 1) is significantly different from that of the pristine capacitor (Figure 4.5). The C-E loop of the pristine capacitor has a butterfly shape – a characteristic behavior of ferroelectric devices. The C-E loop of the fatigued capacitor is strongly asymmetric along the field axis. Under the negative field, the C-E curve shows a butterfly-like behavior with a clear peak as a consequence of a polarization switching. However, under the positive field, the C-E curve shows a broaden shoulder over a wide

range of fields. This is in agreement with the observation from the P-E loop that the polarization switching under positive field (field directs towards the SRO bottom electrode) takes place over a wide range of fields. Therefore, based on the C-E data, it is concluded again that the polarization switching of the fatigued capacitor is asymmetric between the two polarization directions. Moreover, one can see that the static capacitance of the capacitor at $+200 \text{ kV/cm}$ is unchanged after field cycling, but the capacitance at -200 kV/cm and at zero-field is slightly increased after field cycling.

Figure 4.5: *C-E loops of the pristine and fatigued Pt-sputtered/PZT/SRO capacitor.*

Our findings on the change of the capacitance after field-cycling are different from previous reports [10, 11], which observed that fatigued Pt/PZT/Pt capacitors show smaller capacitances than the pristine one. The decrease of capacitance by field cycling was attributed to the structure changes of the Pt/PZT interfaces during field cycling, forming a low permittivity layer in the fatigued capacitor. Our data indicate that there might be another scenario happening in the investigated Pt-sputtered/PZT/SRO capacitor during field cycling rather than structure changes at the capacitor interfaces.

4.3.5 Fatigue dependence on field cycling conditions

To characterize the role of field cycling on the polarization fatigue, we fatigued the Pt-sputtered/PZT/SRO capacitors under field cycling with different field amplitudes, cycling frequencies, operating temperatures, and unipolar cycling

modes. In these measurements, the P-E loop of the capacitors at different cycling states were measured with a triangular field of 200 kV/cm (and frequency of 1 kHz) so that the eventual fatigue effect caused by the square field cycling is clearly observed. The fatigue profile strongly depends on the field cycling amplitude (at the cycling frequency fixed at 1 kHz) (Figure 4.6a). In the range below 120 kV/cm, the higher field causes more fatigue than the lower field. In the range from 120 to 160 kV/cm, the fatigue is practically independent of the field amplitude. In the range above 200 kV/cm, the variation of the polarization as a function of field cycles becomes complicated. The polarization first decreases, showing a fatigue effect, but then increases under further cycling, showing the so-called rejuvenation effect [12]. The onset of the rejuvenation stage depends on the field amplitude; a higher field leads to an earlier rejuvenation. More details on the rejuvenation stage and what happens to the capacitor under further prolonged field cycling will be discussed in chapter 6. In the following sections, we focus on the fatigue behavior of the capacitor, i.e. with the field cycling amplitude in a range from 120 to 200 kV/cm. When the field amplitude was fixed at 160 kV/cm (which is sufficient for complete polarization switching in the pristine PZT), the fatigue profile is almost independent of the cycling frequency and only depends on the number of field cycles (Figure 4.6b). In the range from 25 to 140°C, the fatigue is also nearly independent of operating temperature (Figure 4.6c). In these measurements, the capacitor was first heated to a specific temperature and then the field cycling was applied. The P-E loops were also measured at the same set temperature. However, one can also see that, at the high temperatures, the polarization of the fatigued capacitor starts increasing again, indicating that the rejuvenation effect is a temperature-dependent process (which will be further discussed in chapter 6).

In contrast to the strong fatigue under bipolar field cycling, the fatigue under unipolar field cycling is relatively little (Figure 4.6d). This well agrees with previous studies, which reported little unipolar fatigue as compared to strong bipolar fatigue in PZT sol-gel films and PZT ceramics [13–16]. The results suggest that the strong bipolar fatigue behavior is directly related to the switching of the polarization domains, which only happens under bipolar field cycles. In other words, the mechanism(s) involved in the strong bipolar fatigue is initiated by the domain switching.

Figure 4.6: *Fatigue behavior of the Pt-sputtered/PZT/SRO capacitor under bipolar field cycling with different field amplitudes (a), cycling frequencies (b), and operating temperatures (c). (d) Fatigue behavior under unipolar field cycling.*

4.3.6 Interface structure during field cycling

To gain further insight into the fatigue mechanism, the microstructure of the capacitor before cycling (pristine state), after middle fatigue (2×10^3 cycles), and after complete fatigue (10^6 cycles) were characterized by TEM (Figure 4.7). The field cycling was performed with an amplitude of 160 kV/cm and a cycling of 1 kHz. The PZT lattice structure is visible with a high-resolution. The Pt structure is not resolved due to an intentional contrast enhancement to visualize the PZT structure. Most important, one can observe an interfacial layer between the Pt and PZT layer in the pristine capacitor (Figure 4.7a). This layer appears to be non-structured with an estimated thickness of about 1.5 nm. More details on the nature of this defective layer can be found in chapter 3. The middle fatigued and fully fatigued capacitor also show clearly

an interfacial layer between Pt and PZT (Figure 4.7b,c). It is clear that the interfacial defective layer is microstructurally unchanged during field cycling. No structure modification/degradation was observed in the PZT structure nearby the interface in the fatigued samples. Figure 4.7d shows the PZT/SRO bottom interface of the fully fatigued capacitor, which is also the same to the pristine bottom interface (not shown here). The PZT grows epitaxially (cube-on-cube) on top of the SRO layer with misfit dislocations due to the in-plane lattice mismatch between these two materials ($a_{PZT} \approx 4.10\text{\AA}$, $a_{SRO-strained} = a_{STO} \approx 3.95\text{\AA}$).

Figure 4.7: *STEM investigation on the capacitor interfaces at different fatigued states. (a) pristine Pt-sputtered/PZT interface, (b) middle fatigued Pt-sputtered/PZT interface, (c) fully fatigued Pt-sputtered/PZT interface, and (d) fully fatigued PZT/SRO bottom interface. The while-line circles in (d) address misfit dislocations.*

Our microstructure findings are different from the findings in previous studies [2, 17, 18]. By scanning electron microscopy, Lou *et al.* [2] observed degradation in

Pt electrodes of fatigued PZT sol-gel films. Also by scanning electron microscopy, Balke *et al.* [17] found a molten layer at the PZT/electrode interface in the cycled PZT ceramic capacitors. In a recent study, using time-of-flight mass spectrometry, levlev *et al.* [18] observed that Cu electrode ions diffuse into the PZT lattice of the fatigued PZT epitaxial thin-film. These differences suggest that, depending on the details regarding the fabrication of the devices, i.e. crystallization of the ferroelectric layer (ceramics vs sol-gel polycrystalline layers vs epitaxial single-crystalline layers), the type of electrode material and its fabrication, the capacitors will response to field cycling in different ways. As a consequence, the resulting fatigue behavior in the capacitors fabricated in different ways, might be governed by different dominant mechanisms.

4.4 Discussion

Previously in chapter 4, we have shown that the defective layer at the Pt-sputtered/PZT interface has a relative dielectric constant $\varepsilon_i \approx 9.2$. This finding directly supports the proposition of Lou *et al.* [1] that there is a significant injection of electrons at the defective metal/PZT interfaces during field cycling. If we assume that the electron injection is the initial step in the mechanism for fatigue, logically one would expect the following fatigue related effects: (1) The large transient local depolarization field $E_{bc/i}$, which control the injection of electrons, is present only if reverse domain nucleation occurs at the interface. This happens only under bipolar cycling. Therefore, electron injection and the subsequent fatigue happen significantly only under bipolar field cycling and not under unipolar cycling. (2) The cycling field amplitude E_{cy} (in order of kV/cm) is orders of magnitude lower than the depolarization field $E_{bc/i}$ (of the MV/cm) [1]. Hence, the cycling field parameters (field amplitude and cycling frequency) would not affect the charge injection. The only role of the bipolar field cycles is to switch the polarization in the film, creating the reverse domains with unscreened bound charges nearby the Pt/PZT interface. The fatigue as a consequence of charge injection will be therefore only determined by the number of polarization reversals, i.e. the number of field cycles, as long as the cycling field amplitude is sufficiently high to allow for the nucleation of domain reversal. (3) Assuming that Fowler-Nordheim tunneling can describe the charge injection [1], tunneling probability of the electrons is negligibly affected by temperature. The operating temperature

therefore also would not strongly affect the injection of electrons and the resulting fatigue behavior. We clearly observe that these deduced characteristics of fatigue as a consequence of electron injection are consistent with our experimental observations presented above. Therefore, we qualitatively conclude that electron injection at the Pt-sputtered/PZT interface is the initial step (scenario) in the mechanism for polarization fatigue of the capacitor.

However, the subsequent mechanism(s) behind the polarization switching suppression in cycled capacitors still need to be discussed. Based on the asymmetric polarization switching and the unchanged microstructure of the cycled capacitor, we propose that the injected electrons during every field cycle might be trapped in the interfacial defective layer. Generally speaking, the trapped charges can change the interfacial energy of the Pt-sputtered/PZT interface. In terms of the interface-stimulated nucleation model by Gerra *et al.* [19], this would increase the energy required for the nucleation of a reverse domain at this top interface. Increasing field cycle number will increase density of trapped electrons at the top interface, leading to a higher activation energy for reverse domain nucleation. An external field of 200 kV/cm therefore cannot provide enough energy for the domains to nucleate at the top interface. However, an external field of 600 kV/cm can overcome this energy barrier, leading to a polarization switching. Moreover, the nucleation energy at a nucleating site depends on the local density of trapped electrons at and around that site, so the domain nucleation energy is inhomogeneous over the top interface. All of these result in slanting and positively shifting of the P-E loop (or depressing and broadening of the I-E peaks) of the cycled capacitor under the positive external field (Figure 4.3c-e). In contrast, the PZT/SRO bottom interface is structurally and electrically unchanged with field cycling. Domain nucleation at this interface therefore can occur routinely as indicated by well-defined switching peaks under negative field.

Another possibility is that a certain number of interfacial trapped electrons can combine with positively charged defects (for example oxygen vacancies) to form interfacial electrical dipoles (Figure 4.8). The interfacial dipoles might strongly pin the adjacent polarization domains and make these domains non-switchable even under external fields as high as 600 kV/cm. This thin top PZT layer (still having a good crystalline structure but polarized non-switchable) just acts as a dielectric layer connected in series with the switchable PZT part underneath. This results in several consequences. First, the fatigued capacitor

will shows slightly less saturation polarization compared to the pristine capacitor under 600 kV/cm. Second, the fatigued domain switching under negative field will occur at a slightly higher field amplitude compared to the pristine domains due to the field screening. These are well consistent with the observations from the P-E loop measurements above. Moreover, the downward polarization state P_{down} in the fatigued capacitor detected by the PFM measurements is indeed the signal from the trapped electrons and electrical dipoles in the top PZT layer. Note that a thin top layer of the ferroelectric film was reported to be responsible for the signal (polarization state) read by the PFM tip [20]. Because the domain nucleation at the bottom interface happens routinely during field cycling, we conjecture that the remaining PZT thick layer underneath will show an upward polarization state [20].

Figure 4.8: (a) Schematic visualisation for the domain state in pristine and fatigued capacitor. Electrons are injected and trapped at the Pt-sputtered/PZT interface. They combine with oxygen vacancies (V_O) to form electrical dipoles at the top interface, which can pin adjacent domains. The trapped electrons and interfacial dipoles can inhibit the domain switching of the PZT layer. The figure is not to scale.

In the case of SRO/PZT/SRO capacitor with epitaxial interfaces, the available trap (predominantly dislocations) density is very low. In the case of Pt-inPLD/PZT/SRO, the available trap cites at the clean Pt-inPLD/PZT interfaces are also expected to be much lower than in the defective Pt-sputtered/PZT interface. Moreover, the charge injections at the SRO/PZT and Pt-inPLD/PZT interfaces are also much smaller than that at the Pt-sputtered/PZT interface

(because of a much smaller depolarization field). The number of trapped electrons and the consequent effect of these trapped electrons on domain switching are therefore negligible, resulting in a high fatigue-resistance behavior in these two capacitor structures, as previously shown in chapter 3. However, the Pt-inPLD/PZT/SRO capacitor still becomes strongly fatigued under sufficiently prolonged field cycling, indicating another fatigue mechanism in this sample. Overall, the defective layer of carbon contaminants at the *ex situ* metal/PZT interface not only induces the electron injection but also induces the electron trapping, which all consequently give rise to an early, strong fatigue.

4.5 Conclusion

We have experimentally investigated fatigue behavior of Pt-sputtered/PZT/SRO capacitors. The capacitor shows commonly strong fatigue under bipolar field cycling and little fatigue under unipolar field cycling. The bipolar fatigue is practically independent of the cycling frequency. These behaviors of fatigue support that electron injection at the Pt-sputtered/PZT interface might be the initial step in the mechanism for the fatigue. Furthermore, the non-switchable polarization domains in fatigued capacitor were found to be switchable again under sufficiently high field amplitude, but the switching is asymmetric between the two polarization directions. Guided by these findings, we proposed that the injected electrons are trapped at the Pt-sputtered/PZT interface, consequently inhibit the reverse domain nucleation at this interface. Overall, the dominant mechanism for fatigue in the Pt-sputtered/PZT/SRO capacitor is a sequence of electron injection - electron trapping at interfaces - inhibition of domain nucleation.

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Chapter 5

Mechanisms of fatigue in $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ capacitors with in situ Pt top-electrodes*

As shown in chapter 3, $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ capacitors with *in situ* metal electrodes show clean interfaces and a fatigue resistance up to $10^7 - 10^8$ field cycles. However, such capacitors still strongly fatigue after prolonged field cycling above 10^8 cycles with unknown mechanisms yet. Here, we aim to identify the fatigue mechanism(s) of these capacitors by investigating their domain switching and interface microstructure during field cycling. The Pt-inPLD/ $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ /SrRuO₃ samples with Pt top electrodes made by *in situ* pulsed laser deposition were chosen as a benchmark. We found that the cycled capacitor is switchable but the switching field is significantly higher than that for the pristine capacitor. The Pt-inPLD/PZT interface is structurally degraded and formed a 5-10-nm thick non-structured layer after the fatigue field cycling. Based on these findings, we proposed that local decomposition happens at the Pt-inPLD/PZT interface due to the transient depolarization field during the polarization switching under field cycles, resulting in an interfacial non-ferroelectric PZT-degraded layer. This PZT-degraded layer subsequently screens the applied field over the capacitor, leading to a suppression of polarization switching in the cycled capacitor.

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5.1 Introduction

In chapter 3, we have shown that polarization fatigue of PZT capacitors strongly depends on the electrode/PZT interface microstructure. PZT capacitors with *ex-situ* fabricated metal electrodes exhibit strong fatigue within $10^3 - 10^4$ field cycles. The main origin of this low fatigue resistance turns out to be a 1.5-nm thick defective layer at the *ex-situ* metal/PZT interface, which forms during the *ex-situ* fabrication steps. We then discussed in chapter 4 the mechanism of how this defective layer can lead to fatigue effect. In short, the defective layer induces a transient, local depolarization field, which is produced by the bound charges of nucleating reverse domains, to extremely high values (in the order of several MV/cm). This transient field then induces the injection of electrons from the metal into the ferroelectric layer through the interface. The injected electrons are trapped in the defective interface layer and subsequently inhibit the nucleation of reverse domains at this interface, suppressing the polarization switching of the cycled capacitor. Based on these mechanisms, we suggested to use *in situ* fabricated metal electrodes or *in situ* ferroelectric surface cleaning to enhance the purity of the metal/ferroelectric interfaces and thereby improve the fatigue resistance of the capacitors. As shown in chapter 3, the PZT capacitors with *in situ* metal electrodes are indeed free of fatigue until 10^7 cycles, which is four orders of magnitude longer than the capacitors with *ex situ* metal electrodes. However, such capacitors with *in situ* metal electrodes still strongly fatigue after prolonged field cycling above 10^8 cycles. Understanding of this fatigue behaviour would allow one to further improve the fatigue resistance of metal-electrode ferroelectric capacitors.

