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Knowledge about phase transitions in doped HfO_2 and ZrO_2 -based films is crucial for developing future ferroelectric devices. These devices should perform in ambient temperature ranges with no degradation of device performance. Here, the phase transition from the polar orthorhombic to the nonpolar tetragonal phase in thin films is of significant interest. Detailed electrical and structural characterization is performed on 10 nm mixed $Hf_xZr_{1-x}O_2$ binary oxides with different ZrO_2 in HfO_2 and small changes in oxygen content. Both dopant and oxygen content directly impact the phase transition temperature between the polar and nonpolar phase. A first-order phase transition with thermal hysteresis is observed from the nonpolar to the polar phase with a maximum in the dielectric constant. The observed phase transition temperatures confirm trends as obtained by DFT calculations. Based on the outcome of the measurements, the classification of the ferroelectric material is discussed.

1. Introduction

Fluorite-structured materials like doped $HfO_2^{[1]}$ and ZrO_2 radically changed the development of ferroelectric semicon-

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ductor devices like ferroelectric capacitors, transistors, and tunnel junctions in recent years. Capacitor-based ferroelectric random access memory^[2,3] and ferroelectric field effect transistors^[4] using HfO₂based ferroelectrics have already been integrated into state of the art CMOS processes to prove the potential of this new ferroelectric material system. However, a detailed understanding of the ferroelectric phase formation process, including phase transitions, is necessary for continued development because such phase transitions determine ferroelectric device temperature stability. Several phases were reported to be present or coexisting in doped HfO₂ or ZrO₂ films ranging from monoclinic (space group $P2_1/c$), tetragonal ($P4_2/nmc$), cubic ($Fm\overline{3}m$), rhombohedral (R3m), and different

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orthorhombic phases that can be nonpolar (*Pnma*), antipolar (*Pbca*), nonpolar (*Pbca*), or polar (*Pca2*₁).^[5,6] A remarkable property of the material is the phase coexistence between the nonpolar tetragonal and polar orthorhombic phase. The conditions of this phase coexistence are little investigated because the participating phases have very similar structural properties, and the investigation requires correlated measurement of film properties like the remanent polarization and the dielectric constant. But the phase coexistence over a wide range of conditions causes unusual and interesting material properties. The phase change driven by temperature over a wide range is the cause of the giant pyroelectric effect, the phase change driven over a wide range of the giant piezoelectric effect. Little is known about the relation between phase coexistence and phase transformation.

When amorphous layers are present, crystallization follows Ostwald's rule starting from a cubic/tetragonal nucleus.^[7] Depending on dopant and oxygen vacancy content in the film, the nonpolar tetragonal (t) or the ferroelectric orthorhombic (o) phase can be found.^[8,9] For high oxygen content/oxygen interstitials, activation barriers for a transition from the t- to the o-phase prevent the phase change and the monoclinic (m) phase can be formed. Accordingly, dopant and oxygen vacancy content are two main causes of ferroelectric phase formation in this material system. In addition, surface energy related to grain size^[10] and quenching during cool down after crystallization^[11] are other reported factors. Since all four factors can



impact stress and strain in the fluorite films, internal stress and strain also underlie the emergence of ferroelectricity.

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So far, little is known on phase transitions at or beyond the Curie temperature for the complete compositional range. Tashiro et al. reported a significant thermal hysteresis for epitaxially grown $Hf_xZr_{1-x}O_2$ films on a YSZ substrate when the layers were heated just below Curie temperature.^[12] Here, similar to the Y:HfO₂ system, a thermal hysteresis in the o- to t-phase conversion of 50–200 K was reported. The thermal hysteresis is consistent with a first-order phase transition, whereas second-order phase transitions exhibit no thermal hysteresis.

