Influence of oxygen source on the ferroelectric properties of ALD grown Hf$\text{1-}_x\text{Zr}_x\text{O}_2$ films

Ruben Alcala$^1$, Claudia Richter$^1$, Monica Materano$^1$, Patrick D Lomenzo$^1$, Chuanzhen Zhou$^2$, Jacob L Jones$^3$, Thomas Mikolajick$^{1,4}$ and Uwe Schroeder$^1$

$^1$NaMLab gGmbH, Noethnitzer Strasse 64 a, 01187, Dresden, Germany
$^2$Analytical Instrumentation Facility, North Carolina State University, Raleigh, NC, United States of America
$^3$Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC, United States of America
$^4$Chair of Nanoelectronics, TU Dresden, Noethnitzer Strasse 64, 01187, Dresden, Germany

E-mail: ruben.alcala@namlab.com

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Abstract
Hafnium oxide (HfO$_2$), zirconium oxide (ZrO$_2$), and the solid-solution (Hf$_{1-x}$Zr$_x$O$_2$) system continue to be some of the most relevant ferroelectric materials, in particular, for their promising application in CMOS integrated ferroelectric memories. Recent understanding of the influence of oxygen supplied during film deposition on the structural phase formation process in Hf$_{1-x}$Zr$_x$O$_2$ films has drawn attention to a commonly overlooked parameter for tuning ferroelectric and electrical properties of these films. In this paper, a comparison of O$_3$ and O$_2$ plasma used as the oxygen source in an atomic layer deposition process for Hf$_{1-x}$Zr$_x$O$_2$ films within the full compositional range is discussed. A combination of structural and electrical characterization methods grant insight on the influence of each of the oxygen sources on the crystalline phase formation during deposition of Hf$_{1-x}$Zr$_x$O$_2$ films. These observations are then correlated to the material’s behavior regarding its ferroelectric and electrical properties; mainly, dielectric constant, ferroelectric remanent polarization, and number of electric field cycles to breakdown.

Keywords: ALD, PEALED, hafnium oxide, zirconium oxide, ferroelectric, ozone, oxygen plasma

(Some figures may appear in colour only in the online journal)

1. Introduction

In 2011, Böscke et al discussed a ferroelectric crystalline phase stabilization in doped HfO$_2$ films with thicknesses on the order of nanometers [1]. Almost simultaneously, ferroelectric behavior in Hf$_{0.5}$Zr$_{0.5}$O$_2$ thin films was also discussed [2]. These findings came at a time when traditional ferroelectrics, such as PZT and SBT, were struggling with scalability and Si compatibility issues [3]. In addition, the integration of HfO$_2$ and ZrO$_2$ as high-k dielectrics into microelectronic devices had already been adopted for dynamic random access memory and high-k gate dielectrics in metal oxide semiconductor transistors [4, 5]. Since then, HfO$_2$-ZrO$_2$ based oxides have gained widespread interest as ferroelectric materials; particularly for their application in novel ferroelectric memory technologies [6].
Under ambient conditions, both pure hafnia (HfO$_2$) and pure zirconia (ZrO$_2$) crystallize into a monoclinic structure ($m$-phase) with space group $P2_1/c$ when bulk materials are considered [7, 8]. Nevertheless, it has been long known that additional high-temperature phases of these fluoride-structured oxides, that is, a tetragonal (t-)$P4_2/mmc$ and cubic (c-)$Fm\bar{3}m$ phase, can be stabilized at room temperature in the form of thin films or nanocrystallites. This comes as a result of a significant difference in the surface to bulk free energy relation for grain sizes in the nanoscale and due to dopant distribution across grain boundaries [9–13]. In a similar fashion, the orthorhombic ($o$-) $Pca2_1$ phase, responsible for the ferroelectric behavior in HfO$_2$–ZrO$_2$ oxides, is also expected to be influenced by size and surface related effects. The origin of this ferroelectric phase has been extensively discussed in literature [14–16].

Nanometer-scale thin films of simple Hf$_{1-x}$Zr$_x$O$_2$ ($x = 0–1$) oxide compositions have already been reported to present ferroelectric behavior [17, 18]. Even so, additional doping of the oxide films, in an attempt to understand the ferroelectric behavior and improve the reliability of the material, has also been widely researched [19–21]. At the same time, factors such as the influence of the substrate [22, 23], the choice of electrode material [24, 25], and the annealing treatment [26, 27] have all been identified to influence the ferroelectric behavior of Hf$_{1-x}$Zr$_x$O$_2$ oxide films. Recently, the impact of oxygen and nitrogen vacancies on the phase formation process has been reported [28].