This chapter aims to identify the fatigue mechanism(s) of PZT capacitors with *in situ* fabricated metal electrodes. The model sample for investigation is the Pt-inPLD/PZT/SRO structure fabricated by *in situ* pulsed laser deposition. We characterized the domain switching and the interface microstructure of the capacitor at different cycling states. The cycled capacitors were found to be switchable at sufficiently high applied fields. More importantly, the Pt-inPLD/PZT interface was found to be structurally degraded during field cycling, become a non-ferroelectric layer. Based on these findings, we propose that structural decomposition happens locally at the Pt/PZT interface because of the depolarization during prolonged field cycling. The broken and degraded PZT interfacial layer

then screens the external field, consequently suppresses polarization switching of the cycled capacitor, resulting in the observed fatigue effect.

5.2 Methods

5.2.1 Capacitor fabrications

The Pt-inPLD/PZT/SRO capacitors (Pt and SRO are respectively the top and bottom electrode) were *in situ* grown on SrTiO₃ (STO) (001)-oriented substrate by pulsed laser deposition (using a home-built system, NanoLab, MESA+). More details on the growth conditions of all the layers can be found in chapter 3 (Method section). The thicknesses of the Pt, PZT, and SRO layers are 100, 250, and 100 nm, respectively.

5.2.2 Sample characterizations

Ferroelectric properties were measured with an aixACCT TF-2000 Analyzer. Fatigue behaviour was investigated under bipolar rectangular electric field cycling with a variable field amplitude and cycling frequency. At different field cycle numbers, polarization hysteresis (P-E) loops were measured with a triangular electric field with a frequency of 1 kHz and various field amplitudes. Small-signal capacitance-field (C-E) loops were measured with a slow scanning staircase DC bias superimposed with a low-field (2.6 kV/cm), 10-kHz AC modulation signal. In all electrical experiments the capacitor bottom electrode was grounded.

Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) were performed to characterize interfaces between PZT layers and electrodes using the X-Ant-Em instrument at the University of Antwerp. Cross-sectional cuts on the samples along the [001] direction of the STO substrate were prepared by a FEI Helios 650 dual-beam focused ion beam device.

5.3 Results

5.3.1 Fatigue-profile dependence on P-E loop measurements

Two identical capacitors were subjected to the same bipolar field cycling of 200 kV/cm and 100 kHz. At different cycling states, the P-E loops of the first capacitor were measured by a triangular field of 200 kV/cm and 1 kHz, and of the second capacitor by a triangular field of 800 kV/cm and 1 kHz (Figure 5.1a). The resulting remnant polarization profiles of the two capacitors as function of the field cycle number are substantially different (Figure 5.1b). Capacitor 1 (P-E loops measured at 200 kV/cm) loses about 90% of the initial polarization after 10^9 cycles; however, capacitor 2 (P-E loops measured at 800 kV/cm) keeps the polarization nearly unchanged during field cycling. Note that these two investigated capacitors are on the same wafer so they are supposed to have an identical layer microstructure and that the bipolar square field cycles over the two capacitors are the same so the impact of the field cycles on the capacitors must also be equal. We therefore conclude that the evolution profile of the remnant polarization under field cycling, which has been commonly used to present fatigue effect, is strongly sensitive to how one measures the P-E loop at cycling states. Hence, in order to understand more exactly what happens to the capacitors under field cycling, we need to further characterize the polarization switching loops of the cycled capacitors.

5.3.2 Domain switching of fatigued capacitors

The P-E loops and I-E loops measured at different cycling states provide more insight into the switching behavior of the cycled PZT layers. For capacitor 1 (measured at 200 kV/cm), the P-E loop becomes more suppressed and slanted with increasing field cycles, corresponding to the depression of the switching peaks in the I-E loops (Figure 5.2a,c). These data would lead us to the usual conclusion that the cycled ferroelectric capacitor becomes non-switchable. However, for capacitor 2 (measured at 800 kV/cm), the P-E loops show clear ferroelectric switching behavior, corresponding to prominent switching peaks in the I-E loops (Figure 5.2b,d). But there are some major differences between the polarization switching of the cycled capacitor and the pristine capacitor:

- (i) The pristine capacitor shows “non-fatigued” switching peaks at around

Figure 5.1: (a) The field cycling fatigue treatments on two capacitors. The field cycling is the same (200 kV/cm at 100 kHz) for both capacitors. The P-E loops were measured with a maximum field of 200 kV/cm for capacitor 1 and 800 kV/cm for capacitor 2. (b) The obtained remnant polarization profiles as function of the field cycle number of the two capacitors.).

+/- 45 kV/cm, but in the cycled capacitors these peaks become suppressed and there are new “fatigued” switching peaks at higher applied field. For example, the capacitor after 2×10^7 cycles shows fatigued switching peaks at +/- 170 kV/cm (the red curve in Figure 5.2d); after 3×10^7 cycles shows fatigued switching peaks at +/- 200 kV/cm (the blue curve in Figure 5.2d). The capacitor at these two cycling states still shows clear non-fatigued switching peaks at +/- 45 kV/cm, explaining the double-stepped behavior in their P-E loops (the red and blue loop in Figure 5.2b). This behaviour is interpreted as being due to inhomogeneous, region by region fatiguing of the capacitor under the cycling: the non-fatigued regions show polarization switching at +/- 45 kV/cm and the fatigued regions show polarization switching at higher applied fields. After further cycling, the non-fatigued switching peaks at +/- 45 kV/cm almost completely disappear and the fatigued switching peaks shift to values around +/- 240 kV/cm after 10^8 cycles and +/- 300 kV/cm after 10^9 cycles (the pink and green loop in Figure 5.2d, respectively). The single-step behavior of the P-E loops at these cycling states suggests that the whole area of the capacitor now becomes fatigued.

(ii) The fatigued switching peaks are broad as compared to the non-fatigued switching peaks. It means that the applied field required for polarization switching

(the local coercive field) in the fatigued regions of the capacitor is distributed over a wide range. This implies that even in the fatigued region the degree of fatigue at different locations is also different.

(iii) The fatigued switching peak under positive field (when the Pt electrode is positively biased) is broader and lower compared to the fatigued switching peak under negative field (when the Pt electrode is negatively biased). Under positive field, the polarization switching starts by nucleation of downward-oriented domains at the Pt/PZT top interface, whereas under negative field the polarization switching starts by nucleation of upward-oriented domains at the PZT/SRO bottom interface. Generally, the activation energy for reverse domain nucleation at a specific nucleation site at the capacitor interface depends on the local microstructure of and the applied field at that site. Therefore the data above indicate that during field cycling the top Pt/PZT interface becomes more structurally modified than the bottom PZT/SRO interface. This will be verified in the following sections.

Figure 5.2: P - E loops and I - E loops of capacitor 1 (a, c) and capacitor 2 (b, d) at different cycling states.

5.3.3 Fatigue dependence on field cycling conditions

We applied field cycling with various field amplitudes and cycling frequencies to investigate the characteristic dependences of the fatigue on the field cycling conditions. The P - E loops were measured with a triangular field of 200 kV/cm and a frequency of 1 kHz, so that the eventual fatigue effect caused by the square field cycles can be clearly observed. With the cycling frequency, f_{cy} , fixed at 10 kHz, the final fatigue (at 10^8 cycles) is slightly stronger under higher field amplitude. However, in the investigated field range from 120 to 280 kV/cm, the fatigue onset is almost the same, at about 10^7 cycles for all amplitudes (Figure 5.3a). With the field amplitude, E_{cy} , fixed at 200 kV/cm, the fatigue is almost independent of cycling frequency (Figure 5.3b), and only depends on the number of field cycles. Overall, it can be concluded that the fatigue effect is just slightly affected by the field cycling amplitude and frequency, but is dominantly determined by the field

cycle number.

Figure 5.3: *Fatigue profile of the capacitor under field cycling with various field amplitudes (a) and cycling frequencies (b). The P-E loops were measured with a triangular field of 200 kV/cm and frequency of 1 kHz, so the eventual fatigue effect caused by the square field cycling is clearly observed. The fatigue effect is just slightly affected by the field cycling amplitude and frequency, but dominantly affected by the field cycle number.*

5.3.4 Interface structure during field cycling

To understand what happens to the capacitor microstructure during field cycling, we performed cross-sectional transmission electron microscopy (TEM) on the pristine capacitor and the 10^9 -field-cycle fatigued capacitor. The bottom PZT/SRO interface is atomically sharp because of the epitaxial growth and appears to be unchanged during field cycling, similarly to the interfaces of the SRO/PZT/SRO capacitors (see chapter 3). The Pt/PZT top interface of the pristine capacitor is sharp and clean, without any signature of a contaminant and/or defective layer (Figure 5.4a) (in this figure the Pt lattice structure is not clearly visible due to an intentionally enhanced image contrast). However, the Pt/PZT top interface of the fatigued capacitor shows some new features as compared to the top interface of the pristine capacitor: (i) a dark-contrast layer at the Pt/PZT interface with a thickness varying from a few nm up to 10 nm, (ii) “blobby” areas with slightly different contrasts extending to a depth of 30-40 nm into the PZT layer (Figure 5.4b,c). The PZT at larger depths remains undisturbed and shows no changes in the crystalline structure.

Zoom-in TEM images show that the dark-contrast layer at the Pt/PZT interface largely consists of amorphous or structureless material and some nano-sized crystalline grains (Figure 5.4d-f). We performed Fast Fourier Transform (FFT) analysis of different regions close to and inside the Pt/PZT interfacial layer (marked by rectangular boxes labeled from (1) to (4) in Figure 5.4c-f). FFT of region (1) (inside the crystalline PZT structure) provides fringe spacings equal to PZT lattice parameters, $d_{(001)} \approx 4.10\text{\AA}$ and $d_{(100)} \approx 4.06\text{\AA}$ (ICSD 98-009-0478). Regions (2) and (4) (inside the interfacial layer) show similar FFT with fringe spacings of $2.65\text{\AA}$ and $2.55\text{\AA}$, which are respectively comparable with interplanar spacings of (002) and (110) planes of the ZrO_2 tetragonal structure (ICSD 98-000-9993). We therefore conclude these regions to be $(\text{Zr,Ti})\text{O}_2$ grains. Region (3) (inside the interfacial layer) seems to be a metallic Pt grain as its FFT fringe spacing $2.32\text{\AA}$ is equal to the spacing of the Pt (111) planes (ICSD 98-004-1525). Overall, these data show that there is severe structural degradation of the top Pt/PZT interface during the field cycling treatment. Considering that the interfacial layer consists of amorphous, polycrystalline and decomposed material, and the observed oxides and metallic grains, one can assume that this interfacial degraded layer is non-ferroelectric.

Figure 5.4: TEM investigations on the pristine and cycled capacitor. (a) Pristine Pt/PZT interface. (b-c) 10^9 cycled Pt/PZT interface, (d-f) zoom-in image of the fatigued Pt/PZT interface. The bottom panels show FFT of regions marked by rectangle boxes (1-4).

The elemental maps obtained from energy dispersive X-ray spectroscopy (EDX) further confirms the structural change of the Pt/PZT top interface after field cycling (Figure 5.5). The elemental maps show a few nm thick transition boundary between the two layers. The densities of the compositional elements of PZT vary along the interface and one can also observe the Pt grains in the boundary layer.

Structural degradation in fatigued capacitors for both PZT ceramics and thin films has been previously reported [1–5]. By using optical microscopy, Zhang *et*

Figure 5.5: *EDX mapping for different elements at one location of the fatigued Pt/PZT interface. The dash boxes highlight the interfacial PZT-degraded layer.*

al. [1] observed some delaminated areas on the surface of fatigued PZT ceramics. By using scanning electron microscopy (SEM), Balke *et al.* [4] observed a molten layer at the Pt/PZT interface in fatigued PZT ceramic capacitors. Verdier *et al.* [6] found that ferroelectricity of the PZT ceramic capacitors can be recovered if a thin PZT layer adjacent to the electrodes is mechanically removed. This indicates that only a thin interfacial PZT layer is modified by field cycling, but also that this thin modified layer suppresses the polarization switching of the whole PZT capacitor. Also by using SEM, Lou *et al.* [2, 3] observed that the Pt top electrode in fatigued PZT thin-film capacitors became delaminated and suggested that this delamination is due to the degradation of the PZT layer underneath. By using Raman spectroscopy, this group found that the delaminated spots contained PbO, TiO₂, and pyrochlore material. Recently by using time-of-flight second ion mass spectrometer, levlev *et al.* [5] observed the diffusion of Cu electrode ions into the PZT layer in fatigued PZT thin-film capacitors. Here, by using TEM, we clearly observed both the ferroelectric structural degradation and the electrode material diffusion at the Pt/PZT interface in fatigued capacitors, consistent with all the previous reported observations. From all these data we conclude that prolonged field cycling degrades the Pt/PZT interface, resulting in

a non-ferroelectric interfacial layer, which subsequently suppresses the polarization switching of the cycled capacitor.

5.3.5 Capacitance behavior

A structural modification in the capacitor may change the capacitance value. Small-signal capacitance-field (C-E) measurements on the pristine and fatigued (at 10^9 field cycles) capacitor confirm this statement (Figure 5.6a). The static capacitance value of the pristine capacitor at 200 kV/cm, $C_0 \approx 100pF$, much higher than that of the fatigued capacitor, $C_f \approx 65pF$. This decrease of capacitance by field cycling is consistent with previous data [7, 8], which showed that fatigued Pt/PZT/Pt capacitors show a lower capacitance than pristine capacitors. The decrease of the capacitance was attributed to structural changes and/or the formation of a low permittivity layer at the Pt/PZT interface(s) during field cycling.

As presented above, there is a non-ferroelectric, PZT-degraded layer at the top interface of our fatigued Pt-inPLD/PZT/SRO capacitor. The fatigued capacitor can be modeled as the series connection of a capacitor C_i formed by the interfacial degraded PZT layer and a capacitor $C_{(PZT/f)}$ formed by the remaining ferroelectric PZT-crystalline layer (Figure 5.6b). Hence, one has the following equations for the capacitance of the fatigued device, the capacitance of the remaining crystalline PZT layer and of the interfacial degraded PZT layer, respectively:

$$\frac{1}{C_f} = \frac{1}{C_i} + \frac{1}{C_{PZT/f}} \quad (5.1)$$

with

$$C_i = \frac{\varepsilon_0 \varepsilon_i A}{d_i} \quad (5.2)$$

$$C_{PZT/f} = C_0 \frac{d_{PZT/p}}{d_{PZT/f}} \quad (5.3)$$

Here $d_{PZT/p} = 250nm$ is the PZT thickness in the pristine capacitor, d_i and ε_i are respectively the average thickness and relative dielectric constant of the

interfacial PZT-degraded layer in the fatigued capacitor, $d_{PZT/f} = d_{PZT/p} - d_i$ is the thickness of the remaining PZT-crystalline layer in the fatigued capacitor, $A = 10^{-8} m^2$ is the capacitor area. If we take $d_i \approx 5 nm$ (as determined from the TEM figures), one obtains $\epsilon_i \approx 10$. This seems a plausible dielectric constant value for the interfacial PZT-degraded layer, which mainly contains non-ferroelectric binary oxides.