The picture obtained from thin films is consistent with bulk HfO₂ and ZrO₂, where a first-order diffusionless martensitic phase transition from the t- to the m-phase is well-known.^[13,14] Simulation results indicated no IR-sensitive soft phonon modes for the t-phase at 0 K.^[15] This implies that there are no single instable phonon modes but that a phase transition is activated by coupling of several phonons.^[16] The absence of soft phonons is also an indicator of the nature of a t- to o-phase transition. Similarly, soft phonons are missing for the o-phase at 0 K, precluding a simple explanation for the o- to t-phase transition. Additionally the phononic band structure of the o- and t-phase of HfO₂ and ZrO₂ is calculated. Further characteristics classifying the phase transition are the evolution of polarization and dielectric constant with temperature. In a single crystal, a firstorder phase transition exhibits a discontinuous remanent polarization and a peak in the dielectric constant at the transition temperature.^[17] The conditions are different in a polycrystalline material, the role of surfaces and interfaces possibly allows internal stresses or pressures not feasible in a single crystal. Therefore polycrystalline materials could support conditions for coexisting phases that are absent in single crystals.

In this work, detailed structural and electrical characterization is performed to characterize temperature-dependent phase transitions, leading to a discussion on the classification of different ferroelectric material classes for the HfO_2/ZrO_2 material system.

2. Results and Discussion

2.1. Structure Analysis

As discussed in previous publications^[8,18] and shown in detail in the Supporting Information, the phase formation in thin $Hf_xZr_{1-x}O_2$ (HZO) layers and consequently the ferroelectric properties are strongly impacted by ZrO_2 content and the ozone dose time during the HZO ALD growth. Thin films of $Hf_{0.5}Zr_{0.5}O_2$ with various ozone dose times and $Hf_xZr_{1-x}O_2$ films with 5 s ozone dose time and varied ZrO_2 content are investigated to evaluate the temperature stability of ferroelectric HfO_2 -based thin films (see Figure S1, Supporting Information).

For structural characterization, GIXRD measurements from room temperature up to 1000 K and back to room temperature were performed on a ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ thin film with a high remanent polarization (5 s ozone dose). With increasing temperature, a peak shift of the o(111)/t(101) peak at 30.5° to lower 2 θ positions is observed (**Figure 1**a,b), but the peak position shifts are weaker during cooling. Based on the peak positions, the pseudo-cubic unit cell volume (a³) is calculated using the o(111)/t(101) diffraction peak at $2\Theta = 30.5^{\circ}$ as explained in detail in Section S6 (Supporting Information). This approximation allows one to neglect anisotropy effects. The unit lattice cell volumes (see Figure 1c,d) indicate a linear thermal volume expansion up to 680 K. Values are consistent with measured thermal expansion values of HfO₂ and ZrO₂ for the t-phase but are much larger than values for the m-phase.^[19] For the thermal expansion coefficient of the o-phase no experimental data is available so far.

Above 723 K, the thermal expansion slope increases by a factor of 3, up to 800 K. From Haggerty et al., an expansion coefficient of 3.4×10^{-5} K⁻¹ for the t-phase and 2.1×10^{-5} for the m-phase can be calculated for $Hf_{0.5}Zr_{0.5}O_2$.^[19] In Figure 1c, above 723 K an expansion coefficient of 5.0×10^{-5} K⁻¹ is measured. The measured expansion coefficient is 50% larger than the literature value. Thus, the observed change appears too large to be purely driven by a linear thermal expansion of the t-phase lattice. The silicon expansion with 2.6 \times 10⁻⁶ K⁻¹ is negligible. An abrupt change in the expansion coefficient is typically related to a change in phase, which could be attributed to a possible intermediate phase present in between the transformation from the t- to the m-phase, as reported also for perovskite materials like BaTiO₃ for the transition from the t- to o-phase.^[20] More likely is a temperature driven partial phase change from the t- to the m-phase, whereby additional strain relaxation facilitates the t- to m-phase transition. Since thin ferroelectric HfO2 films contain a high tensile strain of 1-2 GPa, strain relaxation cannot be ruled out.^[21]