Different techniques for ferroelectric Hf$_{1-x}$Zr$_x$O$_2$ film depositions have been studied, such as atomic layer deposition (ALD), sputter deposition (PVD) [29] chemical solution deposition [30], pulsed laser deposition [31], and molecular beam epitaxy [32]. That said, ALD remains the most robust and well established method for the deposition of very thin oxide films, especially for CMOS processes, with a clear advantage in deposition conformity on three dimensional structures [33]. Multiple reports comparing different metal-precursor combinations for Hf$_{1-x}$Zr$_x$O$_2$ film deposition have been published [34–36]. In contrast, a comparison of oxygen sources for the same deposition process is rather uncommon [37, 38]. To better understand the role of the ALD oxygen sources and its link to the recently reported vacancy dependency on phase formation in Hf$_{1-x}$Zr$_x$O$_2$ films, this work focuses on analyzing the effects of O$_3$ and O$_2$ plasma during ALD growth and their influence on the ferroelectric properties of Hf$_{1-x}$Zr$_x$O$_2$ thin films.

2. Experimental

Hf$_{1-x}$Zr$_x$O$_2$ thin-films were deposited on (100) oriented p-Si wafer substrates via ALD in an Oxford OpAL tool. All films had a target thickness of 10 nm. Cyclopentadienyl-amine-based C$_p$-Hf[N(CH$_3$)$_2$]$_3$ and C$_p$-Zr[N(CH$_3$)$_2$]$_3$ were used as metal-organic precursors and were bubbled with Ar gas at 65 $^\circ$C and 70 $^\circ$C, respectively, to assist precursor delivery. Either O$_3$ gas or O$_2$ plasma was employed as the oxidizing agent. O$_3$ gas was obtained from a Sorbios ozone generator and was applied at a volume flow rate of 700 sccm with a 150 g m$^{-3}$ density. O$_2$ plasma was generated via an inductively coupled plasma source at 300 W and a 20 sccm O$_2$ gas flow rate. Key deposition parameters of the ALD process which were varied during this work were deposition temperature and oxidation exposure time. In addition, film composition was varied by modifying the Hf to Zr precursor cycle relation, defined here as Zr/(Zr + Hf), for a specific number of ALD cycles, referred to as a supercycle.

In order to evaluate electrical properties, TiN\(\backslash\)Hf$_{1-x}$Zr$_x$O$_2\backslash$TiN\(\backslash\)Ti\(\backslash\)Pt structured metal-insulator-metal (MIM)-capacitors were fabricated on (100) oriented p-Si substrates. 10 nm TiN layers were used as bottom and top electrodes and were deposited via sputtering in a Bestec ultrahigh vacuum sputter cluster at room temperature using a Ti target and N$_2$ plasma. 10 nm thick Hf$_{1-x}$Zr$_x$O$_2$ layers were deposited via the aforementioned ALD method. A 20 s postmetallization anneal (PMA) at 450 $^\circ$C in a N$_2$ atmosphere was employed to achieve a crystallization of the Hf$_{1-x}$Zr$_x$O$_2$ dielectric layer. Additionally, a 10 nm thick Ti layer and a 25 nm thick Pt layer were deposited via electron beam evaporation through a shadow mask as an adhesion and contact layer, respectively. In a final fabrication step, excess TiN was etched with a SC-1 procedure at 50 $^\circ$C for 5 min in a solution of H$_2$O, H$_3$O$_2$, and NH$_3$ at a 50:2:1 ratio, in order to isolate the contact pads.

Structural characterization of the deposited films was performed with a Bruker D8 Discover XRD Tool using a Cu Ka source with $\lambda = 0.154$ nm. X-ray reflectometry was utilized for film thickness determination; from which the growth per cycle (GPC) could also be extracted. Grazing incidence x-ray diffraction (GIXRD) and further diffraction peak analysis were used for crystalline phase identification and content determination. Furthermore, time-of-flight secondary ion mass spectrometry (TOF-SIMS) analyses were performed using a TOF SIMS V (ION TOF, Inc.) tool.

