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Influence of Oxygen Source on the Ferroelectric Properties of ALD Grown Hf1-xZrxO2 Films

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| 6  7  8 | **Influence of Oxygen Source on the Ferroelectric** | | | | | |
| 9  10 | **Properties of ALD Grown Hf1-xZrxO2 Films** | | | | | |
| 11  12 | | | | | | |
| 13  14  15 | **Ruben Alcala1,4, Claudia Richter1, Monica Materano1, Patrick D. Lomenzo1, Chuanzhen Zhou2, Jacob L. Jones3, Thomas Mikolajick1,4, and Uwe Schroeder1** | | | | | |
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| 25  26 | Accepted for publication xxxxxx  Published xxxxxx | | | | | |
| 27  28 | **Abstract** | | | | | |
| 29  30  31  32  33  34  35  36  37  38  39  40  41  42 | Hafnium oxide (HfO2), zirconium oxide (ZrO2), and the solid-solution (Hf1-xZrxO2) 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 Hf1-xZrxO2 films has drawn attention to a commonly overlooked parameter for tuning ferroelectric and electrical properties of these films. In this paper, a comparison of O3 and O2 plasma used as the oxygen source in an atomic layer deposition (ALD) process for Hf1-xZrxO2 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 Hf1-xZrxO2 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. | | | | | |
| 43  44 | Keywords: ALD, PEALD, Hafnium Oxide, Zirconium Oxide, Ferroelectric, Ozone, Oxygen Plasma | | | | | |
| 45  46  47 | | | | | | |
| 48 | in metal oxide semiconductor (MOS) transistors.[4,5] Since | | | | | |
| 49 | **1. Introduction** | | | | then, HfO2-ZrO2 based oxides have gained widespread interest | |
| 50 | In 2011, Böscke et al. discussed a ferroelectric crystalline | | | | as ferroelectric materials; particularly for their application in | |
| 51 | novel ferroelectric memory technologies.[6] | |
| phase stabilization in doped HfO2 films with thicknesses on | | | |
| 52 | Under ambient conditions, both pure hafnia (HfO2) and | |
| the order of nanometers.[1] Almost simultaneously, | | | |
| 53 | pure zirconia (ZrO2) crystallize into a monoclinic structure (*m*- | |
| ferroelectric behavior in Hf0.5Zr0.5O2 thin films was also | | | |
| 54 | phase) with space group 𝑃21/𝑐 when bulk materials are considered.[7,8] Nevertheless, it has been long known that | |
| discussed.[2] These findings came at a time when traditional | | | |
| 55 |
| ferroelectrics, such as PZT and SBT, were struggling with | | | |
| 56 |
| additional high-temperature phases of these fluorite-structured | |
| scalability and Si compatibility issues.[3] In addition, the | | | |
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| oxides, that is, a tetragonal (*t*-) 𝑃42/𝑛𝑚𝑐 and cubic (*c*-) | |
| integration of HfO2 and ZrO2 as high-k dielectrics into | | | |
| 58 |
| 𝐹𝑚3̅𝑚 phase, can be stabilized at room temperature in the | |
| microelectronic devices had already been adopted for dynamic | | | |
| 59 |
| form of thin films or nanocrystallites. This comes as a result | |
| random access memory (DRAM) and high-k gate dielectrics | | | |
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| Journal **XX** (XXXX) XXXXXX | | | | | Author *et al* | |
| 1  2  3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36  37  38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54  55  56  57  58  59  60 | of a significant difference in the surface to bulk free energy | | | | | which were varied during this work were deposition | |
| relation for grain sizes in the nanoscale and due to dopant | | | | | temperature and oxidation exposure time. In addition, film | |
| distribution across grain boundaries.[9–13] In a similar | | | | | composition was varied by modifying the Hf to Zr precursor | |
| fashion, the orthorhombic (*o*-) 𝑃𝑐𝑎21 phase, responsible for the ferroelectric behavior in HfO2–ZrO2 oxides, is also | | | | | cycle relation, defined here as Zr/(Zr+Hf), for a specific number of ALD cycles, referred to as a supercycle. | |
| expected to be influenced by size and surface related effects. | | | | | In order to evaluate electrical properties, TiN\ Hf1- | |
| The origin of this ferroelectric phase has been extensively | | | | | xZrxO2\TiN\Ti\Pt structured metal-insulator-metal (MIM)- | |
| discussed in literature.[14–16] | | | | | capacitors were fabricated on (100) oriented *p*-Si substrates. | |
| Nanometer-scale thin films of simple Hf1-xZrxO2 (x = 0 – 1) | | | | | 10 nm TiN layers were used as bottom and top electrodes and | |
| oxide compositions have already been reported to present | | | | | were deposited via sputtering in a *Bestec ultrahigh vacuum* | |
| ferroelectric behavior.[17,18] Even so, additional doping of | | | | | *sputter cluster* at room temperature using a Ti target and N2 | |
| the oxide films, in an attempt to understand the ferroelectric | | | | | plasma. 10 nm thick Hf1-xZrxO2 layers were deposited via the | |