Starting at 723 K, a transition to the m-phase is indicated, which becomes more dominant above 800 K. But the film is never completely converted to the m-phase at 1000 K. The expanded lattice volume can make it thermodynamically favorable for part of the film to transform from the t-phase to the m-phase. Since the m-phase has the lowest free energy of the system, a backward transformation into the o/t-phase is energetically not possible at this temperature once the m-phase has been stabilized without high pressure and temperature conditions.^[22] Consequently, during cool down to room temperature, the phase mixture of mand o/t-phase stays constant. The reduction in unit cell volume indicates a partial thermal decrease in cell volume. The unit cell volume of the o/t-phase is enhanced compared to the pristine condition. Similarly, a Hf_{0.5}Zr_{0.5}O₂ film with 0.1 s O₃ dose and higher t-phase content is annealed only to 725 K (Figure S12, Supporting Information). A similar slope of the pseudo-cubic unit cell volume (Figure 1c,d) below 723 K, which corresponds to the thermal expansion coefficient of the material, is present during heating and cooling and seems to be independent of the initial o/t-phase ratio of the layer. Again, this value is consistent to a thermal expansion of the t-phase. Coefficients are so far not reported in literature for the o-phase. As discussed later, up to 680 K, an o- to t-phase transition is expected with a 2θ shift of the o(111)/t(101) peak to higher values. This shift is minor compared to the change by thermal expansion.

2.2. Dielectric and Ferroelectric Properties

The switching current versus electrical field hysteresis loops for $Hf_{0.5}Zr_{0.5}O_2$ capacitors with a 1 s O_3 dose during HZO ALD growth show a dominant switching peak at room temperature

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Figure 1. Temperature-dependent phase changes: a) GIXRD pattern in a temperature range from 300 to 1000 K followed by b) cooling down to 300 K for a $Hf_{0.5}Zr_{0.5}O_2$ film deposited by ALD with 5 s O_3 dose time. Black line corresponds to the o(111) and t(101) reflection peak. The green lines correspond to the m(-111) and m(111) peaks. c,d) Pseudo-cubic unit cell volume for $Hf_{0.5}Zr_{0.5}O_2$ films deposited by ALD with 5 and 0.1 s O_3 dose time as a function of heating and cooling temperature, determined from the d_{111} lattice plane distance of the orthorhombic o(111) GIXRD diffraction peak. The dashed lines are guides to the eye.

(Figure 2a). As described in Section S2 (Supporting Information), peak deconvolution shows two overlaying peak contributions at ≈ 2.5 MV cm⁻¹ of the dominant peak. Additionally, a third minor switching peak at low fields is observed. Up to 520 K, both overlaying switching peaks slightly change their switching field position with temperature. Increasing the temperature to about 723 K causes a drifting apart of the dominant switching peak pair, enhancing the peak distance with higher temperatures. Peak drifting can be tracked by following the deconvoluted switching field position with temperature (Figure 2b), whereas the dominant peak 0 is moving to zero field. Peak 1 and peak 2 indicate additional antiferroelectric-like switching behavior at about 723 K. At high temperatures, peak 1 becomes the switching peak B and peak 2 the back-switching peak A' of the switching peak A. Accordingly, a predominant ferroelectric switching peak is present at 300 K. As the t-phase becomes energetically more stable at higher temperatures, a higher electric field is required to induce a phase transition

from the t-phase portions to the polar o-phase. Cooling back to room temperature reverses the peak splitting, and a slight increase in the switching field is observed when comparing before and after heating, respectively.

The observed peak splitting at high temperatures is similar to the antiferroelectric-like switching behavior of films with high nonpolar t-phase portions (e.g., high ZrO₂ concentrations, see also Figure S6, Supporting Information) which are postulated to arise from a reversible field-induced phase change from the tetragonal to the polar orthorhombic phase.^[23,24] In films with higher ZrO₂ concentration (e.g., 60% and 75% ZrO₂), the peak splitting with increasing temperature becomes more distinct.

The remanent polarization (P_r) was determined as a function of temperature for the two film sets (**Figure 3**, see complete data set in Section S2, Supporting Information). As a result, the temperature stability of the remanent polarization strongly depends on the ZrO₂ and oxygen content. A temperaturedependent drop of P_r from 20 to 0 μ C cm⁻² can be attributed







Figure 2. Temperature-dependent ferroelectric switching. a) Dynamic switching current versus applied electric field at a temperature of 300 K, heated to 723 K and cooled back to 300 K for $Hf_{0.5}Zr_{0.5}O_2$ capacitors with a 1 s O_3 dose time during HZO film growth. Current peak pairs 0-0', 1-1', 2-2', 3-3', A-A' and B-B' denote the coupled switching. b) The switching field position deconvolution of the $Hf_{0.5}Zr_{0.5}O_2$ capacitors with a 1 s O_3 dose time during deposition as a function of temperature. The peak positions are represented by dots. The dot areas represent the deconvoluted peak areas and indicate the amount of switching charge. The dashed lines are guides to the eye.