Electrical characterization was used to determine properties such as remanent polarization ($P_r$), electric field cycles to breakdown and dielectric constant ($k$) of the material, and was performed using an aixACCT TF Analyzer 3000. Dynamic hysteresis measurements (DHM) were performed using a 4 V triangular pulse signal at 1 kHz with additional field cycling performed at 100 kHz. The dielectric constant was extracted from the small-signal capacitance of CV-measurements.

3. Results and discussion

3.1. Mixed Hf$_{0.5}$Zr$_{0.5}$O$_2$ films

Based on previous work on the optimization of the ALD process for ferroelectric Hf$_{1-x}$Zr$_x$O$_2$ films [34, 37], a fixed metal-organic precursor pulse length and oxidation pulse length were evaluated under distinct deposition temperatures for Hf$_{0.5}$Zr$_{0.5}$O$_2$ films deposited using either O$_3$ or O$_2$ plasma as an oxygen source. As depicted in figure 1, the GPC, derived from the complete film thickness and the number of ALD cycles, maintained a mean value of around 0.81 Å/cycle in the case of O$_3$ and 0.92 Å/cycle in the case of O$_2$ plasma, with
initial layer growth on the TiN substrate. Despite the impurity presence, both oxygen sources presented a consistent GPC in the evaluated deposition temperature interval, suggesting a minimal interference with the growth process. The influence of impurities on ferroelectric performance shall be discussed later.

GIXRD analysis of the as-deposited Hf$_{0.5}$Zr$_{0.5}$O$_2$ films shows that these films are amorphous with only some nanocrystallite formation in the order of 1 to 5 nm grain size, as estimated by the Debye-Scherrer formula implemented on the weak diffraction peaks at the expected 2θ values of 28.5°, 30.4°, 30.8°, and 31.6° of the m(−111), o(111), t(011), and m(111) planes, respectively (figure 2) [45]. The slight increase in grain size was directly related to the deposition temperature. An exception to this subtle behavior was the Hf$_{0.5}$Zr$_{0.5}$O$_2$ film deposited at 350 °C with O$_3$ as an oxygen source for which a considerably larger increase in grain size to around 8–10 nm was observed.

Further peak analysis and peak deconvolution identified a trend of higher monoclinic phase (m-phase) fraction for increasing deposition temperatures (figure 3). Partial in-situ crystallization during the ALD process is anticipated, especially for higher deposition temperatures. Nevertheless, a divergence between oxygen source trends for the m-phase fraction at 350 °C can be identified. This observation leads to the assumption of a higher oxygen presence in the Hf$_{0.5}$Zr$_{0.5}$O$_2$ films deposited using O$_2$ as an oxygen source since such correlation has been reported for nanoscale Hf$_{0.5}$Zr$_{0.5}$O$_2$ films [28, 46]. Because the values presented in figure 3 are extracted from the GIXRD patterns, and therefore only represent phase fraction percentage relative to the crystallized portion of the film, the m-phase fraction difference between O$_3$ and O$_2$ plasma at 350 °C, with the additional consideration of the amorphous fraction of the film, is expected to be larger due to the difference in crystallization identified in figure 2. Further diffraction peak deconvolution of the t/o-phase is known to be difficult and was not undertaken in this work.

GIXRD analysis of post-metalization annealed MIM-capacitor stacks with Hf$_{0.5}$Zr$_{0.5}$O$_2$ layers deposited at different ALD temperatures was also performed. Additional determination of the orthorhombic (α-) and tetragonal (t-) phase content, in addition to the m-phase, was now possible due to an increase in diffraction peak intensities and average crystalline grain size. Nevertheless, due to the overlapping nature of the main reference diffraction peaks of these phases, that is, (111)$_o$ at 2θ equal to 30.4° and (011)$_t$ at 2θ equal to 30.8°, a combined phase fraction value was preferred.

As shown in figure 4, the overall phase composition of the Hf$_{0.5}$Zr$_{0.5}$O$_2$ layer when using O$_2$ plasma as an oxygen source presented little relation with respect to deposition temperature, showing only a slight increase in m-phase for higher deposition temperatures. In contrast, for O$_3$, at 250 °C the Hf$_{0.5}$Zr$_{0.5}$O$_2$ layer remained mostly amorphous even after the PMA treatment and, for increasing deposition temperatures, a larger amount of a monoclinic phase was observed. This trend fits well with previous observations in figure 3 for O$_3$ and illustrates how the as-deposited stabilized monoclinic phase limits α- and t-phase formation.