Figure 5.6: (a) *C-E loops of the pristine and fatigued capacitor.* (b) *Schematic presentation of the fatigued capacitor.*

5.4 Discussion

We have investigated the switching behavior and the interface structure of ferroelectric Pt-inPLD/PZT/SRO capacitors during field cycling. The capacitor becomes fatigued inhomogeneously under field cycling, and the fatigued capacitor requires higher external field to switch the polarization as compared to the pristine capacitor. The Pt/PZT interface is structurally degraded by field cycling, forming an interfacial non-ferroelectric PZT-degraded layer (of nano TiO_2 , ZrO_2 , and Pt grains). These observations are clearly different from those for the fatigued Pt-sputtered/PZT/SRO capacitor (see Chapter 4). This suggests that the dominant fatigue mechanism(s) in the Pt-inPLD/PZT/SRO capacitor is different from that in the Pt-sputtered/PZT/SRO capacitor. Regarding the fatigue mechanism of the Pt-inPLD/PZT/SRO capacitor, one needs to answer two major questions: (1) How does field cycling cause microstructural degradation at the Pt/PZT inter-

face? (2) How does the interfacial PZT-degraded layer suppress the polarization switching of the cycled capacitor?

How does field cycling cause the microstructural degradation at the Pt/PZT interface? Although Balke *et al.* [4] and Ilev *et al.* [5] observed microstructural changes at the capacitor interface after field cycling, they did not discuss in detail the mechanisms behind these changes. Lou *et al.* [9] proposed that the changes are related to the transient depolarization field that appears within nanoseconds during the nucleation of reverse domains under bipolar cycles. We think that this is a plausible hypothesis. The transient depolarization field at the interface is produced by unscreened positive polarization charges on the top of the nucleating reverse domains and directs from the PZT layer towards the electrode. The magnitude of this field at the Pt-inPLD/PZT interface, as was estimated in chapter 3, is in the order of MV/cm, which is much higher than the DC breakdown field of many PZT films [10]. The interfacial PZT lattice suffers this transient, high depolarization field every single field cycle. Therefore, at a certain moment during the field cycling – here after about 10^7 cycles, the PZT lattice adjacent to the top interface becomes deteriorated and starts being decomposed by the repeated depolarization field. In general, the initial step right before a field-assisted structure decomposition in any dielectric material is the presence of a large charge carrier current. In this particular case of the Pt/PZT interface, the carrier current is the electron injection from the Pt electrode into the PZT layer, driven by the high transient depolarization field. With high kinetic energies, the injected electrons might strongly heat the interface, subsequently cause local thermal decomposition of the interfacial PZT lattice [3]. The presence of $(\text{Zr,Ti})\text{O}_2$ and non-structure materials and the diffusion of Pt are the results of this thermal decomposition scenario. The "blobby" areas just below the severely degraded interfacial layer are also resulted from the structure deterioration. Note that the decomposition discussed here is the local effect happening within the thin PZT layer adjacent to the interface under the effect of the transient depolarization field. The remaining PZT layer in distance from the interface is still in a crystalline structure. This is different from the capacitor breakdown effect (with structure degradation) commonly discussed in literature, which is under the effect of high external DC biases and occurs all through the whole thickness of the ferroelectric layer, making the capacitor highly leaky or even conductive.

One can think of several reasons why the PZT structure at the PZT/SRO

bottom interface, which is also subjected to the depolarization field during field cycling, remains stable, i.e. is not structurally modified. The most important reason is that the PZT lattice forms a strong chemical bond with the SRO lattice by the continuous oxygen backbone through the bottom interface (apart from a few dislocation defects). In contrast, there is no strong chemical bonding between the Pt and PZT lattices and the Pt/PZT interface can be considered as a large planar lattice defect. Moreover, it was reported that the deposition of Pt on a PZT surface always transforms the Pb^{2+} ions in the PZT top layer into neutral Pb^0 atoms [11–14]. The Pt/PZT interface therefore also contains a certain number of compositional defects and Pb vacancies. Because of all these lattice and compositional defects, the field-assisted structure decomposition, which is strongly mediated by defects, has much more chance to happen at the metal/ferroelectric interface than at the oxide/ferroelectric interface. This is also in a good agreement with the observation that ferroelectric capacitors with oxide electrodes show a higher DC breakdown strength than those with metal electrodes [15, 16].

If there is a defective dielectric layer between the Pt and PZT layer, such as in the case of the Pt-sputtered/PZT interface, the injected electrons will be predominantly trapped in this defective layer. The trapped electrons then quickly suppress the domain switching of the polarization within $10^3 - 10^4$ cycles as seen in chapter 4. Afterwards, there is no domain switching under further field cycling. The total number of times that the interfacial PZT lattice experiences the transient depolarization field is in order of $10^3 - 10^4$ times, much lower than the minimum number for an apparent decomposition in interfacial PZT lattice, $10^7 - 10^8$ times. The structure decomposition at the Pt-sputtered/PZT therefore has no chance to occur, explaining why we did not observe any clear PZT-degraded layer at the fatigued Pt-sputtered/PZT interface.

Then the second question, how can the interfacial PZT-degraded layer suppress domain switching of the capacitor? *levlev et al.* [5] suggested that the Cu-electrode diffusion at the interface forms Cu-doped PZT material and that Cu-doped PZT shows a very low polarization compared to the bare PZT. However, this cannot be the only reason for the suppressed polarization of the capacitor because the Cu diffusion was observed only nearby the Cu/PZT interface; therefore, the Cu doping, if it truly happens, only applies to a thin PZT layer nearby the electrode and the major part of the PZT layer in the

cycled capacitor is still undoped. Balke *et al.* [4] suggested that the interfacial PZT-degraded layer screens the external field applied over the cycled capacitor, reducing the actual field seen by the remaining (ferroelectric) PZT-crystalline layer. Therefore, the field seen by the ferroelectric PZT inside the cycled capacitor is much lower than the external applied field and might not be sufficient to cause a polarization switching. We suggest that a field screening effect also happens in our cycled capacitor. As shown above, the cycled capacitor is non-switchable under 200 kV/cm but is completely switchable under 800 kV/cm. And note that only the top interface has a degraded layer and the bottom interface is completely unchanged, but the applied switching field for both polarization directions, i.e. from upward into downward state and vice versa, are both increased up to 300 - 400 kV/cm. These are the evidence that the non-ferroelectric PZT-degraded layer at the top interface reduces the effective field seen by the remaining ferroelectric PZT-crystalline layer in the cycled capacitor.

Let us quantitatively model this scenario. The continuity of the displacement current across the dielectric layer/ferroelectric interface and the voltage drop across the two layers can be described by the following equations, respectively:

$$\varepsilon_0 E_i + P_i = \varepsilon_0 E_{PZT/f} + P_{PZT/f} \quad (5.4)$$

$$E_i d_i + E_{PZT/f} d_{PZT/f} = E_{appl} d_{PZT/p} \quad (5.5)$$

with E_i , $E_{PZT/f}$, E_{appl} are the field in the interfacial degraded PZT layer, the field in the remaining crystalline ferroelectric PZT layer, and the external applied field, respectively; P_i and $P_{PZT/f}$ are the polarization of the degraded layer and the crystalline PZT layer, respectively. We assume that the interfacial PZT degraded layer is completely non-ferroelectric, so we have $\varepsilon_0 E_i + P_i = \varepsilon_0 \varepsilon_i E_i$ with $\varepsilon_i \approx 10$ is the relative dielectric constant of the interfacial degraded PZT layer. Therefore, from Equation 5.4 and 5.5 one obtains the electric field in the degraded interfacial PZT layer and in the crystalline bulk PZT layer:

$$E_i = \frac{E_{PZT/f}}{\varepsilon_i} + \frac{P_{PZT/f}}{\varepsilon_0 \varepsilon_i} \quad (5.6)$$

$$E_{PZT/f} = \frac{E_{appl} - \frac{P_{PZT/f}}{\varepsilon_0 \varepsilon_i} \frac{d_i}{d_{PZT/p}}}{\frac{1}{\varepsilon_i} \frac{d_i}{d_{PZT/p}} + \frac{d_{PZT/f}}{d_{PZT/p}}} \approx E_{appl} - \frac{P_{PZT/f}}{\varepsilon_0 \varepsilon_i} \frac{d_i}{d_{PZT/p}} \quad (5.7)$$

The last approximation applies for the considered devices in which $d_i \ll d_{PZT/f} \approx d_{PZT/p}$. From Equation 5.7, it is seen that due to the interfacial dielectric layer at the interface, the field seen by the ferroelectric layer, $E_{PZT/f}$, is strongly reduced compared to the applied field. This is the field screening effect caused by the interfacial dielectric layer. At the moment that the remaining ferroelectric PZT-crystalline layer performs a domain switching, i.e. $P_{PZT/f} \approx 40 \mu C/cm^2$, we expect this layer sees a field $E_{PZT/f} \approx 45 kV/cm$ (similar to the switching field of the pristine capacitor). Putting these values into Equation 5.6 and 5.7, one obtains $E_i \approx 48000 kV/cm$ and $E_{appl} \approx 1000 kV/cm$. It means that the domain switching in the fatigued capacitor will occur if the external applied field is at least of 1000 kV/cm. This is a few times higher than the values observed from the I-E loop measurements (Figure 5.2d), within 300-400 kV/cm. A possible reason is that we used a simple model of the cycled capacitor as a series connection of only the degraded interfacial PZT layer and the remaining crystalline ferroelectric PZT layer. In fact, we did not consider the effect of the intermediate PZT layer with blob-structure regions between the interfacial PZT-degraded layer and perfect PZT-crystalline layer. The ferroelectricity of this layer might be not as good as the PZT-crystalline layer. This will make the quantitative model more complicated. However, the field screen effect caused by the interfacial PZT-degraded layer is still the main reason behind the suppression of the polarization switching in the cycled capacitor.

Overall, the mechanism of fatigue in the Pt-inPLD/PZT/SRO capacitor consists of two main scenarios: (i) decomposition of the interfacial PZT lattice adjacent to the Pt electrode into a non-ferroelectric layer by the effect of the transient depolarization field during field cycling and (ii) domain switching suppression caused by field screening of the resulting interfacial PZT-degraded layer. This mechanism model can explain well some observed characteristic behaviors of fatigue as shown in the Results section. First, the structural decomposition happens locally at different spots at the Pt/PZT interface. The spots which are most favorable for domain nucleation will be broken most quickly. The capacitor therefore becomes fatigued inhomogeneously under field cycling. Second, the

thickness d_i and dielectric constant ε_i (which depends on material component) of the interfacial PZT-degraded layer vary from location to location along the interface. As seen from Equation 5.7, this leads to a variation of the $E_{PZT/f}$ in the remaining ferroelectric PZT-crystalline layer. In other words, the applied field required for domain switching in this layer is inhomogeneous, as shown up by the broadening of fatigued switching peaks in the I-E loops. Third, the cycling field amplitude E_{cy} (in the order of kV/cm) is orders of magnitude lower than the transient depolarization field locally at the interface (in the order of MV/cm). Hence, the cycling field parameters (field amplitude and cycling frequency) do not strongly affect the decomposition of the Pt/PZT interface. The only role of the applied field cycles is to switch the PZT polarization, creating reverse domains (with unscreened bound charges on top) at the interfaces. The degree of the Pt/PZT interface caused by the high transient depolarization field is therefore only determined by the number of the polarization reversals, i.e. the number of field cycles, as long as the cycling field amplitude is high enough to allow for the nucleation of reversal domains.

To experimentally verify the field screening of an interfacial non-ferroelectric layer, we suggest to characterize the ferroelectricity of a Pt-inPLD/PZT-a/PZT/SRO capacitor in which the PZT-a is a thin amorphous PZT layer deposited by PLD at room temperature. The PZT-a layer, which is non-ferroelectric, is expected to increase the applied field required for the capacitor polarization switching. From thickness (determined from TEM) and dielectric constant (determined from C-E loops of a Pt-inPLD/PZT-a/SRO capacitor) of the PZT-a layer, one can estimate the switching field of the Pt-inPLD/PZT-a/PZT/SRO capacitor through Equation 5.7. This value is expected to be close to the value taken from the P-E and I-E loops.

The fatigue-mechanism model shows that one logical way to enhance the fatigue resistance is to enhance the bonding between the electrode and the ferroelectric layer, which then strengthens the interface structure against the depolarization field. The first solution is to insert a thin conductive oxide layer at the interface to form strong chemical bonding between the electrode and the ferroelectric layer and reduce the interfacial lattice defects. A 5-nm thick SRO contact layer inserted between Pt and PZT layer makes the capacitor become free of fatigue, proving this concept (Figure 5.7). Another solution is to use an adhesion layer of Ti or Ta, which can also enhance the bonding between the

noble metal (by metal-metal bonding) on the one side and the ferroelectrics (by metal-oxide formation) on the other side, subsequently strengthen the capacitor interfaces. We also believe that the electrode-ferroelectric chemical bonding is the real reason behind the good fatigue resistance in capacitors using Cu [17] and PtFe [18] as electrodes, because of the electrode-metal oxides at the interface.

Figure 5.7: *Fatigue behavior of a PZT capacitor with a 5-nm thick SRO layer inserted at the top interface between the Pt and PZT layer*

5.5 Conclusion

In summary, we have clarified the mechanisms behind the development of polarization fatigue in Pt/PZT/SRO thin-film capacitors fabricated by *in situ* PLD by characterizing their Pt/PZT interface structure and switching behaviour at the non-fatigued and fatigued states. The Pt/PZT interface was observed to become structurally degraded, forming a non-ferroelectric layer of binary oxides and diffused Pt. This interface degradation is attributed to the cyclic occurrence of the transient depolarization field arising from the reverse domain nucleation under bipolar field cycling, causing a large electron injection current which in turn thermally decomposes the interfacial PZT crystalline structure. The resulting interfacial non-ferroelectric PZT-degraded layer screens the external applied field and suppresses the domain switching of the cycled capacitor, leading to the observed fatigue effect. The obtained insight into the mechanisms behind the development of fatigue suggests a practical solution to improve the fatigue

resistance of metal-electrode ferroelectric capacitors by enhancing the chemical bonding between the metal electrodes and the ferroelectric layer.

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Chapter 6

Rejuvenation and second-fatigue of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ capacitors with ex situ Pt top-electrodes

Pt-sputtered/ $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ /SrRuO₃ (Pt-sputtered/PZT/SRO) capacitors became strongly fatigued within $10^3 - 10^4$ bipolar field cycles. However, the fatigued capacitors were observed to recover the polarization under further continued field cycling, which is the so-called rejuvenation effect. The effect has not been explained satisfactorily yet. Moreover, fatigue behavior of the capacitor after being rejuvenated has not been discussed elsewhere. Here, we aim to identify mechanisms behind the rejuvenation of (first) fatigued Pt-sputtered/PZT/SRO capacitors and investigate the following (second) fatigue behavior of the rejuvenated capacitors. We found that the rejuvenation onset depends strongly on the field cycling conditions and the rejuvenated capacitors became fatigued within $10^7 - 10^8$ field cycles. We observed a 20-30 nm thick PZT-degraded layer at the Pt/PZT interface in the second-fatigued capacitor. Based on these findings, we propose (i) charge compensation between interfacial trapped electrons and accumulated oxygen vacancies as the mechanism for the polarization rejuvenation in first-fatigued capacitors, and (ii) field screening by the PZT-degraded layer as the mechanism for the polarization fatigue in the rejuvenated capacitors. Our work helps to construct a more complete picture of how the Pt-sputtered/PZT/SRO capacitor responds to field cycling.

