Origin of Ferroelectric Phase in Undoped HfO₂ Films Deposited by Sputtering

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1. Introduction

Since Böscke et al. reported ferroelectricity (FE) in thin atomic layer deposited (ALD) Si-doped HfO₂ films,[1] many other dopants such as Al, Gd, La, Sr, Y, and Zr are reported to induce ferroelectric properties in HfO₂.[2–7] While bulk HfO₂ crystallizes in a monoclinic phase (m-phase; space group: P2₁/c), it is believed that the FE in doped HfO₂ results from the formation of a non-centrosymmetric Pca₂₁ orthorhombic phase (o-phase).[1–7] For increasing doping concentrations, ALD HfO₂ films undergo a phase transition from a non-ferroelectric m-phase to ferroelectric orthorhombic phase and for higher concentrations to the tetragonal phase (t-phase; space group: P42/nmc) if the dopants are smaller than Hf like Si and Al, or to the cubic phase if the dopants are larger than Hf like Gd, La, Sr, and Y.[8] Besides the influence of doping, four other factors are known to promote the stabilization of the ferroelectric phase: surface or interface/grain boundary energy, film stress, and the presence of oxygen vacancies.[9–13] Oxygen vacancies and the related defect states play an important role in the so-called wake-up effect.[14] Wake-up describes the increase of the remanent polarization during electrical field cycling with opening of an initially pinched polarization-voltage hysteresis.[15] In Hf₁₋ₓZrₓO₂ films, Materlik et al. suggested that the bulk and surface free energy of the o-phase is located between those of the m-phase and t-phase. As a result, the o-phase is stabilized in a specific film thickness and grain size region. This suggestion matches well
with many experimental results on the effect of film thickness and/or grain size for the ferroelectric phase formation.\[9,10,12\] Experimentally, a ferroelectric phase could be formed in undoped HfO$_2$ by tuning the grain size which can be controlled by thermal treatment and film thickness.\[13,16\] Polakowski and Müller\[17\] and Kim et al.\[18\] obtained the ferroelectric phase at reduced ALD deposition temperatures and for decreased film thicknesses below 10 nm. Both methods reduced the grain size and stabilized the o-phase in undoped HfO$_2$. Besides the aforementioned thermodynamic mechanisms, Park et al. recently suggested that the metastable orthorhombic phase formation can be attributed to the kinetic suppression of the formation of the monoclinic phase due to the rather high kinetic activation barrier for the tetragonal/orthorhombic to monoclinic phase transformation.\[19\]

Ferroelectric HfO$_2$-based thin films could be reproducibly deposited using various deposition techniques such as ALD, chemical vapor deposition, chemical solution deposition, pulsed laser deposition and sputtering as physical vapor deposition (PVD) method.\[20\] Among these techniques, the most intensively studied deposition technique is ALD. For the case of ALD, however, there are less deposition parameters which can be controlled, since ALD is based on a self-limiting mechanism with chemical reactions between a metal precursor, oxygen source, and substrate or previously deposited film. Typical parameters are only deposition temperature and precursor/purge pulse times. On the other hand, for PVD, various factors such as sputtering power, sputter atmosphere, and deposition temperature can be easily controlled, suggesting that PVD is an attractive deposition technique to study root causes of the unexpected ferroelectric phase formation in HfO$_2$-based thin films. Contaminants within the film are mainly determined by the target quality. The first report of sputtered ferroelectric HfO$_2$-based films used Y doping and later extensive studies with other dopants followed.\[21–23\] These studies showed improved FE in HfO$_2$ by co-sputtering from oxide targets, but also undoped sputtered HfO$_2$ films showed signs of FE.

In this study, RF sputtering as a PVD method is used to fabricate undoped HfO$_2$ thin films. The fabricated PVD films are compared to ALD films as reported in literature to gain deeper insight into the mechanisms involved in the formation of the ferroelectric phase in undoped HfO$_2$ films.\[17,24\] For ALD HfO$_2$ films, carbon from the residual precursor ligands will be present as a significant source of contamination, whereas in PVD HfO$_2$ films, only a low amount of processing gases were reported.\[18\] In addition, the possibility to grow the films at room temperature together with higher deposition rates changes the deposition kinetics when sputtering is used compared to ALD. The benefit of characterizing the ferroelectric properties in undoped HfO$_2$ films is that the number of factors influencing the formation of the ferroelectric HfO$_2$ phase is reduced. With the effect of doping removed, studies can focus on the impact of the remaining factors responsible for the formation of the ferroelectric phase. In particular, the influence of oxygen content in thin HfO$_2$ films on the phase composition and the according ferroelectric properties will be investigated. Comparable studies were performed for HfO$_2$ powders, which showed similar trends.\[25,26\]

Figure 1. Double remanent polarization 2P$_r$ for sputtered undoped HfO$_2$ films as a function of film thicknesses and annealing temperature. Open symbols represent pristine values and closed symbols are values after wake-up.