Table 1. TOF-SIMS derived impurity comparison for Hf$_{0.5}$Zr$_{0.5}$O$_2$ films deposited at 300 °C using different oxygen sources. C concentration for the bottom electrode (BE) interface is excluded due to interest in carbon contribution only from the deposition process. For the OH$^-$ and TiO$^-$ ions, the values presented are relative to HfO$_2^+$ + ZrO$_2^+$.

| Impurity | Unit | In bulk | At BE interface |
|----------|------|---------|-----------------|
| C        | 10$^{20}$ cm$^{-3}$ | 1.5    | 6.1             |
| OH$^-$   | a. u. | 0.02   | 0.02            |
| TiO$^-$  | a. u. | 0.00   | 0.00            |



Figure 1. Average GPC of Hf$_{0.5}$Zr$_{0.5}$O$_2$ films with respect to different deposition temperatures. GPC was determined from final film thickness divided by number of cycles. All films had a thickness of around 10 nm.
Figure 2. GIXRD patterns of as-deposited Hf$_{0.5}$Zr$_{0.5}$O$_2$ films obtained at different deposition temperatures using (a) O$_3$ and (b) O$_2$ plasma as the oxygen source. Diffraction patterns for pure phase powder samples are included at the bottom of each plot.

Figure 3. Monoclinic phase ($m$-phase) fraction of as-deposited Hf$_{0.5}$Zr$_{0.5}$O$_2$ films when using O$_3$ or O$_2$ plasma as an oxygen source, deposited at distinct temperatures. Phase fraction percentages are with respect to the crystallized portion of the film; the amorphous portion is not considered.

On the same structures, a DHM was used to assess remanent polarization values ($P_r$) at a pristine state (figure 5(a)). For O$_2$ plasma, a lower $P_r$ value was only identified when using a 250 °C deposition temperature. A $P_r$ of around 22.5 μC cm$^{-2}$ is reached at 280 °C and no relevant improvement is obtained for higher deposition temperatures. Considering that no clear change in $m$-phase composition was identified for O$_2$ plasma with respect to deposition temperature in figure 4, it is presumed that a larger $t$-phase stabilization, visible as a peak shift in GIXRD patterns depicted in figure 5(b), is responsible for
the reduced $P_r$ at 250 °C. Regarding O$_3$, the increasing m-phase trend identified in figure 4 is coherent with the decreasing $P_r$ trend in figure 5(a). In addition, the amorphous case at 250 °C correspondingly lacked any ferroelectric behavior.

From this analysis, it was determined that the deposition temperature has little effect on the crystalline phase content and therefore little effect on the $P_r$ of the Hf$_{0.5}$Zr$_{0.5}$O$_2$ layer when using O$_2$ plasma as an oxygen source. In contrast, when using O$_3$ as an oxygen source, crystallization was limited at 250 °C and an underlying trend of increasing m-phase content was identified for increasing deposition temperatures. Both phenomena have a clear detrimental effect on the ferroelectric properties of the film. Regardless, at the 280 °C–300°C deposition temperature range, similar stabilization of the polar o-phase is expected, independent of the oxygen source, due to similar $P_r$ values and $o + t$ diffraction peaks observed in GIXRD.

The influence of the oxidation exposure length during the ALD process on the ferroelectric properties of Hf$_{0.5}$Zr$_{0.5}$O$_2$ films was also studied for both O$_3$ and O$_2$ plasma. First, PMA treated MIM-capacitor stacks with a 10 nm Hf$_{0.5}$Zr$_{0.5}$O$_2$ dielectric layer deposited at 300 °C and varying oxidation exposure lengths were characterized using GIXRD. Once more, diffraction peak deconvolution and intensity comparison were used to determine the phase fraction distribution in the Hf$_{0.5}$Zr$_{0.5}$O$_2$ layer. For O$_3$, an oxidation exposure length of 10 s presented a weak diffraction peak pattern indicating limited crystalline phase development and a shorter 5 s time interval lacked any relevant crystalline phase development. In effect, both pulse lengths are excluded from figure 6. The underlying reason behind these deficiencies for O$_3$ is expected to be insufficient exposure time to achieve a full reaction with the substrate surface during the half-cycle of the ALD process. Regarding O$_2$ plasma, no effect of reduced crystallization in the Hf$_{0.5}$Zr$_{0.5}$O$_2$ films was observed at any of the evaluated oxidation exposure lengths. Longer oxidation exposure lengths led to increased m-phase fraction, regardless of the oxygen source (see figures 6 and 7(a)). This is due to the direct relation between oxidation exposure length and oxygen content in the Hf$_{0.5}$Zr$_{0.5}$O$_2$ layer [47].