6.1 Introduction

It has been noted in chapter 4 that the Pt-sputtered/PZT/SRO capacitors firstly became fatigued but then recovered the polarization under field cycling (Figure 4.6a). This is consistent with previous observations that fatigued ferroelectric capacitors could recover the polarization under further continued field cycling [1, 2]. The recovery of polarization of a fatigued capacitor is called the rejuvenation effect. Despite the observations that were reported, mechanism(s) behind the rejuvenation are still unclear yet. Moreover, the subsequent fatigue of the capacitor after being rejuvenated has not been discussed in literature. For clarity, the fatigue behavior of the pristine capacitor is called "first-fatigue" and the fatigue behavior of the rejuvenated capacitor is called "second-fatigue". Understanding of the rejuvenation and the second-fatigue behavior will construct a more complete picture of how ferroelectric capacitors respond to field cycling, which subsequently may help to further enhance the stability of ferroelectric devices.

In this chapter, we discuss the mechanism(s) of the rejuvenation effect in the first-fatigued Pt-sputtered/PZT/SRO capacitors and investigate the subsequent second-fatigue behavior of the rejuvenated capacitors. We characterized the rejuvenation effect under various field cycling/DC-bias conditions and proposed that accumulated oxygen vacancies compensate the interfacial trapped electrons, subsequently enabling domain switching in the capacitors, resulting in the polarization rejuvenation. Under further field cycling, the Pt/PZT interface is decomposed to form a non-ferroelectric PZT-degraded, which subsequently screens the applied field over the capacitor, leading to domain switching suppression and resulting in the second-fatigue behavior.

6.2 Methods

6.2.1 Capacitor fabrications

The (as-grown) pristine Pt-sputtered/PZT/SRO capacitors (see chapter 3 for more details on the capacitor features and the growth conditions) were fatigued under 10^5 bipolar field cycles of 120 kV/cm and 1 kHz. After this field cycling, the (first-fatigued) capacitor shows a suppressed P-E loop as compared to the pristine capacitor (the red and the blue curve in Figure 6.2a). The first-fatigued

capacitors were then subjected to DC bias/field cycling for the investigations into the rejuvenation and second-fatigue behavior.

6.2.2 Sample characterizations

The ferroelectric properties of the samples were investigated with the aixACCT TF-2000 Analyzer. Polarization hysteresis (P-E) loops were measured with a triangular AC-electric field with an amplitude of 200 kV/cm and a frequency of 1 kHz. The field cycle used for fatigue treatment and rejuvenation investigation has a square, bipolar profile and variable field amplitude and cycling frequency. Small-signal capacitance-field (C-E) loops were measured with a slow scanning staircase DC bias superimposed with a low-field (2.6 kV/cm), 10-kHz AC modulation signal. In all electrical experiments the capacitor bottom electrode was grounded.

High-resolution transmission electron microscopy (TEM, Philips CM300ST-FEG) and scanning electron microscopy (SEM, Zeiss-1550) were employed to characterize the microstructure (cross-sectional and top view, respectively) of the capacitor at different cycling states. Sample lamellas for TEM measurements were made by using focused ion beam (Nova 600 Nanolab Dualbeam SEM/FIB).

6.3 Results

6.3.1 Rejuvenation and second-fatigue under field cycling

Dependence on field cycling amplitude and frequency

The (first-) fatigued capacitors were subjected to field cycling with various field amplitudes E_{cy} and cycling frequencies f_{cy} . With a f_{cy} fixed at 1 kHz, field cycling at a higher amplitude field sets an earlier rejuvenation (Figure 6.1a). Field cycling at 120 kV/cm cannot rejuvenate the polarization at least up to 10^7 cycles. Field cycling at 200 kV/cm sets in the rejuvenation rather abruptly at about 4×10^5 cycles, whereas field cycling at 320 and 400 kV/cm almost immediately start the rejuvenation but the degree of rejuvenation gradually increases with increasing field cycle number. For all cases, the capacitors achieve a maximally rejuvenated state at around 5×10^5 cycles, with almost the same remnant polarization as in the pristine state. With a E_{cy} fixed at 200 kV/cm, a field cycling at lower

frequency cycling sets an earlier rejuvenation onset (Figure 6.3b). This suggests that the rejuvenation is sensitive to the total duration of the applied field over the capacitor, T_{field} , calculated as the ratio of the cycle number n and the field frequency f_{cy} , $T_{field} = n/2f_{cy}$.

It is seen that the rejuvenated capacitor strongly decreases its polarization after field cycling of $10^7 - 10^8$ cycles, indicating the second-fatigue behavior of the Pt-sputtered/PZT/SRO capacitor (Figure 6.1b). The fatigue of the rejuvenated capacitors appears to be independent of the field cycling frequency, i.e. only depends on the field cycle number.

Figure 6.1: Rejuvenation behavior of fatigued Pt-sputtered/PZT/SRO capacitors under field cycling for various field amplitudes (a) and cycling frequencies (b). The cycling states for the SEM and TEM characterizations shown in the following sections are indicated.

The results above show that, under field cycling, the first-fatigue and the rejuvenation effect can be overlapped, depending on the cycling field and frequency used. Therefore, the remnant polarization profile as a function of the field cycle number is a competition between fatigue and rejuvenation and it can become complex, depending on the field cycling conditions. Hence, one needs to carry out experiments carefully to differentiate these two effects and to get accurate characteristic dependence of each effect on the field cycling conditions, which can be subsequently used to establish models for the effect mechanism(s).

Domain switching behavior

Although the remnant polarization of the fully rejuvenated capacitors (after 10^6 cycles) is nearly equal to that of the pristine capacitor, the P-E loops of these two states are substantially different (the black and red curve in Figure 6.2a). First, the average measured coercive field ($E_{cm,av} = (E_{c+} - E_{c-})/2$) of the rejuvenated capacitor (88 kV/cm) is larger than that of the pristine capacitor (46 kV/cm). This corresponds to the shift of the switching peaks to higher field amplitudes in the I-E loops (the black and red curves in Figure 6.2b). Second, the polarization of the rejuvenated capacitor at maximum applied field of 200 kV/cm ($P_{max} = 44 \mu C/cm^2$) is slightly smaller than that of the pristine capacitor ($48 \mu C/cm^2$). Further on we will show that the rejuvenated capacitor shows an interfacial dielectric layer at the ferroelectric electrode interface, to which we attribute these changes in the ferroelectric behavior.

The P-E loops and I-E loops of the capacitor at different cycling states during the second-fatigue stage are also shown in Figure 6.2(a,b). The state at 2.5×10^7 cycles (and other states within 10^7 - 10^8 cycles – not shown here) shows indications of a double-step P-E loop, which corresponds to double switching peaks in the I-E loops. This indicates that the fatigue stage develops inhomogeneously from region to region in the rejuvenated capacitor. At even higher field cycles, the P-E loop becomes completely suppressed, indicating that the whole capacitor becomes non-switchable. However, if the applied field is increased to 800 kV/cm, the second-fatigued capacitor is switchable again (as shown by the yellow curve in Figure 6.2c). The coercive field taken from this loop is about 315 kV/cm, almost 10 times larger than that in the pristine capacitor. The P-E loops measured with a maximum field of 200 kV/cm before and after the field pulse of 800 kV/cm show almost the same remnant polarization (the cyan and blue curves in Figure 6.4c). Moreover, we observed that the second-fatigued capacitors do not recover the polarization under further field cycling/DC bias even at an operating temperature as high as $200^\circ C$ (not shown here). These results imply that the mechanism(s) of the second-fatigue stage is (are) different from that of the first-fatigue stage, which is the domain switching inhibition due to interfacial trapped electrons at the defective Pt-sputtered/PZT interface.

Figure 6.2: *P-E loops (a) and I-E loops (b) of the pristine, maximally rejuvenated, and second-fatigued capacitors. (c) P-E loops of the second-fatigued capacitor at 10^9 cycles measured with different fields (inset).*

6.3.2 Rejuvenation under DC-bias poling

First-fatigued PZT capacitors also rejuvenated under application of DC bias (Figure 6.3a). The rejuvenation induced by DC bias is dependent on bias direction; negative bias (on the Pt top electrode) rejuvenates the film more efficiently than positive bias with the same amplitude. Rejuvenation is also sensitive to bias amplitude, higher bias results in stronger rejuvenation. It is noted that rejuvenation of polarization under DC bias is much less efficient than that under field cycling with the same field amplitude and effective field duration.

Rejuvenation induced by DC-bias poling was tested at different temperatures up to 200°C (Figure 6.3b). In these measurements, the first-fatigued capacitors were subjected to the bias and the temperature simultaneously for 30 minutes. P-E loops were then measured at room temperature. It is obvious that rejuvenation under negative bias becomes more efficient with increasing applied temperature.

At 200°C , a bias of -5 V (-200 kV/cm , on Pt electrode) can rejuvenate the remnant polarization ($2P_r$) to $62\text{ }\mu\text{C/cm}^2$, achieving 86 % of its maximum value (Figure 6.3c). In contrast, rejuvenation under the positive bias is practically unchanged with temperature and still little compared to the other case. Note that a fatigued capacitor heated at 200°C without application of bias shows no rejuvenation. All of these data indicate that DC poling under negative bias and at high temperature can release most of the non-switchable domains, and this is a slow process, which is possibly related to the moving ionic defects. We will further explain these observations in the discussion section.

Figure 6.3: (a) Rejuvenation of first-fatigued Pt-sputtered/PZT/SRO capacitors under various DC biases in comparison with that under field cycling. (b) Rejuvenation of the fatigued capacitor under bias of -5 V (-200 kV/cm) and $+5\text{ V}$ ($+200\text{ kV/cm}$) for 30 minutes at different testing temperatures. (c) P-E loops of the rejuvenated capacitor under $\pm 5\text{ V}$ poling at 200°C .

6.3.3 Microstructure characterizations

Rejuvenated capacitor at 10^6 cycles of 400 kV/cm and 1 kHz

The cross-sectional microstructure of the rejuvenated capacitor after 10^6 cycles of 400 kV/cm field strength and 1 kHz cycling frequency (as marked in Figure 6.1a) was characterized by transmission electron microscopy (TEM) (Figure 6.4a,b). One can observe a 5-nm thick interfacial layer (with a lighter contrast) between the Pt electrode and the PZT layer. This is different from the top interface in the pristine and the first-fatigued capacitor, which show only a 1.5-nm thick interfacial layer of carbon contaminants which initially forms during *ex situ* capacitor fabrication (Figure 4.7a-c in chapter 4). Zoom-in images show that the interfacial layer contains some embedded nano-sized grains with random crystalline orientations (Figure 6.4c-e). Based on the fringe spacings of the corresponding Fast Fourier Transform (FFT), we determined these grains to be $(\text{Zr,Ti})\text{O}_2$ with a tetragonal structure: $3.01\text{\AA} \approx d_{(001)}$, $1.83\text{\AA} \approx d_{(020)}$, $2.64\text{\AA} \approx d_{(002)}$ (ICSD 98-000-9993). The nature of the remaining polycrystalline materials in the interfacial layer could not be determined exactly, but we expect that they are mixtures of different metal (Pb, Ti, Zr) oxides.

Figure 6.4: *Cross-sectional TEM studies of the structure of the rejuvenated Pt-sputtered/PZT/SRO capacitor. (a) Low-resolution image of the capacitor structure. (b) Higher resolution image of the 5-nm thick interfacial layer. (c, e) Enlarged images of two locations in the interfacial layer showing the presence of crystalline grains. The yellow boxes mark the locations for the Fast Fourier Transform (FFT) in (d, f), respectively. The indicated lattice spacing are consistent with those of ZrO_2 tetragonal structure.*

Second-fatigued capacitor at 10^9 cycles of 200 kV/cm and 100 kHz

Microstructure degradation was observed in the second-fatigued capacitor (at 10^9 cycles) by SEM (Figure 6.5). Blisters and holes appear in the Pt layer together with degraded spots on the PZT surface. Note that the rejuvenated capacitors (at 10^6 cycles) have a good microstructure. Therefore, the observed degradation of

the capacitor microstructure is due to the field cycling from 10^6 up to 10^9 cycles. Looking more closely to the holes in the Pt layer, it is obvious that the Pt layer at these locations was melted, indicating that there is thermal degradation/explosion of the PZT material underneath. Note that the leakage current of the second-fatigued capacitor, which can be seen from the I-E loops, is as low as that of the pristine capacitor. This implies that the microstructure degradation occurs locally at particular locations in the second-fatigued capacitor and there is no conductive channel through the whole thickness of the PZT layer.

Figure 6.5: *Top-view SEM images of two Pt-sputtered/PZT/SRO capacitors fatigued by 10^9 cycles (at 200 kV/cm and 100 kHz). Thickness of the Pt top electrode is 100 nm (a) and 30 nm (b). There are numerous blisters and delaminated spots in the Pt top electrodes and PZT surfaces.*

A cross-sectional sample lamella along the STO [001] orientation was cut across a blister area for TEM characterizations. One can see that the Pt layer at the center of the blister area becomes detached from the PZT layer underneath (Figure 6.6a). Some layers with different contrasts can be observed in the detached gap between the Pt and the PZT surface (Figure 6.6b). These layers can be the degraded PZT, but also re-deposited material during the lamella preparation by FIB. Away from the blister center, the Pt layer is still attached to the PZT surface and there is an interfacial layer (with a lighter contrast), with a thickness

in the range 20-30 nm, between the Pt electrode and the PZT layer (Figure 6.6c). Enlarged TEM images show that the interfacial layer contains nano-sized grains with random crystalline orientations surrounded by non-structured materials (Figure 6.6d,e). Based on the fringe spacings their corresponding FFT (Figure 6.6f), we determined some crystalline grains inside the interfacial to be $(\text{Zr,Ti})\text{O}_2$ and Pt crystals. There are also numerous smaller grains inside the non-structured layer of which we cannot determine the lattice structure, however, we expect that these are the oxides of Pb, Ti, and Zr.

Figure 6.6: TEM studies showing the cross-sectional structure of a second-fatigued Pt-sputtered/PZT/SRO capacitor. (a-c) Low-resolution images of the capacitor structure. In the center of the blister area, the Pt layer becomes detached from the PZT surface. At a position far away from the blister area, the Pt layer is still attached to the PZT surface but a 20-30 nm thick interfacial layer is visible. (d-e) Enlarged TEM images showing clearly the interfacial PZT-degraded layer. (f) Fast Fourier Transforms (FFT) of the labeled locations in (d-e), show crystalline structures of PZT, (Zr,Ti)O₂, and Pt, respectively.

6.3.4 Capacitance behavior

The static capacitance at ± 200 kV/cm (where contribution from polarization switching is negligible) of the rejuvenated capacitor (at 10^6 cycles) is about $C_{re} \approx 78$ pF and of the second-fatigued capacitor (at 10^9 cycles) $C_{fa2} = 30$ pF (Figure 6.7). These are smaller than the capacitance of the pristine Pt-sputtered/PZT/SRO capacitor, $C_0 \approx 85$ pF and of the PZT layer in the SRO/PZT/SRO capacitor, $C_{PZT/0} \approx 100$ pF (see chapter 3).

Figure 6.7: C - E loops of the pristine, maximally rejuvenated, and second-fatigued capacitors.