to a phase change from the polar o- to the nonpolar t-phase, as discussed in detail below. During heating and subsequent cooling, P-E measurements reveal a temperature hysteresis in the remanent polarization. It ranges from 10% to 30% of the remanent polarization depending on varying oxygen vacancy concentration achieved by changing the O_3 dose time and ZrO_2 concentration. For both cases (Figure 3a,b) a slightly reduced remanent polarization after the heating and cooling cycle is observed. The thermal hysteresis can be assumed to be below 50 K if the heating and cooling rates are fast enough. The thermal hysteresis of the remanent polarization increases only for thin films with a higher initial m-phase/content, which means either low ZrO_2 content or low oxygen vacancy content or lower heating rates (Figure 5a).

Caused by this specific dopant or oxygen vacancy content, the activation barrier for a t- to m-phase transition at elevated

temperatures is reduced.^[8] A transition to the m-phase is more likely and is enhanced with increasing temperature. The m-phase fraction slightly increases and subsequently reduces the remanent polarization. This effect is drastically enhanced for lower heating and cooling rates, where the system has more time for a transition to the m-phase (see Figure 5a).

To get an overall understanding of the temperaturedependent changes of the measured parameters during heating, all available data is plotted in **Figure 4** for a $Hf_{0.5}Zr_{0.5}O_2$ film deposited with 1s O₃ dose time. Due to the to the different temperature ramp rates of the conducted measurements, changes in the phase transition temperatures are expected. Slower ramp rates for GIXRD compared to impedance spectroscopy measurements lead to a slight increase in the transition temperature in the former. Accordingly, transition regions are introduced as marked in grey in Figure 4. Changes of the parameters can be



Figure 3. Temperature hysteresis of the remanent polarization. a) Remanent polarization as a function of temperature during heating and cooling for $Hf_xZr_{1,x}O_2$ with different ZrO_2 content and 5 s ozone dose time. b) Remanent polarization as a function of temperature for $Hf_{0.5}Zr_{0.5}O_2$ and different O_3 dose times. The dashed lines are guidelines for the eyes.



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Figure 4. Overview of temperature dependencies: a) Pristine remanent polarization, b) switching fields, c) pseudo-cubic cell volume, FWHM of $2\Theta = 30.5^{\circ}$ o(111) peak, d) dielectric constant ε_r , and e) $1/\varepsilon_r$ as function of temperature during heating of the $Hf_{0.5}Zr_{0.5}O_2$ with 1 s. The dashed lines are guidelines for the eyes.

separated into four temperature regimes. Up to 520 K, a predominately ferroelectric o-phase is present in the dielectric layer having a remanent polarization of about 20 μ C cm⁻² slightly decreasing to 17 μ C cm⁻² at 520 K. This reduction might be related to the linear thermal expansion of the unit cell volume from 128 to 129 Å³. Both dielectric constant and the switching field are stable at about 25 and 2 MV cm⁻¹, respectively.

Between 520 and 729 K, a continuous phase transition from the polar o-phase to the nonpolar t-phase is assumed, as indicated by the drop in remanent polarization from 17 to 0 μ C cm⁻² with no significant changes in the GIXRD pattern (Figure 1). This phase transition is consistent with an increase in dielectric constant from 25 to 50 (Figure 4d). The pinching of the hysteresis loop progresses with temperature (Figures S7



and S8, Supporting Information), as revealed by an increase in switching field from 2 to 3 MV cm⁻¹ and the appearance of the back-switching peak at 0 MV cm⁻¹. Here, a reversible fieldinduced phase transition from the t- to the o-phase is assumed. Interestingly, only a slight increase in the thermal expansion coefficient of the unit cell volume with no change in the FWHM of the main 2θ peak at about 30.5° occurs between room temperature and 723 K (Figure 4c). Since the o- and t-phase have a similar pseudo-cubic Hf lattice structure with mainly differences in the O position, a change in slope is not expected (also see Sections S4 and S8, Supporting Information). Moreover, there are only minor atomic displacement differences in O positions and the cell metrics are all nearly cubic, so a major change in thermal expansion characteristics and a change in slope of an equivalent pseudo-cubic lattice constant are not expected. Since the o(111)- and t(101)- reflection at about 30.5° have slightly different 2θ positions, a peak broadening is assumed but not visible due to a superposition of a linear volume mixture of o- and t-phase plus a linear thermal expansion of the t-phase and o-phase fractions with temperature.