| behavior and improve the reliability of the material, has also | | | | | aforementioned ALD method. A 20 s post-metallization | |
| been widely researched.[19–21] At the same time, factors such | | | | | anneal (PMA) at 450°C in a N2 atmosphere was employed to | |
| as the influence of the substrate,[22,23] the choice of electrode | | | | | achieve a crystallization of the Hf1-xZrxO2 dielectric layer. | |
| material,[24,25] and the annealing treatment[26,27] have all | | | | | Additionally, a 10 nm thick Ti layer and a 25 nm thick Pt layer | |
| been identified to influence the ferroelectric behavior of Hf1- | | | | | were deposited via electron beam evaporation through a | |
| xZrxO2 oxide films. Recently, the impact of oxygen and | | | | | shadow mask as an adhesion and contact layer, respectively. | |
| nitrogen vacancies on the phase formation process has been | | | | | In a final fabrication step, excess TiN was etched with a SC-1 | |
| reported.[28] | | | | | procedure at 50 °C for 5 min in a solution of H2O, H2O2, and | |
| Different techniques for ferroelectric Hf1-xZrxO2 film | | | | | NH3 at a 50:2:1 ratio, in order to isolate the contact pads. | |
| depositions have been studied, such as atomic layer deposition | | | | | Structural characterization of the deposited films was | |
| (ALD), sputter deposition (PVD)[29] chemical solution | | | | | performed with a *Bruker D8 Discover XRD Tool* using a Cu | |
| deposition (CSD),[30] pulsed laser deposition (PLD),[31] and | | | | | Kα source with λ = 0.154 nm. X-ray reflectometry (XRR) was | |
| molecular beam epitaxy (MBE).[32] That said, atomic layer | | | | | utilized for film thickness determination; from which the | |
| deposition (ALD) remains the most robust and well | | | | | growth per cycle (GPC) could also be extracted. Grazing | |
| established method for the deposition of very thin oxide films, | | | | | incidence x-ray diffraction (GIXRD) and further diffraction | |
| especially for CMOS processes, with a clear advantage in | | | | | peak analysis were used for crystalline phase identification | |
| deposition conformality on three dimensional structures.[33] | | | | | and content determination. Furthermore, time-of-flight | |
| Multiple | reports | comparing | different | metal-precursor | secondary ion mass spectrometry (TOF-SIMS) analyses were | |
| combinations for Hf1-xZrxO2 film deposition have been | | | | | performed using a TOF SIMS V (ION TOF, Inc.) tool. | |
| published.[34–36] In contrast, a comparison of oxygen | | | | | Electrical characterization was used to determine properties | |
| sources for the same deposition process is rather | | | | | such as remanent polarization (*Pr*), electric field cycles to | |
| uncommon.[37,38] To better understand the role of the ALD | | | | | breakdown and dielectric constant (*k*) of the material, and was | |
| oxygen sources and its link to the recently reported vacancy | | | | | performed using an *aixACCT TF Analyzer 3000*. Dynamic | |
| dependency on phase formation in Hf1-xZrxO2 films, this work | | | | | hysteresis measurements (DHM) were preformed using a 4 V | |
| focuses on analyzing the effects of O3 and O2 plasma during | | | | | triangular pulse signal at 1 kHz with additional field cycling | |
| ALD growth and their influence on the ferroelectric properties | | | | | performed at 100 kHz. The dielectric constant was extracted | |
| of Hf1-xZrxO2 thin films. | | | | | from the small-signal capacitance of CV-measurements. | |
| **2. Experimental** | | | | | **3. Results and Discussion** | |
| Hf1-xZrxO2 thin-films were deposited on (100) oriented *p*-Si wafer substrates via atomic layer deposition (ALD) in an *Oxford OpAL tool*. All films had a target thickness of 10 nm. Cyclopentadienyl-amine-based Cp-Hf[N(CH3)2]3 and Cp-Zr[N(CH3)2]3 were used as metal-organic precursors and were bubbled with Ar gas at 65°C and 70°C, respectively, to assist precursor delivery. Either O3 gas or O2 plasma was employed as the oxidizing agent. O3 gas was obtained from a *Sorbios ozone generator* and was applied at a volume flow rate of 700 sccm with a 150 g/m³ density. O2 plasma was generated via an inductively coupled plasma source at 300 W and a 20 sccm O2 gas flow rate. Key deposition parameters of the ALD process | | | | | *3.1 Mixed Hf0.5Zr0.5O2 films*  Based on previous work on the optimization of the ALD process for ferroelectric Hf1-xZrxO2 films, [34,37]a fixed metal-organic precursor pulse length and oxidation pulse length were evaluated under distinct deposition temperatures for Hf0.5Zr0.5O2 films deposited using either O3 or O2 plasma as an oxygen source. As depicted in **Figure 1**, the growth per cycle (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 O3 and 0.92 Å/cycle in the case of O2 plasma, with a ± 0.015 Å/cycle one-sigma interval for both | |