As depicted in figure 7(a), $o + t$-phase fraction appears to remain constant between the 3 s and 5 s oxidation exposure lengths when using O$_2$ plasma as an oxygen source. Nevertheless, a closer analysis of the combined (111)$_o$/(011)$_t$ diffraction peak (figure 7(b)) clearly identifies a right-shift in the peak position for the 3 s exposure length with respect to the 5 s exposure length. This qualitatively confirms a larger t-phase fraction in the Hf$_{0.5}$Zr$_{0.5}$O$_2$ layer when using the shorter exposure length. As a result, the O$_2$ plasma exposure length series exhibits a transition from a film with high t-phase stabilization at 3 s, through a film with mostly o-phase stabilization at 5 s, up to films with increasing m-phase content for longer exposure lengths. This coincides with the previously reported phase development dependence on the oxygen content in the Hf$_{0.5}$Zr$_{0.5}$O$_2$ film [28].

DHM were also performed on these structures to assess remanent polarization ($P_r$) in the pristine state (figure 8). For both oxygen sources, the $P_r$ values fit well with the trends observed in the structural analysis: for O$_3$, the mostly amorphous Hf$_{0.5}$Zr$_{0.5}$O$_2$ layer obtained from a 5 s oxidation exposure length deposition showed no remanent polarization ($P_r$) and the Hf$_{0.5}$Zr$_{0.5}$O$_2$ layer with reduced crystalline phase development at 10 s presented only a small $P_r$. With regard to the rest of the exposure lengths, a maximum $P_r$ is reached at a 20 s exposure length after which only equal or smaller $P_r$ values are obtained due to increasing m-phase fraction or, rather, a decrease in o-phase content (see figure 6). Similarly, for O$_2$ plasma, a peak $P_r$ value is reached at 5 s after which a decreasing trend is observed, also in accordance with the increasing 

![Figure 5](image1.png)

**Figure 5.** (a) $P_r$ values of annealed Hf$_{0.5}$Zr$_{0.5}$O$_2$ films, when using O$_3$ and O$_2$ plasma as an oxygen source, as a function of deposition temperature. A 4 V triangular signal at 1 kHz was applied for the hysteresis measurement. (b) A Diffraction peak shift between two Hf$_{0.5}$Zr$_{0.5}$O$_2$ films deposited at 250 °C and 280°C using O$_2$ plasma. A different t-phase fraction for the different deposition temperatures is observed.

![Figure 6](image2.png)

**Figure 6.** Phase fraction percentage of O$_3$-based Hf$_{0.5}$Zr$_{0.5}$O$_2$ films after annealing as a function of the oxidation exposure length used during deposition.
Figure 7. (a) Phase fraction percentage of O\textsubscript{2}-plasma-based Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} films after annealing as a function of the oxidation exposure length used during deposition. (b) GIXRD patterns of two Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2} films after annealing, deposited using O\textsubscript{2} plasma exposure lengths of 3 and 5 s. A shift in the main diffraction peak is observed, likely indicating a variation in \(\alpha\)- and \(t\)-phase fraction between the two films.

Despite having similar combustion-like ALD reaction mechanisms [39, 43, 44], O\textsubscript{2} plasma presented only a minor relation to the deposition temperature and oxidation exposure length in comparison to O\textsubscript{3}. This suggests that the reaction mechanism when using O\textsubscript{2} plasma is dependent on the plasma conditions. In contrast, film deposition can be controlled through the aforementioned parameters if O\textsubscript{3} is employed. In addition, O\textsubscript{2} plasma presents faster reactivity than O\textsubscript{3} in view of the fractional oxidation exposure length required to achieve a full surface reaction with the substrate.