Between 729 and 823 K a clear transition region is present in the x-ray diffraction pattern. The unit cell volume increases from 130 to 133 Å³ with a peak broadening of the t(101) peak at \approx 30.5° for temperatures above 723 K (Figure 4c). Beyond 723 K a small shoulder, and above 823 K a clear peak of the non-polar m-phase appears. In the whole temperature range above 723 K, the remanent polarization is 0 µC cm⁻² and in cases where a field-induced phase transition is possible, the switching field needs to be higher than 3 MV cm⁻¹ (Figure 4a). A drastic increase of ε_r to about 10 000 (and a corresponding drop in $1/\varepsilon_r$ to almost 0) is present at 732 K (Figure 4d).

The sharp permittivity peak at 732 K is attributed to the ferroelectric-paraelectric phase transition at the Curie temperature, $T_{\rm c}$. The permittivity maximum, $\varepsilon_{\rm r,max}$ is $\approx 10\ 600$ but its height was frequency-dependent (see Figure S10, Supporting Information). This frequency dependence is one indication for a first order phase transition in a proper ferroelectric. Relaxor ferroelectric materials would show a frequency dependent shift of the permittivity maximum.^[25] For a short range of temperatures above T_c , the permittivity decreased, as expected from Curie-Weiss behavior. However, a change of slope occurred at \approx 760 K. This permittivity behavior, with a sharp maximum, is characteristic for a first order ferroelectric such as BaTiO₃,^[26] Due to the polycrystalline nature of the HZO film, the polar to nonpolar transition has a gradual temperature dependence coming from grain size effects. According to the Landau-theory of phase transitions, the permittivity peak occurs at the end of the overall orthorhombic to tetragonal phase transition in the film. At the end, the Curie temperature is superimposed with the transition regime between t- and m-phase according to the GIXRD data. Due to the nonpolar to nonpolar phase transition of the tetragonal to monoclinic phase, no sharp permittivity peak of this transition is expected.^[27]

Phase transitions can be either first or second-order, where first-order phase transitions exhibit thermal hysteretic behavior (see Section S3, Supplementary Information). Such behavior was reported in literature for Y:HfO₂ and Hf_{0.5}Zr_{0.5}O₂ epitaxial films with a temperature hysteresis $\Delta T = T_1 - T_0$ between 85 and 200 K, respectively.^[28] Following this assumption, the dielectric



constant (ε_r) and $1/\varepsilon_r$ were plotted (Figure 4d,e and Figure S10, Supporting Information), and a Curie temperature (T_c) of 735 K was extracted. Assuming Curie–Weiss behavior, extrapolation of $1/\varepsilon_r$ to zero determines the maximum temperature T_1 where the polar phase can be present (Figure S11, Supporting Information). A T_1 value of 700–750 K is extrapolated depending on the fitted temperature range. According to the Landau theory, T_1 has to be larger than T_c .^[17] Thus T_1 is ≈15 K above T_c .

2.3. Simulation Results

Phase transformation temperatures extrapolated from the drop of the P_r value to $0 \,\mu\text{C} \,\text{cm}^{-2}$ can also be compared to simulation results by Kersch et al.^[22] Based on DFT thermodynamic calculations (for details see Section S7, Supporting Information) of the free energy for different phases, neglecting activation barrier and thus temperature hysteresis, o- to t-phase transition temperatures can be calculated for HfO₂ layers with different ZrO₂ content at 0 K. A similar calculation can be performed to study the effect of oxygen defects (6% oxygen vacancies in HZO) on the transition paths between the different crystalline phases in Hf_xZr_{1-x}O₂ films. Simulated phase transition temperatures are plotted in Figure 5b and compared to phase transition temperatures extracted from when the dynamic remanent polarization vanishes (see Figure 3 and Figure S2, Supporting Information). A correlation between experimental data and theoretical calculations is found. Experimental results for samples with different HfO₂/ZrO₂ ratio show a parallel trend to simulation results with values about 200 K lower to a perfect lattice structure without defects. When an oxygen vacancy level

of 6% is simulated, T_c would drop by 200 K, similar to experimental data in Figure 3b, where decreasing O₃ dose times with enhanced V_o content also changes T_c by about 200–300 K. Nonetheless, the oxygen vacancy level of 6% V_o as predicted by simulation is significantly higher than the one obtained experimentally, which are in the range of 0.1–1% as determined elsewhere via XPS measurements.^[29]