2. Discussion

The capacitors described above were investigated regarding their ferroelectric properties. Figure 1 shows the switchable polarization 2P$_r$ of various films with different HfO$_2$ thicknesses from 8 to 30 nm and annealed at different temperatures from 500 to 1000 °C. It can be seen that 500 and 600 °C anneals are not sufficient to induce FE in any of the examined thicknesses. For higher anneal temperatures, films show a stable remanent polarization. The highest 2P$_r$ of 20.2 μC cm$^{-2}$ nearly matches the results reported for ALD deposited films at an electric field of 4 MV cm$^{-1}$ (see Figure 3).\[13\] The impact of the annealing temperature on the remanent polarization changes with film thickness. From 8 to 20 nm, 2P$_r$ increases with increasing
temperature. In contrast, the 800 °C annealing seems to be the optimal annealing temperature for thicker films. This is caused by a lowered crystallization temperature and a preferred transformation to the monoclinic phase for thicker films, as will be discussed later.[13,28] Additionally, the 800 °C annealed samples exhibit the most stable polarization at different thicknesses in the pristine state and after wake-up cycling. However, samples annealed at this temperature possess a much stronger polarization increase with electrical field cycling than the 1000 °C annealed films (see Figure 1). The higher annealing temperature causes a more homogeneous distribution of defects and ferroelectric domains in the film.[11] This effect increases the initial number of switchable domains within the ferroelectric film and thus the pristine remanent polarization is increasing (see Figures S1 and S2, Supporting Information). In previous studies, a similar effect could be shown for ALD Hf0.5Zr0.5O2 thin films.[16]

In Figure 2 the number of field cycles to breakdown (endurance) for different film thicknesses and annealing temperatures is shown. To keep the measurement time in a reasonable range, the maximum number of applied cycles was 10⁸. Therefore, the endurance of samples reaching 10⁸ cycles is equal to or greater than 10⁸. The number of electric field cycles before the dielectric breakdown decreases for increasing annealing temperature from 600 to 1000 °C and with increasing film thickness. Higher temperatures not only result in a more homogenous defect distribution, but also in an increased defect concentration, diffusion of defects, and migration of titanium/nitrogen ions from the electrode along grain boundaries into the film.[29] The significantly increased leakage current density with higher annealing temperature (Figure S10, Supporting Information) confirms the assumption of more defects for higher annealing temperatures. The number of field cycles to breakdown of these films is accordingly decreasing. In addition, the higher polarization of films annealed at temperatures above 800 °C leads to a higher charge injection and increased defect generation during electrical field cycling.[30,31] Samples annealed at 500 °C show an opposite behavior because of the changed crystalline properties. As determined by grazing-angle incidence X-ray diffraction (GIXRD), the 10 nm thick sample is crystalline for anneals at 600 °C and above (see Figure 4) and only an amorphous background signal is detected for

**Figure 3.** Number of cycles to break down HfO₂ films as a function of film thickness and annealing temperature. Cycling was stopped after 10⁸ electrical field cycles were reached.