The interfacial layer is largely non-structured, which is expected to be non-ferroelectric. The presence of such a layer can explain the capacitance decrease of the rejuvenated and second-fatigued state as compared to the pristine state. The rejuvenated capacitor can be attributed to the series connection of the remaining PZT crystalline layer $C_{PZT/1} \approx C_{PZT/0}$ and the (5-nm thick) interfacial non-ferroelectric layer $C_{i/re}$ with the following equation:

$$\frac{1}{C_{re}} = \frac{1}{C_{PZT/1}} + \frac{1}{C_{i/re}} = \frac{1}{C_{PZT/0}} + \frac{d_{i/re}}{\varepsilon_{i/re}\varepsilon_0 A} \quad (6.1)$$

$$\varepsilon_{i/re} = \frac{d_{i/re}}{\varepsilon_0 A} \left(\frac{1}{C_{re}} - \frac{1}{C_{PZT/0}} \right)^{-1} \quad (6.2)$$

where $\varepsilon_{i/re}$ and $d_{i/re}$ ($= 5$ nm) are the relative dielectric constant and thickness

of the interfacial layer in the rejuvenated capacitor, and A is the area of the capacitor ($10^{-8}m^2$). Hence, one finds $\varepsilon_{i/re} \approx 18$. This is a plausible value for the dielectric constant of a PZT-non-structured material.

Similarly, the second-fatigued capacitor C_{fa2} can be considered as the series connection of the interfacial PZT-degraded layer, $C_{i/fa2}$, and the remaining PZT-crystalline layer, $C_{PZT/2}$. One has the following equations:

$$\frac{1}{C_{fa2}} = \frac{1}{C_{PZT/2}} + \frac{1}{C_{i/fa2}} \quad (6.3)$$

$$C_{i/fa2} = \frac{\varepsilon_0 \varepsilon_{i/fa2} A}{d_{i/fa2}} \quad (6.4)$$

$$C_{PZT/2} = \frac{d_{PZT/0}}{d_{PZT/2}} C_{PZT/0} \quad (6.5)$$

with $C_{PZT/0} = 100pF$ is the capacitance of the SRO/PZT/SRO capacitor. With $A = 10^{-8}m^2$, $d_{i2} = 25nm$, $d_{PZT/2} = 225nm$, $d_{PZT/0} = 250nm$, one obtains $\varepsilon_{i2} \approx 12$. This value is in the same order to ε_{i1} of the interfacial layer in the rejuvenated capacitor, implying the similar material nature (PZT-degraded) of the two layers.

6.4 Discussion

It was shown above that first-fatigued Pt-sputtered/PZT/SRO capacitors rejuvenated the polarization under application of DC biases or bipolar field cycles. The rejuvenated capacitors then became fatigued again under prolonged field cycling. The rejuvenated capacitor shows a 5-nm thick interfacial layer and the second-fatigued capacitor shows 20-30-nm thick interfacial layer at the top interface.

Before discussing the possible mechanisms of the rejuvenation effect, we revisit the mechanisms of how the pristine Pt-sputtered/PZT/SRO capacitor becomes fatigued. In chapter 3, we found strong indications that the cause of the first fatigue in the Pt-sputtered/PZT/SRO capacitor is the 1.5 – nm thick defective layer of carbon contaminants at the Pt-sputtered/PZT interface. This interfacial layer increases the depolarization field at the interface, accelerating

the injection of electrons from the Pt electrode into the PZT layer. In chapter 4, we proposed that the injected electrons are trapped in the defective interfacial layer. Over time the growing trapped charge density increasingly interacts with polarization charges of reverse domains and finally prevents polarization domains from switching. The first-fatigued capacitor therefore expects to have a defective, space-charged interfacial layer between the Pt and the PZT layer.

What can be the mechanism(s) behind the polarization rejuvenation of first-fatigued Pt-sputtered/PZT/SRO capacitors? We propose the following hypotheses as the mechanisms for polarization rejuvenation under DC bias and field cycling:

(i) The polarization rejuvenation under a negative bias is due to charge compensation between trapped electrons and accumulated oxygen vacancies at the top interface. In general, oxygen vacancies in perovskites were observed to migrate toward electrodes under effect of external electric field [3, 4]. The migration and accumulation of these defects would be accelerated by a higher negative bias voltage, a longer the application time, and a higher operating temperature. The rejuvenation of capacitor polarization therefore becomes more effective under higher bias, longer application, and higher operating temperature. In contrast, a positive bias forces the oxygen vacancies to migrate towards the bottom interface, giving rise to no effect on the trapped electrons at the top interface.

(ii) The polarization rejuvenation under field cycling might also follow the charge compensation of trapped electrons and accumulated oxygen vacancies at the top interface. However, the scenarios are more complex. Under the first half of the field cycle (i.e. when Pt is positively biased, the external field points toward the bottom electrode and is opposite to the field caused by the trapped electrons), oxygen vacancies move toward the bottom interface. Under the second half of the field cycle (i.e. when Pt is negatively biased, the external field points toward the top electrode, in a same direction with the field caused by the trapped electrons), oxygen vacancies would move more efficiently to the top interface. Therefore, there is an effective amount of oxygen vacancies that migrate and accumulate at the top interface after every single field cycle, subsequently compensate the trapped electrons and consequently reduce the domain pinning effect. Moreover, when there are some switchable domains in the capacitor, the switching of these domains might accelerate the migration of oxygen vacancies toward the electrodes.

Oxygen vacancies prefer to locate at domain walls rather than inside the domain interior because of a lower formation energy at domain walls [5–8]. Hence under field cycling, the domain walls, which move forward and backward, can enhance the diffusion rate and thus the accumulation of oxygen vacancies at the top interface. In addition, when the domain switching happens, the PZT layer is repeatedly deformed due to the piezo-electric effect, which may also enhance the defect motion and accumulation. Overall, there is an effective number of oxygen vacancies moving towards the top interface under field cycling, and the consequent charge compensation of the trapped electrons by accumulating oxygen vacancies is the mechanism behind the polarization rejuvenation effect.

The mechanisms suggested above can well explain the main observed characteristic features of the polarization rejuvenation under field cycling. First, migration of oxygen vacancies toward the top interface is a field amplitude and field duration dependent process. Therefore, charge compensation at the top interface and the resulting rejuvenation of polarization is dependent on the field cycling conditions, as observed above. Second, the accumulation of oxygen vacancies at the top interface might give rise to the decomposition of the top PZT lattice. Note that the capacitor rejuvenated by 10^6 field cycles of 400 kV/cm and 1 kHz, which shows 5-nm thick interfacial layer, has continuously performed repeated domain switching (because the rejuvenation onset starts almost together with the field cycling application). Therefore, thermal decomposition of the top PZT atomic layers can also occur due to the heat of the injected electrons, contributing to the formation of the 5-nm thick interfacial layer. We expect that the rejuvenated capacitor under DC negative bias will show less interfacial layer than the rejuvenated capacitor under field cycling.

What can be the mechanism(s) behind the fatigue in rejuvenated capacitors? The fatigue onset of the rejuvenated Pt-sputtered/PZT/SRO capacitor is within $10^7 - 10^8$ cycles, which is similar to the fatigue onset of the Pt-inPLD/PZT/SRO capacitor. The fatigued Pt-sputtered/PZT/SRO capacitor at 10^9 cycles also shows a thick PZT-degraded layer adjacent to the Pt electrode. Based on these data, we conclude that the rejuvenated Pt-sputtered/PZT/SRO capacitor and the Pt-inPLD/PZT/SRO capacitor have a similar fatigue mechanism. There are two main scenarios involved into this mechanism. First, electron injection happens at the top interface, thermally decomposing the top PZT layer into a non-ferroelectric degraded layer. The degraded layer becomes thicker with

increasing field cycle number. Second, the thick PZT-degraded layer screens the external field, reducing the effective field seen by the remaining PZT-crystalline structure, leading to the polarization non-switching in the cycled capacitor. Detail discussions for these scenarios can be found in chapter 5. However, we notice that the PZT-degraded layer observed in the second-fatigued Pt-sputtered/PZT/SRO capacitor is around 20-30 nm, which is several times thicker than the PZT-degraded layer in the fatigued Pt-inPLD/PZT/SRO, which is around 5-10 nm. We currently cannot explain this difference between the two capacitor structures.

6.5 Conclusion

We have investigated the rejuvenation effect in the first-fatigued Pt-sputtered/PZT/SRO capacitors and the second-fatigue behavior of the rejuvenated capacitors under field cycling. Charge compensation of trapped electrons by the accumulating oxygen vacancies at the Pt-sputtered/PZT interface is proposed as the main mechanism for the rejuvenation effect. The rejuvenated capacitors then fatigue within 10^7 - 10^8 cycles, which is 10^4 times more fatigue resistant than the pristine as-grown capacitors. The second-fatigued capacitor shows a relatively thick PZT-degraded layer at the top interface. We propose that during the prolonged field cycling, the injected electrons thermally decompose the PZT crystalline structure into a non-ferroelectric PZT-degraded layer, which consequently screens the applied field over the PZT layer, leading to the polarization switching suppression in the cycled capacitor. This chapter, together with the chapters 3 and 4, provides a more complete picture on how the Pt-sputtered/PZT/SRO capacitors respond to field cycling.

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Chapter 7

Polarization fatigue of $\text{SrRuO}_3/\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3/\text{SrRuO}_3$

$\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) capacitors with conductive oxide electrodes are often observed to show excellent fatigue resistance against field cycling, and therefore are considered to be potential candidates for high-endurance ferroelectric-based devices. However, some particular aspects of the fatigue of these capacitors have not been discussed yet, for example, the effect of the film composition (Zr/Ti ratio) and harsh cycling conditions (high field amplitude and high operating temperature) on the fatigue behaviour. This chapter discusses these topics. The fatigue observed in the $\text{SrRuO}_3/\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3/\text{SrRuO}_3$ (SRO/PZT/SRO) capacitor depends on the Zr/Ti ratio; Zr-rich (Zr/Ti = 80/20) and morphotropic phase boundary (Zr/Ti = 52/48) samples are free of fatigue, while the Ti-rich (Zr/Ti = 20/80) sample is strongly fatigued. We propose that the strong fatigue in the $\text{SrRuO}_3/\text{PbZr}_{0.20}\text{Ti}_{0.80}\text{O}_3/\text{SrRuO}_3$ capacitor is related to the presence of 90° domain walls in this sample, which become charged during the field cycling and consequently hinder the polarization switching in the cycled capacitor. Further, we observed that the $\text{SrRuO}_3/\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3/\text{SrRuO}_3$ capacitor only shows little fatigue under increasing cycling field amplitude and operating temperature. However, under increasingly harsh conditions, the capacitor starts to show electrical breakdown with permanent structural degradation.

7.1 Fatigue dependence of SRO/PZT/SRO on the Zr/Ti ratio

7.1.1 Introduction

A $\text{SrRuO}_3/\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3/\text{SrRuO}_3$ (SRO/PZT/SRO) capacitor with $x = 0.52$ is free of fatigue, as presented in chapter 3. This is consistent with all of the data in literature on oxide-electrode $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ capacitors (see chapter 2). However, Pentilie *et al.* [1] observed that an epitaxial $\text{SrRuO}_3/\text{PbZr}_{0.20}\text{Ti}_{0.80}\text{O}_3/\text{SrRuO}_3$ (SRO/PZT-20/80/SRO) thin-film capacitor strongly fatigues under field cycling. The fatigue mechanism(s) in this $\text{PbZr}_{0.20}\text{Ti}_{0.80}\text{O}_3$ capacitor was not discussed in detail. To the best of our knowledge, there is no any other investigation further confirming this observation and clarifying the mechanism(s) behind the fatigue.

In this section, we aim to investigate and compare the fatigue behaviour of $\text{SrRuO}_3/\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3/\text{SrRuO}_3$ capacitors with three different Zr/Ti ratios: 80/20 (PZT-80/20), 52/48 (PZT-52/48), and 20/80 (PZT-20/80). This allows us to draw a more complete picture of the fatigue of $\text{SrRuO}_3/\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3/\text{SrRuO}_3$ capacitors and to verify the observation of Pentilie *et al.* [1].

7.1.2 Methods

The SRO/PZT/SRO with Zr/Ti = 80/20, 52/48, 20/80 were all grown on SrTiO_3 (001)-oriented substrates by PLD. The thicknesses of the SRO and PZT layers are 100 and 250 nm, respectively. The detailed growth conditions of the layers can be found in Chapter 3 (Method section).

Fatigue measurements were carried out under bipolar field cycling at room temperature. Details on other characterization techniques can be found in the previous chapters.

7.1.3 Results

Structural characterizations

Reciprocal space map (RSM) measurements around the PZT (013) reflection were performed to characterize the crystalline structure of the three investigated

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capacitors (Figure 7.1). The obtained reflections of the STO substrates and the SRO layers are the same for the different samples and used as references. The RSM results for the PZT layers with three Zr/Ti ratios are clearly different. The PZT-80/20 and PZT-52/48 capacitor show only one single PZT reflection peak of the rhombohedral structure while the PZT-20/80 capacitor shows several separate PZT peaks, which correspond to reflections from in-plane oriented *a*-domains and out-of-plane *c*-domains of the tetragonal structure. Some further features on the PZT-20/80 domain structure such as domain fraction and domain tilting angle, which are out of the scope of this work, can however be obtained by an interpretation presented in previous works [2, 3].

Figure 7.1: Reciprocal space maps around the (013) reflection of the PZT layers (SRO-t and SRO-b correspond to the top and bottom electrode, respectively). In the PZT-20/80 sample, reflection signals from both *a*- and *c*-oriented domains are observed.

The in-plane (ip) and out-of-plane (oop) lattice parameters of the PZT layers and the STO substrates (as reference) calculated from the reflection peaks are summarized in Table 7.1. The lattice parameters confirm the rhombohedral structure of the PZT-80 and PZT-52 layer and the tetragonal structure of the PZT-20 layer.

Material-lattice	PZT-80/20	PZT-52/48	PZT-20/80
STO-ip	3.905	3.906	3.906
STO-oop	3.905	3.905	3.905
PZT-ip	4.119	4.087	3.971
PZT-oop	4.121	4.107	4.145
PZT-tetragonality (oop/ip)	≈ 1.000	≈ 1.004	≈ 1.044

Table 7.1: Lattice parameters of different materials calculated from the RSM data.

Ferroelectric behaviour

The (pristine) SRO/PZT/SRO capacitors show P-E loops that depend on the Zr/Ti ratio (Figure 7.2a). The remnant polarization P_r and the average coercive field E_C ($E_C = (E_C^+ + E_C^-)/2$) increase with increasing Ti content (Figure 7.2b). These findings are consistent with previous observations on PZT epitaxial films grown by metal-organic chemical vapor deposition [4] and sputtering [5, 6] and on PZT polycrystalline films [7]. The shape of the P-E loop depends not only on the crystalline orientation but also on the film thickness; therefore, we do not compare the exact values of P_r and E_C from different studies on the films with different thicknesses.

Figure 7.2: (a) P-E loops and (b) remnant polarization P_r and coercive field E_C of the SRO/PZT/SRO capacitors with various Zr/Ti ratios.

Generally, the polarization of PZT depends on the tetragonality of the

7.1. Fatigue dependence of SRO/PZT/SRO on the Zr/Ti ratio

material unit cell [6], which depends on the Zr/Ti ratio. The PZT layers with Ti-rich compositions have tetragonal structures with high tetragonalities; therefore, they are expected to show higher polarizations than PZT at morphotropic phase boundary and PZT with Zr-rich compositions, which have rhombohedral structures. The composition dependence of E_C follows unclear mechanisms [7], which is out of scope of this work.