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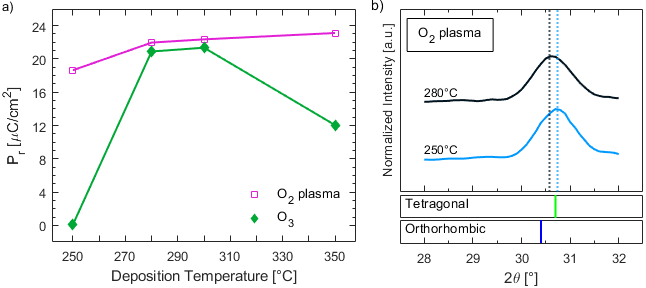
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| 3 |  | | | | | | Table I. TOF-SIMS derived impurity comparison for Hf0.5Zr0.5O2 films | | | | | | | | | | | | | | |
| 4 | deposited at 300°C using different oxygen sources. C- concentration | | | | | | | | | | | | | | |
| 5 | for the bottom electrode (BE) interface is excluded due to interest | | | | | | | | | | | | | | |
| 6 | in carbon contribution only from the deposition process. For the OH- | | | | | | | | | | | | | | |
| 7 | and TiO- ions, the values presented are relative to HfO2-+ZrO2-. | | | | | | | | | | | | | | |
| 8 |
| **Impurity Concentration** | | | | | | | | | | | | | | |
| 9 |
| In Bulk | | | | | | | | | | At BE Interface | | | | |
| 10 |
| Impurity | | | | Unit | O3 | | O2 | | | | | | O3 | O2 |
| 11 |
| 12 | Plasma | | | | | | Plasma |
| 13 | C- | | 1020 | | | 1.5 | | | 6.1 | | | | - | | - |
| 14 | cm-3 | | |
| 15 |
| OH- | | | a. u. | | 0.02 | | | 0.02 | | | 0.35 | | | 0.02 |
| 16 |
| TiO- | | | a. u. | | 0.00 | | | 0.00 | | | 0.42 | | | 0.22 |
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| the weak diffraction peaks at the expected *2Θ* values of 28.5°, | | | | | | | | | | | | | | |
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| 19 |
| Fig. 1. Average GPC of Hf0.5Zr0.5O2 films with respect to different | | | | | |
| 30.4°, 30.8°, and 31.6° of the m(-111), o(111), t(011), and | | | | | | | | | | | | | | |
| 20 |
| deposition temperatures. GPC was determined from final film | | | | | |
| m(111) planes, respectively (**Figure 2**).[45] The slight increase in grain size was directly related to the deposition | | | | | | | | | | | | | | |
| 21 |
| thickness divided by number of cycles. All films had a thickness of | | | | | |
| 22 | around 10 nm. | | | | | |
| temperature. An exception to this subtle behavior was the | | | | | | | | | | | | | | |
| 23 | oxygen sources, extracted from the GPC values at different | | | | | |
| Hf0.5Zr0.5O2 film deposited at 350°C with O3 as an oxygen | | | | | | | | | | | | | | |
| 24 |
| deposition temperatures. An increased GPC is commonly | | | | | | source for which a considerably larger increase in grain size | | | | | | | | | | | | | | |
| 25 |
| reported for O2 plasma use as a result of its reaction | | | | | | to around 8-10 nm was observed. | | | | | | | | | | | | | | |
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| mechanism along with possible emergent background | | | | | | Further peak analysis and peak deconvolution identified a | | | | | | | | | | | | | | |
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| 28 | chamber variations.[39–42] | | | | | | trend of higher monoclinic phase (*m*-phase) fraction for | | | | | | | | | | | | | | |
| 29 | Considering the organic nature of the metal-organic | | | | | | increasing deposition temperatures (**Figure 3**). Partial *in-situ* crystallization during the ALD process is anticipated, | | | | | | | | | | | | | | |
| 30 | precursors used, carbon-ligand derived impurities are | | | | | |
| 31 | expected to be found in the film.[34] Additionally, specific | | | | | especially for higher deposition temperatures. Nevertheless, a | | | | | | | | | | | | | | | |
| 32 | oxygen group contamination has been reported for each of the | | | | | divergence between oxygen source trends for the *m*-phase | | | | | | | | | | | | | | | |
| 33 | oxygen sources.[39,43,44] As a result, interference in the | | | | | fraction at 350°C can be identified. This observation leads to | | | | | | | | | | | | | | | |
| 34 | growth process of the film is expected, especially for lower | | | | | the assumption of a higher oxygen presence in the Hf0.5Zr0.5O2 | | | | | | | | | | | | | | | |
| 35 | deposition temperatures which are prone to higher impurity | | | | | films deposited using O3 as an oxygen source since such | | | | | | | | | | | | | | | |
| 36 | concentrations. | Time-of-flight | secondary | ion | mass | correlation has been reported for nanoscale Hf0.5Zr0.5O2 films. | | | | | | | | | | | | | | | |
| 37 | spectrometry was used to determine impurity concentrations | | | | | [28,46] Because the values presented in **Figure 3** are extracted from the GIXRD patterns, and therefore only represent phase | | | | | | | | | | | | | | | |
| 38 |
| resulting from the use of each of the oxygen sources for | | | | |
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| Hf0.5Zr0.5O2 films deposited at 300°C. Concentration of | | | | | fraction percentage relative to the crystallized portion of the | | | | | | | | | | | | | | | |
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| impurities for two regions of the film, a bulk or mid-film | | | | | film, the *m*-phase fraction difference between O3 and O2 | | | | | | | | | | | | | | | |
| 41 |
| region and at the interface with the bottom electrode, are | | | | | plasma at 350°C, with the additional consideration of the | | | | | | | | | | | | | | | |
| 42 |
| presented in **Table I**. O2 plasma presented higher carbon related impurities with a concentration of around 6.1×1020 | | | | | amorphous fraction of the film, is expected to be larger due to | | | | | | | | | | | | | | | |
| 43 |
| the difference in crystallization identified in **Figure 2.** Further diffraction peak deconvolution of the t/o-phase is known to be | | | | | | | | | | | | | | | |
| 44 |
| cm-3. For O3, the corresponding concentration was around | | | | |
| 45 |
| 1.5×1020 cm-3. O3 based films also show a higher OH- content | | | | | difficult and was not undertaken in this work. | | | | | | | | | | | | | | | |
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| at the interface to the bottom electrode as an effect of the initial | | | | | GIXRD analysis of post-metallization annealed MIM- | | | | | | | | | | | | | | | |
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| layer growth on the TiN substrate. Despite the impurity | | | | | capacitor stacks with Hf0.5Zr0.5O2 layers deposited at different | | | | | | | | | | | | | | | |
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| presence, both oxygen sources presented a consistent GPC in | | | | | ALD | | temperatures | | | | was | also | | | performed. | | | | | Additional |
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| the evaluated deposition temperature interval, suggesting a | | | | | determination of the orthorhombic (*o*-) and tetragonal (*t-*) | | | | | | | | | | | | | | | |
| 50 |
| minimal interference with the growth process. The influence | | | | | phase content, in addition to the *m*-phase, was now possible | | | | | | | | | | | | | | | |
| 51 |
| of impurities on ferroelectric performance shall be discussed | | | | | due to an increase in diffraction peak intensities and average | | | | | | | | | | | | | | | |
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| later. | | | | | crystalline grain size. Nevertheless, due to the overlapping | | | | | | | | | | | | | | | |
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| GIXRD analysis of the as-deposited Hf0.5Zr0.5O2 films | | | | | nature of the main reference diffraction peaks of these phases, | | | | | | | | | | | | | | | |
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| shows that these films are amorphous with only some | | | | | that is, (111)o at *2Θ* equal to 30.4° and (011)t at *2Θ* equal to | | | | | | | | | | | | | | | |
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| nanocrystallite formation in the order of 1 to 5 nm grain size, | | | | | 30.8°, a combined phase fraction value was preferred. | | | | | | | | | | | | | | | |
| 56 |
| as estimated by the Debye-Scherrer formula implemented on | | | | |
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| 58  59  60 | | | | | | | | | | | | | | | | | | | | | |