3.2. Hf\textsubscript{1-x}Zr\textsubscript{x}O\textsubscript{2} films with various compositions

As reported previously, the ideal oxide composition for ferroelectric MIM-capacitors, corresponding to a high \(\alpha\)-phase fraction in the Hf\textsubscript{1-x}Zr\textsubscript{x}O\textsubscript{2} dielectric layer, appears to be around identical Hf and Zr content (Hf\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2}) for ALD deposited layers of around 10 nm thickness, characterized by the highest obtainable \(P_r\) around this oxide composition [16, 34, 48]. A decrease in \(P_r\) is commonly observed when deviating from this composition, with increasing Hf or Zr content; although it is not always the case [49]. Increasing Hf content leads to a monotonic decrease in \(P_r\) until a paraelectric behaved monoclinic HfO\textsubscript{2} layer is reached. In the opposite direction, an increase in Zr content produces a strong pinching effect in the hysteresis loop around the 0 MV cm\textsuperscript{-1} electric field region, leading to an anti-ferroelectric-like behavior. This effect consistently increases as a pure ZrO\textsubscript{2} composition with a high \(t\)-phase fraction is approached (see figure 9) [14]. In this section, the influence of the oxygen source of the ALD process on the behavior of Hf\textsubscript{1-x}Zr\textsubscript{x}O\textsubscript{2} films is examined.

Based on the previous ALD process optimization discussed above, Hf\textsubscript{1-x}Zr\textsubscript{x}O\textsubscript{2} layers in the complete HfO\textsubscript{2} to ZrO\textsubscript{2} composition range with a thickness of 10 nm were deposited at 300 °C with a MIM-capacitor structure and given a PMA treatment at 450 °C for 20 s. The oxidation exposure lengths...
when employing O$_3$ or O$_2$ plasma as the oxygen source in the ALD process were 20 s and 5 s, respectively. To achieve a specific oxide composition, a supercycle formatted ALD process was used, in which the metal-organic precursors was alternately used for a defined fraction of cycles. To avoid a nanolaminate structure formation [34, 50, 51], a maximum of three continuous ALD cycles of a single metal organic precursor during any deposition process was used. Due to oxide composition discrepancies as a result of the ALD growth process, rather than using the expected Zr content in the Hf$_{1-x}$Zr$_x$O$_2$ layer, the ratio of the Zr metal-organic precursor to the total number of cycles in the supercycle, defined as Zr/(Zr + Hf) and referred to as the ‘Zr precursor ratio’, was the preferred reference value.

GIXRD diffraction patterns of the obtained annealed structures are presented in figure 10. Starting with the pure HfO$_2$ case (0.0 Zr precursor ratio), the dielectric layer presents predominantly monoclinic phase crystallization in the case of O$_3$ and remains mostly amorphous when using O$_2$ plasma. For increasing Zr precursor ratios, the reference peak for the (111)$_o$/(011)$_o$ planes at a 2θ value of about 30.6° becomes the sole discernable diffraction peak.

Hf$^{4+}$ and Zr$^{4+}$ ions have different ionic radii. Therefore, a unit cell volume expansion is expected when transitioning from pure HfO$_2$ to ZrO$_2$ [52]. This may be observed as a left-shift in the diffraction peaks when comparing GIXRD patterns of films with increasing Zr content. Simultaneously, a right-shift in the overlapping (111)$_o$/(011)$_o$ reference peak at the 2θ value of about 30.6° when increasing Zr content is expected due to an increase in t-phase stabilization [15]. This leads to an irregular (111)$_o$/(011)$_o$ peak shifting. As depicted in figure 11, the observed (111)$_o$/(011)$_o$ peak shifting resulted independent of the oxygen source. The strong right-shift in the observed peak position at the transition in Zr precursor ratio from 0.5 to 0.6 suggests a meaningful change in t-phase fraction in the dielectric film. For all other cases, the unit cell volume expansion seemingly has a larger influence on the detected (111)$_o$/(011)$_o$ peak-shift since a negative trend, or rather a left-shift, is maintained for increasing Zr precursor ratios. Despite this simple model, additional factors such as strain/stress in the film are also expected to impact the 2θ peak position [28], one of the clearest external influences being the choice of the electrode material. For this work, TiN was chosen due to its known mechanical constraint that allows for higher non-monoclinic phase stabilization [53]. Nevertheless, other materials have shown a similar behavior [54–56].