Fatigue behaviour

The capacitors were subjected to field cycling at 140 kV/cm and 100 kHz. It is seen that the PZT-80/20 and PZT-52/48 capacitors are free of fatigue, while the PZT-20/80 capacitor is fairly strongly fatigued, with 60% polarization loss after 10^9 cycles (Figure 7.3a). The P-E loop of the latter device becomes suppressed in P-direction and narrow in E-direction with increasing field cycle number (Figure 7.3b). However, the fatigued capacitors still show square loops, well-developed ferroelectric behaviour, with only a small increase of the loop slanting.

Figure 7.3: (a) Fatigue behaviors of SRO/PZT/SRO capacitors with various Zr/Ti ratios. (b) P-E loops of the PZT-20/80 capacitor at different cycling states.

Our data confirm the observations of Pentilie *et al.* [1] that the PZT-20/80 is strongly fatigued even with SRO electrodes. Until now, there is no research which directly studies the dependence of fatigue behaviour of SRO/PZT/SRO epitaxial thin-film capacitors on the Zr/Ti ratio. However, it was reported that metal/PZT/metal polycrystalline capacitors become fatigued more severely with increasing Ti content [8, 9]. This indicates that Ti-rich PZT films fatigue more

than Zr-rich PZT films, irrespective of the electrode materials and the film crystallinity.

The fatigue behaviour of the PZT-20/80 capacitor was further investigated under field cycling with various field amplitudes, cycling frequencies, and pulse durations. When the field amplitude was fixed at 140 kV/cm, the field cycling with a higher frequency causes an earlier fatigue to the capacitor (Figure 7.4a). When the frequency was fixed at 100 kHz, the field cycling with a higher field amplitude causes a less fatigue (Figure 7.4b). However, one can see that under high field-amplitude cycling (200 and 300 kV/cm), the capacitor first becomes fatigued and then rejuvenates the polarization under continued field cycling. This means that the fatigued PZT-20/80 also exhibits the rejuvenation effect. We fixed the field amplitude at 140 kV/cm and the frequency at 1 kHz but varied the applied pulse duration (Figure 7.4c). The capacitor was found to be more severely fatigued under field cycling with shorter pulse duration (Figure 7.4d).

Pentilie *et al.* [1] also observed the rejuvenation effect in their fatigued SRO/PZT-20/80/SRO capacitors. However, they observed a more complicated dependence of the fatigue on the field cycling frequency: no fatigue under 1MHz cycling, strong fatigue under 100 kHz, and strong fatigue followed by complete rejuvenation under 10 kHz and 1 kHz. Currently, we cannot explain the differences between the studies.

The fatigued SRO/PZT-20/80/SRO capacitors were found to rejuvenate about 95% of the pristine remnant polarization after storage for 3 days in ambient conditions (without any electrical and thermal treatment) (Figure 7.5a, the red curve). Another fatigued capacitor rejuvenated completely the polarization after only 2 minutes placing on a hot plate of 200°C (Figure 8a, the blue curve). Under field cycling (140 kV/cm and 100 kHz), this rejuvenated capacitor becomes fatigued again, although slightly less than the pristine capacitor (Figure 7.5b).

7.1.4 Discussion

We have shown that the fatigue behavior of SRO/PZT/SRO capacitors depends on the Zr/Ti ratio, with strong fatigue in PZT-20/80 and no fatigue in PZT-52/48 and PZT-80/20. Characteristic features of the fatigue behavior of the PZT-20/80 device are the following: (i) the fatigue strongly depends on the field cycling amplitude, frequency, and pulse duration; (ii) fatigue and rejuvenation

7.1. Fatigue dependence of SRO/PZT/SRO on the Zr/Ti ratio

Figure 7.4: Fatigue profiles of PZT-20/80 capacitor under field cycling with various cycling frequencies (a), field amplitudes (b), applied pulse durations (c-d).

can occur concurrently under field cycling; (iii) self-rejuvenation (without field cycling) of fatigued capacitors already occurs at room temperature and is much accelerated at higher temperatures. The SRO/PZT-52/48/SRO capacitor is structurally unchanged during field cycling, see Chapter 4 for the TEM data. We did not characterize the microstructure of the PZT-80/20 and PZT-20/80 capacitor after field cycling, but we think that these capacitors are also structurally unchanged during the field cycling treatment. Although the PZT-20/80 capacitor shows strong fatigue, the fatigued capacitor then can rejuvenate the polarization completely and the rejuvenated P-E loop is similar to the pristine loop. This only happens if the microstructure of the sample is unchanged.

Let us discuss the difference in microstructure and domain structure of the pristine PZT-80/20, PZT-52/48, and PZT-20/80 capacitors. First, the PZT/SRO interfaces of the all investigated capacitor are epitaxial, irrespective of the Zr/Ti

Figure 7.5: (a) P - E loops of the rejuvenated PZT-20/80 capacitors compared to the pristine P - E loop. (b) Fatigue profile of the pristine capacitor and the rejuvenated capacitor (by 2 minutes at 200°C).

ratio. As shown in 7.1, the PZT-20/80 layer shows a better in-plane lattice matching with the SRO/STO stack than the PZT-52/48 and the PZT-80/20 layer. Therefore, the PZT-20/80/SRO interface is expected to be less defective than the PZT-52/48/SRO and PZT-80/20/SRO interface. Hence, we think that the observed fatigue in the PZT-20/80 capacitor does not originate from the capacitor interfaces. Second, the PZT-20/80 film shows a tetragonal structure while the PZT-80/20 and PZT-52/48 film show a rhombohedral structure. As discussed above, the tetragonal structure of the PZT-20/80 epitaxial film grown on SRO/STO leads to a formation of a/c domain pattern, in which a -domains have the polarization vector in the film plane direction and c -domains have the polarization vector in the out-of-plane direction [10, 11]. These a/c polydomain structures help to release the epitaxial strain inside the film. As a consequence, the domain walls inside the PZT-20/80 film can be 180° domain walls (between the c -domains with up- and down-oriented polarization) and 90° domain walls (between a -domains and c -domains). The rhombohedral-structure PZT-52/48 film shows random structures of grain domains with dimensions in the range from few nm to a few tens of nm [11, 12]. In the rhombohedral PZT-80/20, the domain walls are 71° or 101° . Generally, to maintain a minimum statistic electrical energy, the domain walls inside the ferroelectric sample are electrically neutral. For example, in the PZT-20/80 capacitor, the 90° domain walls are electrically neutral because of the head-to-tail polarization configuration of the adjacent a -

7.1. Fatigue dependence of SRO/PZT/SRO on the Zr/Ti ratio

and c -domains, which minimizes the bound charges at the domain walls [13] (Figure 7.6a).

We propose that the origin of the fatigue in the PZT-20/80 lies in the 90° domain walls (a/c domain walls). We suggest as a possible fatigue mechanism that during repeated field cycles, the 90° domain walls become electrically charged by forming temporary head-to-head configurations of the polarization vectors at the domain walls, which subsequently hinder a complete polarization switching of the cycled capacitor. A possible sequence of events occurring in the PZT-20/80 capacitor during the field cycling is the following:

(i) When a positive bias is applied to the top electrode of the pristine capacitor, upward oriented c -domains will be switched into downward oriented domains. Under the applied field, the 180° -switching of a -domains is normally much harder, which takes longer switching time than the 180° -switching of c -domains [14]. As a consequence, a transient charged 90° -domain wall is formed between the a -domain and the downward-oriented c -domains (Figure 7.6b). This charged 90° -domain walls is not energetically favorable because of the high density of the bound charges. P. Gao *et al.* [13] indeed observed that there is a few-nm thick transition layer with low polarization formed between the a -domain and the downward-oriented c -domain (Figure 7.6c). The authors showed that this transition layer consists of tiny domains with random polarizations, which helps to minimize the bound charge density at the domain walls. The effective (out-of-plane measured) polarization of this transition layer is low and therefore the layer acts as a transient dead layer. Although the authors did not discuss the endurance of this transition layer with time, they did observe that this layer can be removed under a higher external field through a switching of the a -domains into the opposite polarization state.

(ii) Now imagine that the field cycle is repeatedly applied over the capacitor, the domains inside the PZT layer repeatedly undergo polarization switching. The polarization switching of the a -domains are harder than the switching of the c -domains. Therefore, if the field duration in one direction of every field cycle is not long enough, the c -domains become switched but the a -domains have not become switched yet. As a consequence, a charged 90° domain wall (together with a transition layer with low net polarization) is formed between the two domains. Under field cycling, the switching of c -domains takes place repeatedly, the number of charged 90° domain walls is expected to increase with increasing

field cycle number. A large number of these charged domain walls then hinder the complete polarization switching of the c-domains, resulting in an obvious fatigue effect.

Figure 7.6: Schematic visualization of a/c domain pattern in the PZT-20/80 film. In a stable state, the a/c-domain walls are electrically neutral because of the head-to-tail arrangement of the polarization vectors. When a c-domain switched (into the downward direction), the domain wall between this switched domain and the adjacent a-domain becomes electrically charged. A zoom-in at this charged domain wall shows a few nm thick transition layer with low polarization, which acts as a ferroelectrically dead layer in the film.

Although the validity of the above speculative model is still an open question, some of the characteristic behaviors of the fatigue observed above can be qualitatively explained. First, if the field cycling has high field amplitude (as in Figure 7.4b) or the pulse duration is long enough (as in Figure 7.4d), the formation of relatively thick transition layers is less likely because the a-domains can be switched also, following the switching of the c-domains. Therefore, under these conditions the cycled capacitor is expected to have a smaller number of transition layers at charged 90° domain walls, resulting in a small or no fatigue effect. Second, the same argumentation holds for the frequency dependence (as in Figure 7.4a). For high frequencies the pulse length is short and there is no time to annihilate the transition layer by a-domain reversal. Third, the transition layers between the a-domains and the c-switched domains are not energetically favorable because of the same sign of the bound charges on the domain walls. Therefore, they will be erased by time (probably through the 180° switching of the a-domains) to form more stable head-to-tail domain configurations. Therefore, after a few days, the number of transition layers inside the cycled capacitor

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can also be substantially reduced by thermal activation of *a*-domain reversal. Obviously at high temperature, the erasure of the transition layers will be much quicker; therefore, the self-rejuvenation is strongly accelerated by temperature. These were shown up in Figure 7.5.

It appears challenging to directly experimentally verify the proposed model for the origin and mechanism of the fatigue in the PZT-20/80 device. However, to verify the role of the 90° domain walls to fatigue behavior, we suggest to investigate the fatigue behavior of the compressive strained PZT-20/80 film with only *c*-domains (without 90° *a/c* domain walls). This domain configuration of the PZT-20/80 thin film might be obtained by engineering the epitaxial strain of the film by choosing the substrate material or by varying the thickness of the PZT-20/80.

7.1.5 Conclusions

The fatigue behaviour of SRO/PZT/SRO capacitors depends on the Zr/Ti ratio; the PZT-20/80 shows strong temporary fatigue while PZT-52/48 and PZT 80/20 show no fatigue up to 10⁹ field cycles. The fatigue in the PZT-20/80 capacitor is proposed to relate to the presence of 90° domain walls, between *a*-domains and *c*-domains. Under field cycling, the domains are repeatedly switched, giving rise to the formation of transient low-polarization layers at the charged domain walls between *a*- and *c*-domains. These layers then act as dead layers inside the cycled capacitor, and subsequently hinder further polarization switching of the domains. The transient dead layers can be easily removed either by applying a high external field or an increased temperature, resulting in the rejuvenation of the fatigued capacitor.

7.2 Fatigue of SRO/PbZr_{0.52}Ti_{0.48}O₃/SRO under harsh conditions

7.2.1 Introduction

We previously showed that the SrRuO₃/PbZr_{0.52}Ti_{0.48}O₃/SrRuO₃ (SRO/PZT-52/48/SRO) capacitor is completely free of fatigue up to 10⁹ cycles, and this fatigue-free behaviour is likely to be continued under further prolonged cycling.

The fundamental reason behind this excellent fatigue resistance is that the PZT-52/48/SRO interfaces are epitaxial and atomically sharp without many lattice and compositional defects (except misfit dislocations). Therefore, the PZT-52 lattice is stable and unmodified by the field cycling and the cycled capacitor has the same structural and electrical behaviours as compared to the pristine capacitor.

Such fatigue-free SRO/PZT-52/48/SRO capacitors are promising for practical ferroelectric-based devices, which operate under alternating voltage cycles. However, in practice, the devices sometimes operate under harsh working conditions, such as very high drive fields (kV/cm up to MV/cm) or intermediate temperatures (up to 200°); and these harsh working conditions might affect the fatigue resistance of the capacitor. Until now, there are – to our best knowledge – no studies into the fatigue resistance of oxide-electrode PZT capacitors under harsh field-cycling conditions. This section therefore aims to investigate the fatigue behaviour of the SRO/PZT-52/48/SRO capacitor under field cycling with various field amplitudes and operating temperatures.

7.2.2 Methods

The investigated samples are $\text{SrRuO}_3/\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3/\text{SrRuO}_3$ (SRO/PZT-52/48/SRO) capacitors, which were epitaxially grown on SrTiO_3 (001)-oriented substrates. Thicknesses of the SRO and PZT layers are respectively of 100 and 250 nm. More details on the growth conditions can be found in chapter 3.

To investigate the effect of field cycling amplitude, the devices were cycled under field cycling with various field amplitudes at room temperature (25°C). To investigate the effect of operating temperature, the devices were cycled at various temperatures up to 140°C at constant field amplitude of 200 kV/cm.

7.2.3 Results

The polarization of the SRO/PZT-52/48/SRO capacitor is almost unchanged under field cycling at room temperature with the field amplitude up to 480 kV/cm, indicating an excellent fatigue-resistant behavior (Figure 7.7a). However, when the field amplitude is increased to 560 kV/cm, the capacitor remains fatigue free until about 10^7 cycles, but then shows a sudden event that causes an anomalously large increase of (apparent) remnant polarization values. Note that these remnant

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polarization values were automatically extracted from the measured P-E loop by the Aixacct software. As discussed later, this event is the electrical breakdown of the capacitor. After this event the (apparent) polarization varies randomly. Several other capacitors tested under field cycling of 560 V/cm also showed the (breakdown) event, but the event onset, i.e. the field cycle number at which it happens, varied widely (not shown here). Under cycling of higher field above 560 kV/cm, the capacitor showed breakdown at lower field cycle number, but more measurements need to be performed on a large number of capacitors to statistically determine a dependence of the breakdown onset on the field cycling amplitude.

To explain these observations, we take closer look into the P-E and I-E loops of the capacitor at different cycling states (Figure 7.7b,c). After being cycled with the field of 200 kV/cm, the capacitor has the P-E loop and the I-E switching peaks shifted slightly to the left (change from the dashed to the solid black curves) and the loops become more symmetric with respect to the axis origin than the pristine ones. There is no change in the slanting of the P-E loop. After being cycled with the field of 480 kV/cm, the capacitor shows the P-E loop also shifted to the left but also slightly more slanted with a small reduction in the remnant polarization as compared to the pristine loop. The switching peaks in the corresponding I-E loops becomes broader and the amplitude is reduced, reflecting the increased slanting of the P-E loop. However, the polarization value at the maximum measured field (200 kV/cm) is unchanged during field cycling. The P-E loop of the broken capacitor (cycled at 560 kV/cm for more than 10^7 cycles) has a double parabolic shape, corresponding to a nearly resistive I-E relation (the pink curves in Figure 7.7b,c, respectively). This indicates that high conductivity channels through the whole thickness of the PZT layer have been formed, which shunt the switching PZT capacitor and dominate the electrical behaviour. Therefore, after the breakdown moment, the capacitor shows non-ferroelectric behaviour and the measured polarization value becomes ferroelectrically meaningless.