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| Fig. 2. GIXRD patterns of as-deposited Hf0.5Zr0.5O2 films obtained at different deposition temperatures using (a) O3 and (b) O2 plasma as the oxygen source. Diffraction patterns for pure phase powder samples are included at the bottom of each plot. | | |
| Fig. 3. Monoclinic phase (*m*-phase) fraction of as-deposited Hf0.5Zr0.5O2 films when using O3 or O2 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. | Fig. 4. Phase fraction of annealed Hf0.5Zr0.5O2 films, when using O3 or O2 plasma as an oxygen source, as a function of deposition temperature. | |

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21 Fig. 5. (a) *Pr* values of annealed Hf0.5Zr0.5O2 films, when using O3 and O2 plasma as an oxygen source, as a function of deposition temperature. 22 A 4 V triangular signal at 1 kHz was applied for the hysteresis measurement. (b) A Diffraction peak shift between two Hf0.5Zr0.5O2 films 23 deposited at 250°C and 280° using O2 plasma. A different *t*-phase fraction for the different deposition temperatures is observed.

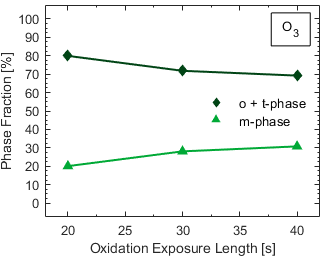
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25 As shown in **Figure 4**, the overall phase composition of the was identified for increasing deposition temperatures. Both

26 Hf0.5Zr0.5O2 layer when using O2 plasma as an oxygen source phenomena have a clear detrimental effect on the ferroelectric 27 presented little relation with respect to deposition temperature, properties of the film. Regardless, at the 280-300°C deposition temperature range, similar stabilization of the polar *o*-phase is 28   
 showing only a slight increase in *m*-phase for higher 29 deposition temperatures. In contrast, for O3, at 250°C the expected, independent of the oxygen source, due to similar *Pr* 30 Hf0.5Zr0.5O2 layer remained mostly amorphous even after the values and *o*+*t* diffraction peaks observed in GIXRD.

PMA treatment and, for increasing deposition temperatures, a The influence of the oxidation exposure length during the 31   
32 larger amount of a monoclinic phase was observed. This trend ALD process on the ferroelectric properties of Hf0.5Zr0.5O2 33 fits well with previous observations in **Figure 3** for O3 and   
 films was also studied for both O3 and O2 plasma. First, PMA 34 illustrates how the as-deposited stabilized monoclinic phase treated MIM-capacitor stacks with a 10 nm Hf0.5Zr0.5O2 35 limits *o-* and *t-*phase formation. dielectric layer deposited at 300°C and varying oxidation exposure lengths were characterized using GIXRD. Once 36 On the same structures, a DHM was used to assess 37 remanent polarization values (*Pr*) at a pristine state (**Figure**  more, diffraction peak deconvolution and intensity 38 **5a**). For O2 plasma, a lower *Pr*valuewas only identified when   
39 using a 250°C deposition temperature. A *Pr* of around 22.5

47 for the reduced *Pr*at 250°C. Regarding O3, the increasing *m*-48 phase trend identified in **Figure 4** is coherent with the 49 decreasing *Pr* trend in **Figure 5a**. In addition, the amorphous 50 case at 250°C correspondingly lacked any ferroelectric 51 behavior.