For the electrical characterization of the fabricated structures, first, remanent polarization ($P_r$) at a pristine state was evaluated (figure 12). The obtained $P_r$ trends were similar among oxygen sources. Nevertheless, using O$_3$ as an oxygen source favored a slightly higher $P_r$ in this case. As expected, the highest $P_r$ values were obtained around identical Hf and Zr content. Increasing Hf had a stronger effect in reducing $P_r$ than increasing Zr and only pure HfO$_2$ was paraelectric. This implies that, despite the (111)$_o$/(011)$_o$, peak position shift toward higher t-phase percentage depicted in figure 11, the o-phase is presumed to remain present even at high Zr contents. Additionally, the phase change spike in figure 11 does not coincide with the $P_r$ drop in figure 12. Therefore, it is expected that an increase in t-phase fraction in the Hf$_{1-x}$Zr$_x$O$_2$ films, at a Zr precursor ratio from 0.5 to 0.6, is the main reason behind the phase change spike of figure 11 but, only until the Zr precursor ratio interval of 0.6 to 0.75, does the o-phase fraction considerably drop.

Even though similar down trends in $P_r$ can be identified in figure 12 for increasing or decreasing Zr content beyond the 0.5 Zr precursor ratio, this observation does not entirely reflect the hysteresis behavior of the films. As depicted in
Figure 10. GIXRD patterns of annealed Hf$_{1-x}$Zr$_x$O$_2$ films deposited under various Zr precursor ratios and using (a) O$_3$ and (b) O$_2$ plasma as oxygen sources. A shift in the main diffraction peak is observed for increasing Zr presence. Diffraction patterns for pure-phase powder samples are located at the bottom of each plot.

Figure 11. (111)$_o$/(011)$_t$ diffraction peak position, obtained from GIXRD patterns of annealed Hf$_{1-x}$Zr$_x$O$_2$ films deposited using either O$_3$ or O$_2$ plasma as an oxygen source, plotted against the Zr precursor ratio used during the deposition process. An expected predominant peak-shifting phenomenon is identified in the figure. Linear trend-lines are introduced only as a visual aid.
of a developing pinching effect. Depolarization fields resulting from the co-existence of polar and non-polar regions of a mixed $\text{o}-\text{t}\text{-phase}$ dielectric layer, as well as parasitic dead layers present in the film stack, are expected to be the main reasons behind the anti-ferroelectric-like behavior of the film as discussed by Lomenzo et al [58].

Despite certain discrepancies among reported values for the dielectric constant ($k$) of the $m$-, $o$- and $t$-phases for HfO$_2$ and ZrO$_2$ [59], experimental results of Hf$_{1-x}$Zr$_x$O$_2$ thin films indicate that the $t$-phase presents the highest dielectric constant, followed by the $o$-phase, and lastly the $m$-phase with approximate values of 40, 25, and 20, respectively [17]. As depicted in figure 14(b), a clear trend of increasing dielectric constant for increasing Zr precursor ratio was identified for both oxygen sources. The observed trend fits well with the observed paraelectric behavior of monoclinic HfO$_2$ and the increase in $t$-phase stabilization for higher Zr content. Nevertheless, at a Zr precursor ratio of 1.0, the lower than expected $k$ if only pure tetragonal phase ZrO$_2$ were present, as well as the non-zero $P_m/P_r$ relation in figure 14(a), is suggestive of the coexistence of the $o$-phase in the dielectric film. In fact, it is suggested by Lomenzo et al [60] that around 30% of the dielectric film could still present a switchable orthorhombic phase. Additional $t$-phase stabilization doping, such as with Y, may be necessary to achieve pure tetragonal/cubic phase ZrO$_2$ with no switchable polar phases [28].