The shift of $T_{\rm C}$ to lower temperatures of the experimental data could also be explained by the polycrystalline nature of the ferroelectric thin films. The low surface/interface energy of the t-phase relative to the m-phase is known from experiments.^[30] The surface/interface energy of the t-phase could be lower than that of the o-phase, which has been proposed and calculated ab initio.^[10,31] This effect would lower the minimum of free energy of the t-phase and the o-phase (the Curie-temperature) compared to the presented ab initio calculation, which does not contain surface/interface energy effects. Thus the oxygen vacancy concentration in reality would be lower than 6% and supports the similarity of the experimental findings and simulation results. In addition, phase transition temperatures as reported in literature are added to Figure 5b, showing an even lower T_c with changing the HfO₂/ZrO₂ ratio. A possible reason could be a further enhanced V_0 content. In former experiments, shorter O₃ times were used.^[32,33]

Following the P_r and dielectric constant changes with temperature predicted by the Curie–Weiss law, a first-order phase transition from the o- to the t-phase is consistent with the observations. Comparing this to GIXRD results, different phase transitions seem to be present. From room temperature to 729 K, a transition from a polar o- to a nonpolar t-phase is observed. Between 729 and 823 K, a transition to the m- phase includes a global



Figure 5. a) Changes in pristine remanent polarization with temperature for different heating rates ($11-235 \text{ Kmin}^{-1}$) for Hf_{0.6}Zr_{0.4}O₂ deposited with 1 s O₃ dose time. b) Temperature of the phase change as a function of ZrO₂ content in Hf_xZr_{1-x}O₂ films deposited by ALD with a 1 s O₃ dose time compared to Hf_{0.5}Zr_{0.5}O₂ films deposited with different ozone dose times. The dashed lines are guides to the eye.

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strain relaxation. Below 823 K, the volume expansion causes the relaxation of the o/t phase.^[21] Here, for heating below 723 K, a transformation back to the original condition at room temperature is favored. Above 723 K and below 823 K, a non-reversible unit cell volume expansion and transition to the m-phase occurs. Above 823 K, a transition to the m-phase is clearly present, which was reported before for other doped HfO₂ films.^[28,34] Once m-phase appears within the thin films, it cannot be transformed back to the o/t-phase at these temperatures.^[7,8,35]

Based on the experimental and simulation results above, phase changes in ferroelectric HfO2-based thin films can be compared to phase changes in other ferroelectric materials (Table 1). Ferroelectrics are typically classified as proper, improper, and relaxor type.^[36] Focusing on the three main classes, the main discriminating properties can be summarized as follows: 1) the order parameter for the phase change, 2) the validity of the Curie-Weiss law for the material, 3) the presence of a temperature hysteresis, 4) the existence of active soft modes in the infrared regime, and 5) the existence of phase or chemical heterogeneity in the layer. Some differences are present when comparing a proper ferroelectric material like BaTiO₃ to HfO₂. BaTiO₃ shows a clear first-order phase transition with a small temperature hysteresis of 5–10 K.^[37] Soft modes are active in the IR regime, and the primary order parameter using the Landau-Devonshire equation is polarization.

2.4. Classification of Ferroelectric HfO₂

For HfO₂, the frequent adoption of Landau–Devonshire models to describe ferroelectric behavior implies that the polarization is the primary order parameter. Yet strain/stress also seems to be coupled to the magnitude of the remanent polarization, as also observed in ferroelectric BaTiO₃.^[38,39] For thin HfO₂ films, the peak in the dielectric constant was confirmed. The frequency dependence of the maximum in the dielectric constant at the Curie temperature indicates a first-order phase transition. Calculations based on the Landau–Devonshire model have suggested a maximum 100 K thermal hysteresis in Si-doped HfO₂.^[38] For bulk HfO₂/ZrO₂, a first-order martensitic phase transition is