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temperature has little effect on the crystalline phase content and therefore little effect on the *Pr* of the Hf0.5Zr0.5O2 layer when using O2 plasma as an oxygen source. In contrast, when From this analysis, it was determined that the deposition 

40 μC/cm2 is reached at 280°C and no relevant improvement is 41 obtained for higher deposition temperatures. Considering that 42 no clear change in *m*-phase composition was identified for O2 43 44 plasma with respect to deposition temperature in **Figure 4**, it

45 is presumed that a larger *t*-phase stabilization, visible as a peak

46 shift in GIXRD patterns depicted in **Figure 5b**, is responsible

56 using O3 as an oxygen source, crystallization was limited at Fig. 6. Phase fraction percentage of O3-based Hf0.5Zr0.5O2 films after

annealing as a function of the oxidation exposure length used during 57 250°C and an underlying trend of increasing *m*-phase content deposition.

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| Fig. 7. (a) Phase fraction percentage of O2-plasma-based Hf0.5Zr0.5O2 films after annealing as a function of the oxidation exposure length used during deposition. (b) GIXRD patterns of two Hf0.5Zr0.5O2 films after annealing, deposited using O2 plasma exposure lengths of 3 and 5 s. A shift in the main diffraction peak is observed, likely indicating a variation in *o*- and *t*-phase fraction between the two films. | | |
| comparison were used to determine the phase fraction | DHM were also performed on these structures to assess | |
| distribution in the Hf0.5Zr0.5O2 layer. For O3, an oxidation exposure length of 10 s presented a weak diffraction peak | remanent polarization (*Pr*) in the pristine state (**Figure 8**). For both oxygen sources, the *Pr* values fit well with the trends | |
| pattern indicating limited crystalline phase development and a | observed in the structural analysis: for O3, the mostly | |
| shorter 5 s time interval lacked any relevant crystalline phase | amorphous Hf0.5Zr0.5O2 layer obtained from a 5 s oxidation | |
| development. In effect, both pulse lengths are excluded from | exposure length deposition showed no remanent polarization | |
| **Figure 6**. The underlying reason behind these deficiencies for O3 is expected to be insufficient exposure time to achieve a | (*Pr*) and the Hf0.5Zr0.5O2 layer with reduced crystalline phase development at 10 s presented only a small *Pr*. With regard to | |
| full reaction with the substrate surface during the half-cycle of | the rest of the exposure lengths, a maximum *Pr* is reached at a | |
| the ALD process. Regarding O2 plasma, no effect of reduced | 20 s exposure length after which only equal or smaller *Pr* | |
| crystallization in the Hf0.5Zr0.5O2 films was observed at any of | values are obtained due to increasing *m*-phase fraction or, | |
| the evaluated oxidation exposure lengths. Longer oxidation | | |
| exposure lengths led to increased *m*-phase fraction, regardless of the oxygen source (see **Figure 6** and **7a**). This is due to the direct relation between oxidation exposure length and oxygen content in the Hf0.5Zr0.5O2 layer.[47]   As depicted in **Figure 7a**, *o* + *t*-phase fraction appears to remain constant between the 3 s and 5 s oxidation exposure lengths when using O2 plasma as an oxygen source. Nevertheless, a closer analysis of the combined (111)o/(011)t diffraction peak (**Figure 7b**) 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 Hf0.5Zr0.5O2 layer when using the shorter exposure length. As a result, the O2 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 Hf0.5Zr0.5O2 film.[28] | Fig. 8. *P*r values of annealed Hf0.5Zr0.5O2 films, when using O3 and O2 plasma as an oxygen source, as a function of the oxidation exposure length during deposition. A 4 V triangular signal at 1 kHz was applied for the measurement. Predominant phase formation trends are | |
| indicated in the figure, where “*a”* refers to amorphous. | | |