The capacitor, that shows electrically the features of electrical breakdown under field cycling of 560 kV/cm, shows clearly degraded spots on the top surface, as observed in SEM images (Figure 7.8). Because the capacitor shows a conductive I-E curve of the capacitor, we can conclude that the degradation forms conductive channels through the whole thickness of the capacitor.

Figure 7.7: (a) Fatigue profiles of the SRO/PZT-52/48/SRO capacitor under field cycling (at room temperature) with various field amplitudes. The P-E loops (b) and I-E loops (c) of the capacitor at different cycling states.

Figure 7.8: SEM images of the broken SRO/PZT-52/48/SRO capacitor under field cycling of 560 kV/cm.

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The SRO/PZT-52/48/SRO samples become only slightly fatigued under field cycling (at 200 kV/cm amplitude) at increased sample temperatures, in the range from RT to 140° (Figure 7.9a). At 140°, after about 10⁸ field cycles, the capacitor shows electrical breakdown with structural degradation spots in the capacitor spots. The capacitors that were fatigued at elevated temperature but do not show structural degradation show a slight increase of the slanting of the P-E loop (Figure 7.9b). The broken capacitor shows the P-E loop with a double parabolic shape, which corresponds to a nearly resistive I-E relation (not shown here).

Figure 7.9: (a) Fatigue profiles of the SRO/PZT-52/48/SRO capacitor under field cycling at various operating temperatures. The cycling was at 200 kV/cm and 100 kHz. (b) The P-E loops of the capacitor at different cycling states at 100°.

7.2.4 Discussion

The SRO/PZT-52/48/SRO capacitor still shows excellent fatigue resistance as long as the field cycling amplitude is less than some critical value, above which electrical breakdown occurs after prolonged cycling.

The pristine capacitor shows a slight positive imprint (P-E loop shifted to the positive field axis), implying that there is a small intrinsic internal field pointing towards the top electrode. The presence of the internal field can be attributed to several origins such as the epitaxial strain at the bottom part of the PZT layer (through the flexoelectric effect) [15], induced by the strain gradient caused by misfit dislocations at the PZT-52/SRO bottom interface [16], and/or a net excess

positive charge near the bottom electrode, most likely due to oxygen deficiencies at the misfit dislocations [17].

We speculatively propose that the field cycles redistributed the charged defects, which are most likely oxygen vacancies, inside the PZT layer. As discussed previously in chapter 6, the forward and backward motion of the domain walls because of repeated domain switching under field cycling give rise to motions of the oxygen vacancies inside the layer. Upon field cycling, these charged defects might be redistributed in such a way to reduce the internal field in the capacitor. For example, a larger density of oxygen vacancies is in the top part than in the bottom part of the PZT layer. By this way, the positively charged defects produce an effective field pointing toward the bottom electrode, reducing the effect of the intrinsic internal field, as shows up in the more symmetric P-E loop of the cycled capacitor. Under high-field cycling and/or at high operating temperature, the SRO/PZT/SRO capacitor shows a little polarization fatigue with some increased slanting of the P-E loop. Currently, we cannot draw definite conclusions on what additionally happens in these cycled capacitors. However, we suspect that these small fatigue features are related to small electrically and microstructurally changes at some local defective locations at the interfaces. These changes might cause a small variation in the nucleation energy of reverse domains at the interface, resulting in an increased spread of switching peaks and a slanting of P-E loop. The breakdown of the capacitor under field cycling is believed to initiate from a single or only a few defective locations at the capacitor interfaces which suffers concurrently the transient depolarization field during the domain switching and the applied field cycle. Characterizations on the cross-sectional structure of the capacitor need to be performed to verify this statement. The statistical breakdown strength, i.e. the field amplitude, and the breakdown onset, i.e. the field cycle number at which the breakdown occurs, of the capacitor is expected to depend strongly on the crystalline orientation and the microstructure (porosity, grain boundaries, interface roughness) of the layers. Further experiments on films with different crystalline structures and microstructures are needed to verify this suggestion.

7.2.5 Conclusion

The SRO/PZT-52/48/SRO epitaxial thin-film capacitor shows excellent fatigue resistance because of the high crystalline quality and epitaxial interfaces. However, the capacitor shows electrical breakdown effect under field cycling with high field amplitude and operating temperature. The electrical breakdown shows up as a local severe structural degradation in the capacitor, which is expected to start at the capacitor interfaces under the effect of the transient depolarization field arising from the switching and the external field.

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Chapter 8

Summary and outlook

8.1 Research summary

Ferroelectric materials have been used in many applications such as non-volatile memory devices, nano- and micro-electromechanical systems, and advanced electronic components. However, these ferroelectric-based devices show instability and deficiency after a prolonged period of working under drive AC voltage. These issues are due to the so-called polarization fatigue, i.e. the loss of polarization of the integrated ferroelectric capacitors upon repeated field cycling. Understanding on the fatigue behavior of ferroelectric capacitors, particularly the characteristic features, the origin(s), and the mechanism(s) of fatigue, will provide practical solutions to enhance the fatigue resistance and consequently the stability of the devices. This project therefore aimed to gain further insight into the origin(s) and the mechanism(s) of how ferroelectric capacitors become fatigued under repeated field cycles.

Since the 1990s, together with the rapid growth of the use of ferro/piezoelectric materials for technological applications, polarization fatigue of the devices has also attracted much research attention. Over three decades, a large body of data on various aspects of the polarization fatigue, such as fatigue onset, field-cycling condition dependence, electrode-material dependence, ferroelectric and structural properties of fatigued capacitors, has been reported, as reviewed in **chapter 2**. However, despite a huge amount of data reported, the picture on the fatigue characteristic features still remains ambiguous and the models on the origins

and mechanisms of fatigue still remains controversial. These problems are due to several factors. First, the ferroelectric films investigated in previous studies, commonly fabricated by chemical solution deposition, contain many different kinds of defects in a highly defective microstructure. It is known that polarization fatigue is a defect-originated phenomenon. Therefore, in such polycrystalline, defective capacitors, there must be multiple scenarios concurrently involved in the development of the observed fatigue. Consequently, they exhibit unpredictable fatigue behaviors due to unknown underlying mechanism(s). Second, the traditional way to interpret the fatigue of the capacitor is based on the graphic profile of the remnant polarization as function of the field cycle number. This sometimes leads to incorrect interpretations because one does not know exactly how the capacitor electrically and structurally responds to field cycling. The deduced models for fatigue origins and mechanisms therefore lack of supporting direct evidence.

To create breakthrough new understanding into the origins and mechanisms of fatigue, the research needs to be performed under the following approaches. First, the ferroelectric sample for investigation should be well controlled in term of defects and microstructures. For this requirement, epitaxial thin-film structures which have dense microstructures and atomically sharp interfaces and fabricated by a well-controlled technique such as pulse laser deposition are promising candidates. Second, together with the investigation into the fatigue profiles of the samples, direct characterizations into the domain switching behavior and the interface structure of capacitors at different cycling states needs to be performed. These measurements will provide strong evidence on how the capacitor reacts with repeated field cycles, from such measurements more realistic and plausible models for the fatigue development can be established. Characterization techniques such as transmission electron microscopy, X-ray photoelectron spectroscopy, and piezoresponse force microscopy can be used for these tasks. Thus we conclude that using the appropriate device structures in combination with suitable characterizations will allow us to gain more insight into what happens in fatiguing ferroelectric samples.

Based on the discussion above, we have performed various experiments on devices of different designs with the aim to gain further understanding of why and how ferroelectric capacitors, particularly with metal electrodes, become fatigued under field cycling (**chapter 3-7**). The benchmark sample for investigation is the $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) epitaxial thin-film capacitor, grown on a SrRuO_3 -buffered

SrTiO₃ substrate by pulse laser deposition (PLD). PZT is the most commonly used ferroelectrics with a high polarization value. By PLD, we are able to control and engineer well the microstructure of the capacitor. Because the fatigue in thin-film capacitor originates mainly from the interface, we first designed the capacitor with different interface structures and investigated the resulting fatigue behavior. Second, we ferroelectrically and structurally characterized the capacitors at different cycling states to understand how they become fatigued. A brief summary on each of the research objectives is given below:

First, we identified the main origin of fatigue in metal-electrode capacitors by investigating the dependence of the fatigue behavior on the top-interface structure. To engineer the capacitor top interface, we varied the material (conductive oxide such as SrRuO₃ vs metal such as Pt, Au) and the fabrication procedure (*in situ* vs *ex situ*) of the top electrode. The fatigue behaviour was found to be directly related to microstructure of the top interface. Capacitors with *ex situ* deposited metal top electrodes showed an as-grown 1.5 nm thick defective dielectric layer at the top interfaces and became rapidly fatigued after only 10³-10⁴ field cycles. Capacitors with *in situ* deposited metal top electrodes show clean top interfaces without any defective layer and became fatigued much later, after about 10⁷-10⁸ field cycles. Capacitors with both SRO electrodes show atomically sharp epitaxial interfaces and were free of fatigue for a least 10⁹ cycles. The defective dielectric layer at the *ex situ* metal/PZT interfaces contains carbon contaminants, which arise from the exposure of the PZT surface to ambient atmosphere during the *ex situ* fabrications. *In situ* removals of this defective layer significantly enhance the fatigue resistance of the capacitor. These results clearly indicate that an interfacial dielectric defective layer is the major origin of polarization fatigue in ferroelectric capacitors with conventional *ex situ* metal electrodes, confirming the previous theoretical proposition in literature. This work also shows that *in situ* fabrication of metal electrodes is a promising solution to enhance fatigue resistance of ferroelectric devices. Details of this research was presented in **chapter 3**.

Second, we answered the question of how a 1.5 nm thick defective layer at the *ex situ* metal/ferroelectric interface can make these capacitors rapidly become fatigued under field cycling. To answer the question, we characterized the fatigue-profile dependence on field cycling conditions, the domain switching, and the interface structure of the Pt-sputtered/PZT/SRO capacitor (with Pt electrode made by *ex situ* sputtering) during field cycling. The polarization fatigue

was observed to be practically independent of the field cycling conditions and only to depends on the number of field cycle. The fatigued capacitors become switchable again under sufficiently high external field (much higher than needed to switch the pristine capacitor), but the switching is asymmetric between the two polarization directions. However, both capacitor interfaces stay structurally unmodified under field cycling, indicating that no degradation in the capacitor structure occurs. Guided by these findings, we proposed that electrons were injected through the interface under the depolarization field and then they became trapped at the defective layer, subsequently inhibited the nucleation of domains at this interface, leading to the polarization fatigue in the device. This work is presented in **chapter 4**.

Capacitors with *in situ* deposited metal electrodes are outperformed in fatigue resistance with several orders of magnitude in field cycle number compared to capacitors with conventional *ex situ* deposited metal electrodes. However, such capacitors still become strongly fatigued after prolonged field cycling. One needs to understand the mechanism behind this fatigue to further increase the fatigue resistance of metal-electrode capacitors. We discuss these topics in **chapter 5** based on investigations into domain switching and the interface microstructure of the Pt-inPLD/PZT/SRO structure (fabricated by *in situ* pulsed laser deposition) at different cycling states. Most importantly, the Pt-inPLD/PZT interface is found to structurally degrade during field cycling to form a non-ferroelectric, degraded layer. This structural decomposition is thought to be caused by the depolarization field during the polarization switching under repeated field cycles. The interfacial PZT-degraded layer is then quantitatively modeled to screen the external field, consequently suppresses polarization switching of the cycled capacitor, resulting in the observed fatigue effect. As a result, to further improve the fatigue resistance of the sample, one needs to improve the adhesion/structural connectivity between the ferroelectric layer and the electrode in order to strengthen the interface against the repeated depolarization field during field cycling. This can be done by inserting a conductive oxide or adhesion layer at the metal/ferroelectric interface.

The capacitors with *ex situ* deposited metal electrodes become rapidly fatigued but then ferroelectrically "revive" again by the so-called polarization rejuvenation process. In this process, the polarization is recovered under the application of field cycling/DC bias. Investigations into this effect will provide more information on how the capacitor has become fatigued priorly and also give

indications how one rejuvenate and reuse the capacitors after the (first) fatigue. We observed that the rejuvenation of fatigued Pt-sputtered/PZT/SRO capacitors strongly depends on the DC-bias/field cycling application conditions. These data lead to the proposition that trapped electrons at the Pt/PZT interface in the fatigued capacitor are compensated by the accumulating oxygen vacancies which migrate under the applied field. The rejuvenated capacitors are then observed to fatigue again after 10^7 - 10^8 cycles, which means 10^4 times more fatigue resistant than the as-grown capacitors. In the second-fatigued state, the capacitor shows a relatively thick PZT-degraded layer at the top interface. This indicates that the fatigue mechanism of the rejuvenated capacitor is similar to that of the *in situ* metal-electrode capacitors, which is sequence of decomposition of the interfacial PZT lattice by the switching depolarization field and the field screening effect causing the polarization switching suppression in the cycled capacitor. This research is presented in **chapter 6**.

Last but not least, we extended some investigations into the fatigue behaviour of SRO/PbZr_xTi_{1-x}O₃/SRO capacitors with respect to the effect of the Zr/Ti ratio of the PZT layer and harsh field cycling conditions on the fatigue. The fatigue of SRO/PbZr_xTi_{1-x}O₃/SRO capacitors is observed to be dependent on the Zr/Ti ratio: PZT with Zr/Ti of 20/80 shows strong temporary fatigue while the ones with 52/48 and 80/20 ratio show no fatigue. We propose that 90° domain walls between in-plane oriented a-domains and out-of-plane oriented c-domains is the origin of fatigue in the PZT-20/80. Under field cycling, the domains are repeatedly switched, giving rise to the formation of transient charged 90° domain walls, which subsequently hinder further polarization switching of the domains. Further, we show that SRO/PbZr_xTi_{1-x}O₃/SRO capacitors with Zr/Ti of 52/58 are promising for application because they showed almost completely fatigue-free behaviour under field cycling with various field amplitude and operating temperature. However, if the conditions become too harsh (with higher field and temperature), the capacitor will show catastrophic electrical breakdown, showing up in some permanent structural degradation spots. All these data are presented in **chapter 7**.

Overall, this thesis provides a wide range of experimental data on the ferroelectric and structural behaviours of PZT capacitors, giving direct evidence for modeling the development of fatigue in these samples. First, the long-standing suggestion based on phenomenological observations that fatigue in ferroelectric

thin films originates mainly from the capacitor interface is now proven. Second, the mechanism of fatigue is clearly shown to be strongly dependent on the specific interface microstructure of the investigated capacitor. This work not only provides new key insight into the physical picture of polarization fatigue but also provides a clear guide on how to interpret existing data in literature.

8.2 Implications and outlook

From the performed studies, we conclude that there are basically two efficient ways to enhance the fatigue resistance of metal-electrode ferroelectric capacitors. One, improve the purity of the metal/ferroelectrics interface by the use of in situ electrode fabrications. Two, strengthen the bonding between electrodes and ferroelectric layers by the use of a conductive oxide and/or adhesion layer. These solutions consequently increase the stability of the ferroelectric-based devices under AC drive voltage.