reported from the t- to the m-phase.^[13] Since a collective martensitic phase transition is difficult to realize in polycrystalline layers, a 20-30 K thermal hysteresis could be confirmed. Overall, a martensitic phase transition possibly involving strain is expected to be easier in polycrystalline than in epitaxial materials. At 0 K no soft modes are active in the IR regime.^[15] The calculated phonon dispersion can be found in Section S9 (Supporting Information). For first-order materials like BaTiO₃, phase transitions can be related to soft modes,^[40] but for HfO₂, Sternik et al. claimed that the phase transition is initiated by the coupling of several phonons.^[15] Finally, BaTiO₃ can be deposited by epitaxial growth even for thick films with larger domain size consisting only of single ferroelectric phase contributions. In contrast, HfO₂ shows the coexistence of different phases in films due to the low activation barriers for phase transitions. Therefore in thin HfO₂ films, epitaxial growth with large domain size and single-phase contributions is more complicated.

Looking at the requirements for improper and relaxor type ferroelectric materials, more differences to experimental observations in HfO2-based ferroelectric materials are seen. For both classes, polarization is not an order parameter. The thermally driven hysteresis is larger than the values reported in this study, and soft phonon modes are not necessarily involved in the phase transition.^[15] For the polycrystalline films, the polar phase may exist as discontinuous clusters. Therefore, the highly localized character of polar regions in HfO2 seems to bear similarities with relaxor ferroelectrics. However, the ferroelectric phase in hafnium oxide is not necessarily confined to such nanoclusters like relaxor ferroelectrics since the polar phase is typically capable of manifesting as an observable macroscopic phase.^[41] Consequently, the classification as relaxor or improper ferroelectric for hafnium oxide is less likely compatible with experimental observation, but further investigations are needed to resolve the question of ferroelectric classification in the HfO₂-based material system.

In summary, most properties of ferroelectric HfO_2 are consistent with the classification as a proper ferroelectric material with first-order phase transition. However, some differences due to the polycrystalline nature of the thin films used in this study are present.

Table 1.	Classification	of different	ferroelectric materia	l classes: Prope	er, improper,	, and relaxo	r ferroelectrics
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	Proper FE	Improper FE	Relaxor FE	Ferroelectric HfO ₂
Example	BaTiO ₃ (BTO) ^[37]	PbTiO ₃ /SrTiO ₃ (PbTO/STO) ^[42]	PbMg _{1/3} Nb _{2/3} O ₃ (PMN) ^[41]	Hf _x Zr _{1-x} O ₂
Order parameter for phase change	Polarization Polarization-strain coupling possible	Polarization not an order parameter	Charge/elemental disorder	Polarization Polarization-strain coupling possible
Curie–Weiss law	Valid	Not valid	Not valid (Burns law applies)	Valid
Phase transition	First- or second-order PT	First- or second-order PT	First-order, missing macroscopic PT	First-order PT
Temperature hysteresis	First order: $\Delta T \approx 5-10 \text{ K}^{[37]}$ Second order: $\Delta T = 0 \text{ K}^{[43]}$	First order: $\Delta T > 10 \text{ K}^{[43]}$ Second order: $\Delta T = 0 \text{ K}^{[43]}$	ΔT > 100 K ^[44]	$\Delta T \ge 15 \text{ K}$
Soft mode active in IR regime	1st order PT: not necessary 2nd order PT: yes	No	Not necessarily involved	Not active at 0 K Coupling of several phonons possible
Phase or chemical heterogeneity	Epitaxial layers/larger domains	Unclear	Nanoregions not visible in XRD	Polycrystalline, small domains