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| 2  3 | | | | | | |
| 4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21  22  23  24  25  26 |  | | | | | |
| 27  28 | Fig. 9. Polarization-electric field hysteresis curves of annealed Hf1-xZrxO2 films, when using O3 and O2 plasma as an oxygen source, at specific Zr/(Zr+Hf) ratios identified for each column. All samples were previously cycled with a 4 V triangular signal at 100 kHz. | | | | | |
| 29 | | | | | | |
| 30 | rather, a decrease in *o*-phase content (see **Figure 6**). Similarly for O2 plasma, a peak *Pr* value is reached at 5 s after which a | | | | | *3.2 Hf1-xZrxO2 films with various compositions* |
| 31 |
| 32 |
| decreasing trend is observed, also in accordance with the | | | | | As reported previously, the ideal oxide composition for |
| 33 |
| increasing *m*-phase fraction (see **Figure 7a**). The *Pr* value for the 3 s oxidation exposure length also decreases with respect | | | | |
| 34 | ferroelectric MIM-capacitors, corresponding to a high *o*-phase |
| 35 |
| fraction in the Hf1-xZrxO2 dielectric layer, appears to be around |
| to the 5 s case due to an increase in non-polar *t*-phase content | | | | |
| 36 |
| identical Hf and Zr content (Hf0.5Zr0.5O2) for ALD deposited |
| in the Hf0.5Zr0.5O2 layer, discussed previously (see **Figure 7b**). Oxidation exposure length plays a significant role in | | | | |
| 37 |
| layers of around 10 nm thickness, characterized by the highest |
| 38 |
| obtainable *Pr* around this oxide composition.[16,34,48] A |
| 39 | determining the structural and electrical properties of the | | | | |
| decrease in *Pr* is commonly observed when deviating from |
| 40 | evaluated Hf0.5Zr0.5O2 layers, that is, the exposure length | | | | |
| this composition, with increasing Hf or Zr content; although it |
| 41 | presents a direct relation with the oxygen content of the | | | | |
| is not always the case.[49] Increasing Hf content leads to a |
| 42 | Hf0.5Zr0.5O2 film;[47] consequently influencing the crystalline | | | | |
| monotonic decrease in *Pr* until a paraelectric behaved |
| 43 | phase | development. | Furthermore, | insufficiently | short |
| monoclinic HfO2 layer is reached. In the opposite direction, an |
| 44 | exposure lengths will limit crystalline phase development as a | | | | |
| increase in Zr content produces a strong pinching effect in the |
| 45 | result of incomplete reactions during the ALD process in the | | | | |
| hysteresis loop around the 0 MV/cm electric field region, |
| 46 | form of inefficient ligand removal. | | | | |
| leading to an anti-ferroelectric-like behavior. This effect |
| 47 | Despite having similar combustion-like ALD reaction | | | | |
| consistently increases as a pure ZrO2 composition with a high |
| 48 | mechanisms,[39,43,44] O2 plasma presented only a minor | | | | |
| *t*-phase fraction is approached (see **Figure 9**).[14] In this section, the influence of the oxygen source of the ALD process |
| 49 |
| relation to the deposition temperature and oxidation exposure | | | | |
| 50 |
| length in comparison to O3. This suggests that the reaction | | | | |
| on the behavior of Hf1-xZrxO2 films is examined. |
| 51 |
| mechanism when using O2 plasma is dependent on the plasma | | | | |
| Based on the previous ALD process optimization discussed |
| 52 |
| conditions. In contrast, film deposition can be controlled | | | | |
| above, Hf1-xZrxO2 layers in the complete HfO2 to ZrO2 |
| 53 |
| through the aforementioned parameters if O3 is employed. In | | | | |
| composition range with a thickness of 10 nm were deposited |
| 54 |
| addition, O2 plasma presents faster reactivity than O3 in view | | | | |
| 55 | at 300°C within a MIM-capacitor structure and given a PMA |
| of the fractional oxidation exposure length required to achieve | | | | |
| 56 | treatment at 450°C for 20 s. The oxidation exposure lengths |
| a full surface reaction with the substrate. | | | | |
| 57 |
| 58  59  60 | | | | | | |

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| Fig. 10. GIXRD patterns of annealed Hf1-xZrxO2 films deposited under various Zr precursor ratios and using (a) O3 and (b) O2 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.    Fig. 11. (111)o/(011)t diffraction peak position, obtained from GIXRD patterns of annealed Hf1-xZrxO2 films deposited using either O3 or O2  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. | |

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| 2 | | | |
| 3 | when employing O3 or O2 plasma as the oxygen source in | | precursor ratio. A 4 V triangular signal at 1 kHz was applied for the |
| 4 | the ALD process were 20 s and 5 s, respectively. To achieve | | *Pr* measurement. |
| 5 |  |
| a specific oxide composition, a supercycle formatted ALD | |
| 6 | process was used, in which the metal-organic precursors was | |
| 7 | alternatingly used for a defined fraction of cycles. To avoid a | |
| 8 |
| nanolaminate structure formation,[34,50,51] a maximum of | |
| 9 |
| three continuous ALD cycles of a single metal organic | |
| 10 |
| precursor during any deposition process was used. Due to | |
| 11 |
| oxide composition discrepancies as a result of the ALD | |
| 12 |
| growth process, rather than using the expected Zr content in | |
| 13 |
| the Hf1-xZrxO2 layer, the ratio of the Zr metal-organic | |
| 14 |
| precursor to the total number of cycles in the supercycle, | |
| 15 |
| defined as Zr/(Zr+Hf) and refered to as the “Zr precursor | |
| 16 |
| ratio”, was the preferred reference value. | |
| 17 |
| GIXRD diffraction patterns of the obtained annealed | |
| 18 |
| structures are presented in **Figure 10**. Starting with the pure HfO2 case (0.0 Zr precursor ratio), the dielectric layer presents | |
| 19 |
| 20 |
| predominantly monoclinic phase crystallization in the case of | |
| 21 |
| Fig. 13. Comparison of polarization-electric field hysteresis curves |
| O3 and remains mostly amorphous when using O2 plasma. For | |
| 22 | for annealed dielectric HfO2, ferroelectric Hf0.5Zr0.5O2 and |
| increasing Zr precursor ratios, the reference peak for the | |
| 23 | antiferroelectric ZrO2 films. Extracted values of remanent |
| (111)o/(011)t planes at a *2Θ* value of about 30.6° becomes the | | polarization (*Pr*) and the maximum attained polarization without the |
| 24 |
| sole discernable diffraction peak. | | linear dielectric contribution (*Pm*)[53] values are marked. |
| 25 |
| Hf4+ and Zr4+ ions have different ionic radii. Therefore, a | | 0.6 suggests a meaningful change in *t*-phase fraction in the |
| 26 |
| unit cell volume expansion is expected when transitioning | |
| 27 |
| dielectric film. For all other cases, the unit cell volume |
| 28 | from pure HfO2 to ZrO2.[52] This may be observed as a left- | |
| expansion seemingly has a larger influence on the detected |
| 29 | shift in the diffraction peaks when comparing GIXRD patterns | |
| (111)o/(011)t peak-shift since a negative trend, or rather a left- |
| 30 | of films with increasing Zr content. Simultaneously, a right- | |
| shift, is maintained for increasing Zr precursor ratios. Despite |
| 31 | shift in the overlapping (111)o/(011)t reference peak at the *2Θ* | |
| this simple model, additional factors such as strain/stress in |
| 32 | value of about 30.6° when increasing Zr content is expected | |
| 33 | due to an increase in *t*-phase stabilization.[15] This leads to an | | the film are also expected to impact the *2Θ* peak position;[28] |
| one of the clearest external influences being the choice of the |
| 34 | irregular (111)o/(011)t peak shifting. As depicted in **Figure 11**, the observed (111)o/(011)t peak shifting resulted independent | |
| 35 | electrode material. For this work, TiN was chosen due to its |
| 36 | known mechanical constraint that allows for higher non- |
| of the oxygen source. The strong right-shift in the observed | |
| 37 | peak position at the transition in Zr precursor ratio from 0.5 to | | monoclinic phase stabilization.[54] Nevertheless, other |
| 38 | materials have shown a similar behavior.[55–57] |
| 39 |  | | For the electrical characterization of the fabricated |
| 40 | structures, first, remanent polarization (*Pr*) at a pristine state |
| 41 | was evaluated (**Figure 12**). The obtained *Pr* trends were similar among oxygen sources. Nevertheless, using O3 as an |
| 42 |
| 43 | oxygen source favored a slightly higher *Pr* in this case. As |
| 44 |
| expected, the highest *Pr* values were obtained around identical |
| 45 |
| Hf and Zr content. Increasing Hf had a stronger effect in |
| 46 |
| reducing *Pr*than increasing Zr and only pure HfO2 was |
| 47 |
| paraelectric. This implies that, despite the (111)o/(011)t peak |
| 48 |
| position shift toward higher *t*-phase percentage depicted in |
| 49 |
| **Figure 11**, the *o*-phase is presumed to remain present even at high Zr contents. Additionally, the phase change spike in |
| 50 |
| 51 |
| **Figure 11** does not coincide with the *Pr*drop in **Figure 12**. Therefore, it is expected that an increase in *t*-phase fraction in |
| 52 |
| 53 |
| the HfxZr1-xO2 films, at a Zr precursor ratio from 0.5 to 0.6, is |
| 54 |
| 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, |
| 55 |
| Fig. 12. Pristine*Pr* values of annealed Hf1-xZrxO2 films when using | |
| 56 |
| either O3 or O2 plasma as an oxygen source as a function of the Zr | |
| does the *o*-phase fraction considerably drop. |
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| 58  59  60 | | | |