Continuous electric field cycling is known to have an effect on the ferroelectric hysteresis loop of Hf$_{1-x}$Zr$_x$O$_2$ films in what is referred to as its electric field cycling behavior [61]. Particularly, a reduction in internal bias fields can be achieved after a certain number of field cycles. This ‘wake-up’ behavior is characterized by an increase in $P_r$ and a reduction or possibly elimination of the pinching effect in the hysteresis loop [61]. In figure 15(a), the ratio between the remanent polarization of a Hf$_{1-x}$Zr$_x$O$_2$ film in a pristine state and after $10^4$ cycles with a 4 V amplitude signal is used as a figure of merit to compare the wake-up behavior of the Hf$_{1-x}$Zr$_x$O$_2$ films with varying Zr content. An increasing wake-up behavior was observed as a Zr precursor ratio of 0.75 was approached from a lower Zr content. Considering the small $P_r$ (figure 12) and increasing $k$ (figure 14(b)) for this precursor ratio, an increase in $t$-phase in the film is expected. From this, the influence of $t$-phase presence on the wake-up behavior is evident. When comparing oxygen sources, the lower oxygen content that was discussed in the first section for O$_2$ plasma use appears to slightly displace the observed trend toward lower Zr content since a larger wake-up behavior is observed at lower Zr ratios and no wake-up effect is present at a pure ZrO$_2$ composition. This is expected to be directly related to higher $t$-phase stabilization in comparison to its O$_3$ counterpart.

In addition to a wake-up effect, remanent polarization fatigue and eventual breakdown of the ferroelectric after additional cycling can occur [61]. The number of field cycles before breakdown is presented in figure 15(b). The field cycles to breakdown for varying Zr precursor ratios presented a similar but inverted trend to remanent polarization (see figure 12). This illustrates how the switching dynamics of the ferroelectric grains inside the film contributes to the breakdown of the...
Figure 14. (a) $P_m/P_r$ ratio of annealed Hf$_{1-x}$Zr$_x$O$_2$ films obtained using O$_3$ or O$_2$ plasma as the oxygen source as a function of the Zr precursor ratio used for the deposition process. The type of dielectric behavior is identified for different ranges. (b) Dielectric constant of annealed Hf$_{1-x}$Zr$_x$O$_2$ films obtained using O$_3$ or O$_2$ plasma as the oxygen source as a function of the Zr precursor ratio used for the deposition process.

Figure 15. (a) Wake-up behavior defined by the ratio $P_{cycled}/P_{pristine}$ and (b) electric field cycles to breakdown of annealed Hf$_{1-x}$Zr$_x$O$_2$ films, obtained using O$_3$ or O$_2$ plasma as the oxygen source, as a function of the Zr precursor ratio. For the cycled samples in (a), all samples were cycled for $10^4$ cycles with a 4 V amplitude signal.

As a result of this analysis, a higher impurity presence in the form of oxygen vacancies and carbon content related to the use of O$_2$ plasma during ALD growth increased hysteresis loop pinching, increased t-phase stabilization at lower Zr precursor ratios, and reduced the number of cycles to breakdown. This was observed as a reduction or shifting of trend values for properties such as $P_r$ and $k$ for varying Zr content in Hf$_{1-x}$Zr$_x$O$_2$ films. Accordingly, an O$_3$ usage would be favored which underscores the relevance of the oxygen source. Nevertheless, it is worth mentioning that the overall trend shape, for example in figures 12 and 14(b), remained intrinsic to the dielectric material.

4. Conclusions

Differences between the oxygen sources, O$_3$ and O$_2$ plasma, for an ALD process to deposit Hf$_{1-x}$Zr$_x$O$_2$ films, were identified. Crystalline phase stabilization during the deposition process was highly sensitive to the deposition temperature when using O$_3$ as an oxygen source. In contrast, deposition temperature had little effect on the film crystalline phase content when using O$_2$ plasma. Additionally, a consistent GPC was always observed for both oxygen sources in the evaluated interval, albeit, not equal among each other. Oxidation exposure length was shown to influence oxygen content in the film. Consequently, a transient preference for t- to o- to m-phase stabilization for increasing oxygen content was observed. In
comparison, $O_2$ plasma clearly allowed for a faster oxidation step as it required only a fraction of the time compared to $O_3$.

Under the optimized ALD conditions regarding deposition temperature and oxidation exposure length, similar trends among oxygen sources were obtained for varying $\text{Hf}_1-x\text{Zr}_x\text{O}_2$ film compositions. This indicates the possibility to use both $O_3$ and $O_2$ plasma during ALD for $\text{Hf}_1-x\text{Zr}_x\text{O}_2$ film depositions. All things considered, $O_3$ is suggested to be the favored oxygen source due to reduced impurity concentrations in the $\text{Hf}_1-x\text{Zr}_x\text{O}_2$ films which lead to longer field cycling until breakdown, reduced hysteresis loop pinching and a reduction in $t$-phase stabilization.

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ORCID ID

Ruben Alcala https://orcid.org/0000-0003-2799-9793

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