3. Conclusion

Phase transitions for polycrystalline 10 nm Hf_vZr_{1-v}O₂ films with different ZrO2 content in HfO2 and minor variations in oxygen content were studied by detailed structural and electrical characterization. Films transformed from a polar orthorhombic to a nonpolar tetragonal to a monoclinic phase with decreasing phase transition temperature for enhanced ZrO₂ content. Below 723 K, the orthorhombic to tetragonal phase transition was reversible for a mixed $Hf_{0.5}Zr_{0.5}O_2$ layer, followed by a stress release with transformation to the m-phase. After clear transformation to the m-phase above 823 K, no back-transformation into the orthorhombic or tetragonal phase was possible during cooling. Fast heating and cooling ramp rates can reduce the thermal hysteresis of the transition and the phase conversion to the monoclinic phase below 823 K. Based on the Curie-Weiss law, maxima in the dielectric constant at orthorhombic to tetragonal phase transition temperature could be experimentally confirmed. DFT calculations could verify measured phase transition temperature trends. Results can be related to a phase transition as expected for a proper first-order ferroelectric material. For device applications, the results indicate that when suitable dopants and oxygen content is incorporated into Hf_xZr_{1-x}O₂-based materials, the phase transition temperature can be increased to about 700 K. This temperature is more than sufficient for typical semiconductor device applications. Enhancing the temperature above 700 K may lead to a non-reversible phase transformation to the monoclinic phase.

4. Experimental Section

 $Hf_xZr_{1-x}O_2$ layers were deposited on a Si substrate via atomic layer deposition (ALD) with $Hf[N(CH_3)(C_2H_5)]_4$ and $CpZr[N(CH_3)_2]_3$ precursors as Hf and Zr sources respectively in a Roth&Rau ALD tool. To change the composition in $Hf_xZr_{1-x}O_2$ binary oxides, the metal precursor cycle ratio between Hf and Zr was varied. Ozone (O₃) was employed as the oxygen source at a deposition temperature of 280 °C. Metalinsulator-metal (MIM) capacitors were fabricated by depositing two titanium nitride (TiN) electrodes with a thickness of about 10 nm via physical vapor deposition (PVD, sputter deposition) in a Bestec UHV sputter cluster at room temperature from a Ti target in N₂ atmosphere. In between these TiN layers, $Hf_xZr_{1-x}O_2$ was deposited. After a postmetallization annealing (PMA) treatment in a nitrogen atmosphere at 600 °C for 20 s a crystalline structure of the dielectric layer was reached. For capacitor structuring, Ti/Pt dots with a diameter of 200 μm and a thickness of 10 and 25 nm for Ti and Pt, respectively, were deposited via e-beam evaporation through a shadow mask. The exposed TiN blanket was wet-chemically etched with a standard clean 1 (SC1: H₂O, H₂O₂ and NH₃ ratio 50:2:1) using the Pt dots as a hard mask.

Grazing incidence X-ray diffraction (GIXRD) measurements were performed as a function of temperature using a Rigaku SmartLab equipped with a Reactor X heating stage. A Cu tube was used as the X-ray source and a point detector was used to measure a 2θ window of $27–38^{\circ}$ at each temperature. GIXRD patterns were measured at various set temperatures during both sequentially increasing and decreasing temperatures. Between set points, the sample was heated at a rate of 30° C min⁻¹. At each set temperature, the sample was aligned in both the vertical dimension (Bragg plane alignment) and made parallel to the beam by rocking the angle ω with respect to parallel incident and diffracted beams. To avoid a strong transition to the m-phase, the heating and cooling rate was kept as high as possible, which reduced the integration time and enhanced the noise level.

Polarization versus electric field (P-E) hysteresis measurements were performed with an aixACCT systems TF Analyzer 3000 using a



measurement frequency of 10 kHz. The P–E hysteresis measurements were done at temperatures from 300 to 800 K in ambient atmosphere. Three different temperature ramps were used as explained in the supporting information and shown in Figure 5a. The capacitance-voltage (C-V) measurements were taken at 0 V to avoid a dielectric breakdown at high temperatures.

For dielectric permittivity measurements, thin film samples were placed between two Pt electrodes in a pressure-contact jig and measured at 4 fixed frequencies of 1, 100, 250 kHz and 1 MHz. Capacitance data corrected for sample geometry were recorded in air every minute from room temperature to 600 °C with heating rate 1 °C min⁻¹ using an LCR meter (Model 4284A, Hewlett Packard, HP). The dielectric permittivity, ε_r was calculated using $\varepsilon_r = C/e_0$, where e_0 is the permittivity of free space, 8.854×10^{-14} F cm⁻¹ and C is the measured capacitance.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

Curie–Weiss law, ferroelectric materials, hafnium oxide, phase transition in doped $\rm HfO_2$ and $\rm ZrO_2,$ zirconium oxide

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