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| **Figure 12** for increasing or decreasing Zr content beyond the 0.5 Zr precursor ratio, this observation does not entirely reflect | Nevertheless, at a Zr precursor ratio of 1.0, the lower than expected *k* if only pure tetragonal phase ZrO2 were present, as | |
| the hysteresis behavior of the films. As depicted in **Figure 13**, both ferroelectric behaved Hf0.5Zr0.5O2 and antiferroelectric | well as the non-zero *Pm/Pr* relation in **Figure 14a**, is suggestive of the coexistence of the *o*-phase in the dielectric | |
| behaved ZrO2 films present a relevant non-linear polarization | film. In fact, it is suggested by Lomenzo et al.[60] that around | |
| contribution under the maximun evaluated electric field | 30% of the dielectric film could still present a switchable | |
| denominated *Pm*.[53] By plotting *Pm/Pr* against the Zr | orthorhombic phase. Additional *t*-phase stabilization doping, | |
| precursor ratio additional insight on the hysteresis loop | such as with Y, may be necessary to achieve pure | |
| behavior is obtained (see **Figure 14a**). Zr precursor ratios ranging from 0.0 to 0.66 presented a small *Pm/Pr* relation | tetragonal/cubic phase ZrO2 with no switchable polar phases.[28] | |
| which is expected for a ferroelectric hysteresis loop. | Continuous electric field cycling is known to have an effect | |
| Nevertheless, from **Figure 12**, a lack of *Pr* for pure HfO2, confirms that oxides with this composition exhibit a purely | on the ferroelectric hysteresis loop of Hf1-xZrxO2 films in what is referred to as its electric field cycling behavior.[61] | |
| paraelectric behavior. An increasing *Pm/Pr* relation for Zr | Particularly, a reduction in internal bias fields can be achieved | |
| precursor ratios of 0.75 and above indicates a transition from | after a certain number of field cycles. This “wake-up” | |
| a ferroelectric to an anti-ferroelectric-like hysteresis loop | behavior is characterized by an increase in *Pr* and a reduction | |
| behavior as a result of a developing pinching effect. | or possibly elimination of the pinching effect in the hysteresis | |
| Depolarization fields resulting from the co-existence of polar and non-polar regions of a mixed *o*/*t*-phase dielectric layer, as | loop.[61] In **Figure 15a**, the ratio between the remanent polarization of a Hf1-xZrxO2 film in a pristine state and after | |
| well as parasitic dead layers present in the film stack, are | 104 cycles with a 4 V amplitude signal is used as a figure of | |
| expected to be the main reasons behind the anti-ferroelectric- | merit to compare the wake-up behavior of the Hf1-xZrxO2 films | |
| like behavior of the film as discussed by Lomenzo et al.[58] | with varying Zr content. An increasing wake-up behavior was | |
| Despite certain discrepancies among reported values for the | observed as a Zr precursor ratio of 0.75 was approached from | |
| dielectric constant (*k*) of the *m*-, *o*- and *t*-phases for HfO2 and ZrO2,[59] experimental results of Hf1-xZrxO2 thin films indicate that the *t*-phase presents the highest dielectric | a lower Zr content. Considering the small *Pr* (**Figure 12**) and increasing *k* (**Figure 14b**) for this precursor ratio, an increase in *t*-phase in the film is expected. From this, the influence of | |
| constant, followed by the *o*-phase, and lastly the *m*-phase with | *t*-phase presence on the wake-up behavior is evident. When | |
| approximate values of 40, 25, and 20, respectively.[17] As | comparing oxygen sources, the lower oxygen content that was | |
| depicted in **Figure 14b**, a clear trend of increasing dielectric constant for increasing Zr precursor ratio was identified for | discussed in the first section for O2 plasma use appears to slightly displace the observed trend toward lower Zr content | |
| both oxygen sources. The observed trend fits well with the | since a larger wake-up behavior is observed at lower Zr ratios | |
| observed paraelectric behavior of monoclinic HfO2 and the | and no wake-up effect is present at a pure ZrO2 composition. | |
| Fig. 14. (a) *Pm/Pr* ratio of annealed Hf1-xZrxO2 films obtained using O3 or O2 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 HfxZr1-xO2 films obtained using O3 or O2 plasma as the oxygen source as a function of the Zr precursor ratio used for the deposition process. | | |