Although the studies in the thesis are performed on PZT epitaxial films, the obtained knowledge can be applied to a certain extent for PZT sol-gel polycrystalline films or ceramics, which are currently used in most practical devices. We expect that the fatigue effect in these devices still mainly comes from the capacitor interfaces. Particularly for the case of Pt/PZT/Pt capacitors grown on a Si substrate in which the PZT layers are made by sol-gel technique and the Pt electrodes made by conventional *ex situ* sputtering, we expect that the top interface will contribute more to the development of fatigue than the bottom interface. This is because the defective contamination layer on the surface of the Pt bottom layer will be (partly) removed during the annealing step needed for the crystallization of the PZT structure. We also expect that the polycrystalline film and ceramics will show a fatigue onset at somewhat higher field cycle number and a slower fatigue rate compared to the epitaxial-film devices discussed in this thesis. This is because in these devices the switching depolarization fields at the interfaces are lower due to a less well defined domain structure and the partly screening by charged defects and grain boundaries, resulting in less electron injection and thus a slower fatigue. However, in such polycrystalline structures, other scenarios such as the migration and accumulation of oxygen vacancies, the presence and/or formation of void defects and grain boundaries can also be involved into the development of fatigue, subsequently resulting in a fatigue

behavior with different features. To further understand the fatigue in these capacitors, one also needs direct characterizations into the microstructure and ferroelectricity of these capacitor at different cycling states.

The knowledge can also be applied to capacitors of other ferroelectric materials since the dominant fatigue mechanism is expected to be related more to the capacitor interfaces and less to the ferroelectric material. For these devices, we also expect that electron injection will happen during the domain switching of the capacitor. The fatigue is dependent on the electron injection at the interface, which depends on the switchable polarization of the ferroelectric material, the microstructure and purity of the electrode/ferroelectric interface. Ferroelectric devices which have less switchable polarization, cleaner interfaces, and stronger ferroelectric-electrode bonding are expect to show more fatigue resistance.

The thesis clarifies some unclear aspects of and provides breakthrough understanding into the origins and mechanisms of polarization fatigue. However, it also raises some new questions that deserve to be investigated further. The first open question is the direct experimental verification of the electron injection across the capacitor interface under field cycling. The second is about direct verification of the electron trapping and charge built-up at the defective metal/ferroelectric interface layer. Then there is the possibility to use *in situ* TEM to characterize and observe domain states of the capacitor under field cycling. The fourth one is whether or not the oxygen vacancy accumulation accelerates the local breakdown of the cycled capacitor interface. The final question is whether one can experimentally verify the proposed fatigue mechanism in the tetragonal PZT (20/80) capacitor.

Samenvatting

Ferroelektrische materialen worden in veel toepassingen gebruikt. Bijvoorbeeld in niet-vluchtige geheugenchips en in micro-mechanische systemen. Echter, dergelijke devices zijn veelal instabiel onder langdurig gebruik, met name onder wisselspannings (AC) bedrijf. Het probleem is de zogenaamde 'polarization fatigue' (vermoeiing van de elektrische polarisatie), d.w.z. het verlies van polarisatie van de ferroelektrische capacitors in deze devices onder langdurige AC operatie. Een beter begrip van het vermoeiingsgedrag van ferroelektrische capacitors zou praktische oplossingen kunnen opleveren om de stabiliteit van devices, die gebruik maken van dergelijke capacitors, te verbeteren. Het doel van dit project is om het inzicht in de mechanismes die leiden tot vermoeiing onder AC operatie te vergroten.

Er is al veel literatuur beschikbaar over verschillende aspecten van polarisatie-vermoeiing, zoals over het begin van de vermoeiing, de afhankelijkheid van AC-elektrisch veld parameters, afhankelijkheid van de materialen die gebruikt worden voor de elektroden van de capacitor, en van de ferroelektrische en kristallijne eigenschappen van het ferroelektrische materiaal (**Hoofdstuk 2**). Echter, er is nog veel onduidelijkheid over de (modellering van de) onderliggende mechanismes die leiden tot vermoeiing. De reden hiervoor is dat de ferroelektrische dunne films die in het verleden zijn onderzocht, veelal gemaakt werden met behulp van depositie vanuit een chemische oplossing, wat over het algemeen de creatie van veel en verschillende types defecten in de dunne laag veroorzaakt. In dergelijke polykristallijne capacitors wordt de polarisatie vermoeiing daarom tegenwoordig toegeschreven aan deze defecten, veelal via verschillende, vaak onbekende scenario's. Ten tweede is de 'traditionele' manier om het vermoeiingsproces te beschrijven gebaseerd op de verandering van de remanente polarisatie als functie van het aantal AC-cycli dat de capacitor heeft ondergaan. Dit leidt soms tot verkeerde

interpretaties en conclusies ten aanzien van het onderliggende vermoeiingsmechanisme. Vanwege deze overwegingen hebben wij er voor gekozen om voor ons onderzoek als referentie capacitor een epitaxiaal gegroeide $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) dunne film capacitor te gebruiken. De PZT laag is gegroeid op een epitaxiaal gegroeide SrRuO_3 onder-electrode, op een éénkristallijn SrTiO_3 substraat. Alle lagen zijn met behulp van gepulste laser depositie (PLD) gededponeerd. Door middel van PLD kunnen we de microstructuur van de lagen, en met name van de PZT laag, controleren en engineren. PZT is het meest gebruikte ferroelektrische materiaal vanwege zijn hoge polarisatie waarde.

Als eerste identificeerden we de voornaamste oorzaak van vermoeiing in capacitors met metaal topelectroden, door de afhankelijkheid van het vermoeiingsgedrag van de microstructuur aan het scheidingsvlak van de top metaal electrode en de ferroelektrische laag te onderzoeken (**Hoofdstuk 3**). We ontwierpen dit scheidingsvlak door verschillende electrode materialen te gebruiken (geleidende oxides zoals SrRuO_3 versus metalen zoals Pt of Au) en de fabricage procedure (*in situ* versus *ex situ* depositie) van de electrode. We vonden dat het vermoeiingsgedrag direct gerelateerd was aan de microstructuur van de ferroelektrische laag aan het scheidingsvlak. Capacitors met een *ex situ* gededponeerde metalen top electrode vertoonden een 1.5 nm dikke defect-rijke laag aan het scheidingsvlak en vermoeiden al snel, d.w.z. na slechts 10^3 - 10^5 AC-cycli. Capacitors met een *in situ* gededponeerde metalen top electrode vertoonden een schoon, defect-vrij scheidingsvlak en vermoeiden pas na 10^7 - 10^8 AC cycli. Capacitors met twee SrRuO_3 elektroden lieten atomair scherpe, epitaxiale scheidingsvlakken zien en vertoonden geen vermoeiing tot tenminste 10^9 cycli. De defect-rijke laag aan het *ex situ* metaal electrode/PZT scheidingsvlak bevatte koolstof verontreinigingen, die werden veroorzaakt door de blootstelling van het PZT oppervlak aan de omgevingsatmosfeer. *In situ* verwijdering van deze defectrijke laag vergrootte de weerstand tegen vermoeiing sterk. Deze resultaten geven duidelijk aan dat een defectrijke, dielectrische laag aan het scheidingsvlak de voornaamste oorzaak is van de polarisatievermoeiing in ferroelektrische capacitors met conventionele *ex situ* gededponeerde metaal electoden.

Vervolgens zochten we een antwoord op de vraag hoe een dergelijke slechts 1.5 nm dikke laag aan het scheidingsvlak een zo snelle vermoeiing van de capacitor kan veroorzaken (**Hoofdstuk 4**). Om deze vraag te kunnen beantwoorden, onderzochten we de afhankelijkheid van het polarisatie-versus-cycli vermoeiings-

profiel van de parameters van de vermoeiingscyclus, polarisatiedomain schakeling (switching) en de microstructuur aan het scheidingsvlak van capacitors met een *ex situ* gesputterde (i.p.v. PLD) top Pt electrode. De polarisatievermoeiing bleek bijna onafhankelijk van de vermoeiingscyclus parameters en alleen maar af te hangen van het aantal cycli. De remanente polarisatie van vermoeide capacitors, dus met sterk gereduceerde remanente polarisatie, kon weer grotendeels worden hersteld wanneer een voldoende grote amplitude van het cyclus elektrisch veld werd gebruikt (veel groter dan nodig om de polarisatie van een niet-vermoeide capaciteit te doen schakelen). Maar we vonden ook dat de polarisatiehystereseloop van de vermoeide capacitor asymmetrisch was voor de twee polarisatie richtingen. Echter, de scheidingsvlakken aan beide elektrodes veranderen structureel niet gedurende de vermoeiing. Geleid door deze observaties veronderstellen we dat elektronen worden geïnjecteerd vanuit de elektrode onder invloed van het sterke depolarisatie veld dat bestaat tijdens polarisatie switching. Deze elektronen worden ingevangen in zogenaamde 'traps' in de defectrijke laag en verhinderen vervolgens de nucleatie van polarisatiedomains aan dit scheidingsvlak, hetgeen leidt tot de polarisatievermoeiing van het device.

Capacitors met *in situ* gedeponeerde metaal elektroden vertonen pas na vele orde groottes meer cycli vermoeiingsgedrag ten opzichte van devices met conventionele *ex situ* gedeponeerde metaal elektroden. Maar zelfs deze capacitors vertonen uiteindelijk vermoeiingsgedrag na een groot aantal cycli. De vraag is wat het mechanisme is dat dit veroorzaakt. We vonden een antwoord op deze vraag op basis van onderzoek naar domain switching en veranderingen in de microstructuur aan het scheidingsvlak van devices met *in situ* gedeponeerde Pt elektroden op verschillende momenten gedurende het vermoeiingsproces (**Hoofdstuk 5**). Het scheidingsvlak bleek structureel te degraderen gedurende de vermoeiing en een niet-ferroelectrische, structureel sterk gedegradeerde laag werd gevormd. We denken dat deze structurele decompositie wordt veroorzaakt door het depolarisatie veld dat ontstaat tijdens de veelvuldig herhaalde polarisatie switching. De niet meer ferroelektrische, gedegradeerde PZT laag schermt het externe aangelegde elektrische veld af, waardoor het switchen van de polarisatie wordt onderdrukt hetgeen tot uiting komt in de geobserveerde vermoeiing.

Dus om het vermoeiingsgedrag te verbeteren is het nodig om de kristalrooster van de ferroelektrische laag aan het scheidingsvlak te beschermen tegen het cyclisch optredende het depolarisatieveld. Dit kan door een geleidend oxide of adhesielaag

aan te brengen op het scheidingsvlak die de hechting tussen het kristalrooster van de ferroelektrische laag en de metaal electrode verbetert.

De capacitors met *ex situ* gedeponeerde metaal elektrodes vermoeien zeer snel, maar de ferroelektriciteit kan weer worden opgewekt door het zogenaamde verjongings-proces. Onderzoek naar dit effect kan aanwijzingen geven hoe dit proces werkt en hoe het gebruikt kan worden om vermoeide capacitors te hergebruiken/'repareren'. We zagen dat de verjonging van vermoeide capacitors met gesputterde Pt elektrodes sterk afhangt van de condities gedurende het vermoeiingsproces, zoals de AC-cyclus parameters of de DC veld amplitude bij DC-veld vermoeiing. Op basis van de deze informatie veronderstellen we dat de lading van de getrapte elektronen aan het Pt/PZT scheidingsvlak in de vermoeide capacitor wordt gecompenseerd door de langzame accumulatie van zuurstof vacatures in het rooster. Deze vacatures migreren onder invloed van het aangelegde veld. De verjongde capacitors vertonen pas opnieuw vermoeiing na 10^7 - 10^8 cycli, dus de weerstand tegen vermoeiing is een factor 10^4 groter dan die van niet-vermoeide capacitors. In deze tweede vermoeiingstoestand vertoont de capacitor een relatief dikke gedegradeerde PZT-laag aan het top scheidingsvlak. Dit duidt er op dat het vermoeiingsproces van de verjongde capacitor bestaat uit de opeenvolging van de degradatie van het PZT kristalrooster aan het scheidingsvlak en de afscherming van het aangelegde veld dat de onderdrukking van de polarisatie tot gevolg heeft in de vermoeide capacitor (**Hoofdstuk 6**).

Tenslotte breidden we het onderzoek uit naar het vermoeiingsgedrag van $\text{SrRuO}_3/\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3/\text{SrRuO}_3$ capacitors met een ferroelektrische PZT laag met een andere Zr/Ti verhouding en naar het gedrag onder hele zware vermoeiings condities (**Hoofdstuk 7**). Capacitors met de verhouding Zr/Ti=20/80 vertonen sterk vermoeiingsgedrag, terwijl die met een verhouding 52/48 en 80/20 geen vermoeiing vertonen. Onze verklaring is dat in de devices met 20/80 compositie de aanwezigheid van een groot aantal 90° domein wanden, met een hoge domein-wandenergie, tussen in-vlak geörienteerde a-domeinen en uit-vlak geörienteerde c-domeinen, de oorzaak is van dit vermoeiingsgedrag. Tijdens de AC-vermoeiing moeten de domeinen voortdurend schakelen tussen de a- en c-orientatie. Dit veroorzaakt de tijdelijke vorming van elektrisch geladen 90° domein wanden, die op hun beurt verdere polarisatie switching bemoeilijken en zelfs verhinderen. We laten verder zien dat $\text{SrRuO}_3/\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3/\text{SrRuO}_3$ capacitors met Zr/Ti=52/58 veelbelovend zijn voor toepassingen omdat ze bijna geen vermoeiing vertonen

onder zware vermoeiingscondities, d.w.z. hoge aangelegde AC velden en verhoogde temperatuur. Maar als de vermoeiingscondities te zwaar worden dan falen de capacitors door elektrische kortsluiting.

Samenvattend bevat dit proefschrift een breed scala aan experimentele gegevens ten aanzien van het ferroelektrische gedrag en veranderingen in de structuur van PZT capacitors, die relevant zijn voor het begrip van het ontstaan van ferroelectrische vermoeiing in deze devices. Gebaseerd op de gewonnen inzichten geven we suggesties voor twee manieren om de gevoeligheid voor vermoeiing van capacitors met metaal electrodes te verminderen: te eerste is het van belang het scheidingsvalk tussen de elektrode en de ferroelektrische laag zo schoon mogelijk te houden, wat kan worden bereikt door in situ depositie van de elektrode laag, of door in situ het top oppervlak van de ferroelektrische laag schoon te maken voor elektrode depositie. En ten tweede door de chemische verbinding tussen ferroelektrische laag en de metaal elektrode te verbeteren door geleidende oxides als elektrode en/of adhesie lagen te gebruiken.

List of publications

1. M. T. Do, N. Gauquelin, M. D. Nguyen, J. Wang, J. Verbeeck, F. Blom, G. Koster, E. P. Houwman, G. Rijnders, "Interfacial dielectric layer as an origin of polarization fatigue in ferroelectric capacitors", Scientific Reports 10, 7310, 2020 (Chapter 3).
2. M. T. Do, N. Gauquelin, M. D. Nguyen, J. Verbeeck, F. Blom, G. Koster, E. P. Houwman, G. Rijnders, "Interface degradation and field screening mechanism of bipolar-cycling fatigue in ferroelectric capacitors", Submitted to Acta materialia (Chapter 5).
3. M. T. Do, M. D. Nguyen, L. Bégon-Lours, F. Blom, G. Koster, E. P. Houwman, G. Rijnders, "Polarization fatigue and rejuvenation under bipolar field cycling of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ thin-film capacitors with sputtered Pt electrodes", in preparation for Journal of European Ceramic Society (Chapter 4 and 6).
4. M. T. Do, M. D. Nguyen, F. Blom, G. Koster, E. P. Houwman, G. Rijnders, "Polarization fatigue of $\text{SrRuO}_3/\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3/\text{SrRuO}_3$ epitaxial thin-film capacitors: Effect of Zr/Ti ratio and harsh cycling conditions", in preparation for AIP Advances (Chapter 7).

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