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| 3  4  5  6  7  8  9  10  11  12  13  14  15  16  17  18  19  20  21 | Fig. 15. (a) Wake-up behavior defined by the ratio Pr,cycled/Pr,pristine and (b) electric field cycles to breakdown of annealed Hf1-xZrxO2 films, obtained using O3 or O2 plasma as the oxygen source, as a function of the Zr precursor ratio. For the cycled samples in (a), all samples were cycled for 104 cycles with a 4 V amplitude signal. | | |
| 22 | | | |
| 23 | This is expected to be directly related to higher *t*-phase | | **4. Conclusions** |
| 24 |
| stabilization in comparison to its O3 counterpart. | |
| 25 |
| 26 | In addition to a wake-up effect, remanent polarization | | Differences between the oxygen sources, O3 and O2 |
| 27 | fatigue and eventual breakdown of the ferroelectric after | |
| plasma, for an ALD process to deposit Hf1-xZrxO2 films, were |
| 28 | additional cycling can occur.[61] The number of field cycles | |
| identified. Crystalline phase stabilization during the |
| 29 | before breakdown is presented in **Figure 15b**. The field cycles to breakdown for varying Zr precursor ratios presented a | |
| deposition process was highly sensitive to the deposition |
| 30 |
| temperature when using O3 as an oxygen source. In contrast, |
| 31 | 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 | |
| deposition temperature had little effect on the film crystalline |
| 32 |
| phase content when using O2 plasma. Additionally, a |
| 33 |
| consistent GPC was always observed for both oxygen sources |
| 34 | breakdown of the material.[46] Nevertheless, increasing the | |
| in the evaluated interval, albeit, not equal among each other. |
| 35 | Zr content leads to a higher number of cycles to breakdown of | |
| Oxidation exposure length was shown to influence oxygen |
| 36 |
| the film compared to increasing the Hf content. Also, the | |
| content in the film. Consequently, a transient preference for t- |
| 37 |
| higher oxygen vacancy concentration in the O2 plasma films | |
| to o- to m-phase stabilization for increasing oxygen content |
| 38 |
| becomes evident when comparing oxygen sources since a high | |
| was observed. In comparison, O2 plasma clearly allowed for a |
| 39 |
| oxygen vacancy concentration is listed among the causes for | |
| faster oxidation step as it required only a fraction of the time |
| 40 |
| early onset of fatigue and a general reduction in the number of | |
| compared to O3. |
| 41 |
| field cycles to breakdown.[46] | |
| Under the optimized ALD conditions regarding deposition |
| 42 |
| As a result of this analysis, a higher impurity presence in | |
| 43 | temperature and oxidation exposure length, similar trends |
| the form of oxygen vacancies and carbon content related to the | |
| 44 | among oxygen sources were obtained for varying Hf1-xZrxO2 |
| use of O2 plasma during ALD growth increased hysteresis | |
| 45 | film compositions. This indicates the possibility to use both |
| loop pinching, increased *t*-phase stabilization at lower Zr | |
| 46 | O3 and O2 plasma during ALD for Hf1-xZrxO2 film depositions. |
| precursor ratios, and reduced the number of cycles to | |
| 47 | All things considered, O3 is suggested to be the favored |
| breakdown. This was observed as a reduction or shifting of | |
| 48 | oxygen source due to reduced impurity concentrations in the |
| trend values for properties such as *Pr* and kfor varying Zr | |
| 49 | Hf1-xZrxO2 films which lead to longer field cycling until |
| content in Hf1-xZrxO2films. Accordingly, an O3 usage would | |
| 50 | breakdown, reduced hysteresis loop pinching and a reduction |
| be favored which underscores the relevance of the oxygen | |
| 51 | in *t*-phase stabilization. |
| source. Nevertheless, it is worth mentioning that the overall | |
| 52 |
| trend shape, for example in **Figure 12** and **14b**, remained intrinsic to the dielectric material. | | **Acknowledgements** |
| 53 |
| 54 |
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| 55 |
| Economic Affairs and Energy (BMWi) project (16IPCEI310) |
| 56 |
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| 57 |
| for their support. TOF-SIMS experiments were performed at |
| 58 |
| 59  60 | | | |

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