**Figure 4.** GIXRD patterns of undoped sputtered HfO₂ for different thicknesses from 8 to 30 nm and for 10 nm thick films with different annealing temperatures. The theoretical peak positions for cubic TiN orthorhombic HfO₂, monoclinic HfO₂, and tetragonal HfO₂ are shown in the lowest panel.
as-deposited samples up to 500 °C annealing temperatures. The samples have a relatively high endurance that drops for lower annealing temperatures than 600 °C where films are mainly amorphous. Overall, the crystallization temperature of PVD HfO₂ is raised relative to ALD samples as explained later in the text. The identified thickness-dependent polarization of the sputtered HfO₂ films is compared with those of published ALD films in Figure 3. The FE in sputtered HfO₂ is retained up to much larger thicknesses for PVD relative to ALD films that exhibit FE only in undoped HfO₂ films thinner than 12 nm. Polakowski and Müller assumed that the decreased grain size for films with a thickness lower than 10 nm stabilizes the ferroelectric phase. Additionally, from DFT simulations and former experiments, it is known that an increase in the grain size in thicker films destabilizes the orthorhombic phase and stabilizes the monoclinic phase as a consequence of an increase of the surface energy to bulk energy ratio. Accordingly, other factors than surface and grain boundary energy play a more prominent role in the stabilization of the ferroelectric phase in undoped HfO₂ deposited by PVD. To prove that the hysteretic behavior of HfO₂ films shown above has a ferroelectric origin, the individual nanometer-scale domains were monitored by piezoresponse force microscopy (PFM) on a 10 nm thick HfO₂ film annealed at 1000 °C. PFM maps of the amplitude and phase of local piezoelectric response have been collected on the HfO₂ capacitors through the TiN/Pt 30 nm top electrode (Figure 5a–f). The measurements have been carried out using the off-resonance PFM technique with the ac signal of 0.5 V/91 kHz. The nanometer-scale switching data in Figure 5 reveal a switching asymmetry; the tip bias of +3 V results in a complete switching (homogeneous phase map) while the opposite bias produces only partial switching with about 30% of non-reversed domains. The PFM maps of this partially switched state clearly show the domain structure where the opposite domains are signaled by bright color (Figure 5a–c: phase map) and outlined by dark zones at the
boundaries (amplitude maps). These PFM results which show partial switching are consistent with the macroscopic switching data (Figure 1) where the initial switching polarization is 22% lower than the value achieved after the wake-up procedure. The FE of the capacitors used in this study is further confirmed by local hysteresis loops of the transverse piezoelectric coefficient $d_{33}$ (Figure 5). The sharp 180° phase change during switching and the saturating voltage dependence of $d_{33}$ loops attest to the true ferroelectric origin of the observed hysteretic behavior.

With the confirmation of ferroelectric switching shown by the PFM results, the crystal structure is examined by GIXRD to identify the polar orthorhombic phase which is the origin of FE in HfO$_2$ as explained above. The investigated HfO$_2$ thin films of various thicknesses annealed at 800 and 1000 °C have polycrystalline structures and Figure 4 evidences that the orthorhombic and/or tetragonal phase is the most prominent phase in all films. Films with film thicknesses above 15 nm have an increasing monoclinic phase fraction. This effect was also investigated for ALD HfO$_2$.[17] For ALD films, a significant increase of the m-phase from 15 to 60% for increasing film thickness from 6 to 20 nm occurred, which was accompanied by a destabilization of the o-phase and a reduction of the remanent polarization. The increase of the m-phase fraction is weaker in PVD HfO$_2$ films.[17] The higher monoclinic phase fraction in 20 and 30 nm thick films annealed at 1000 °C causes the decrease in remanent polarization. From 8 to 30 nm thickness, a slight o(111)-peak shift to higher two theta values is observable (30.5° to 30.65°). This can hint to a phase change from a predominant orthorhombic to a more tetragonal phase, which may also decrease the remanent polarization. However, this peak shift can most likely originate from a change of the film stress with increasing thickness. Thus, no clear separation between film stress and phase transformation can be made here. Films annealed at 600 °C exhibit a strong o(111)/t(011) peak at ~30.65° but only a small remanent polarization.[32] The MIM capacitors annealed at 600 °C had a pinched hysteresis loop which slightly opened up during field cycling. Capacitance-voltage measurements result in a $k$-value of ~37 (Figure S13, Supporting Information). Accordingly, a mixture of the tetragonal ($k = 40$) and orthorhombic phase ($k = 28$) can be assumed.[33] In the GIXRD pattern of Figure 4 the o(111)-peak is shifting from 30.65° to 30.5° for increasing annealing temperature. This shift indicates a phase transformation from the tetragonal to the orthorhombic phase.[16] To distinguish between the o- and t-phases, a Rietveld refinement was performed. The orthorhombic phase fraction is increasing from ~40 to ~95% with increasing annealing temperature, whereas the tetragonal phase is decreasing from ~40 to 0% (see Figure S14, Supporting Information). In the low-temperature annealed films, an equal mixture of the orthorhombic and tetragonal phases prevails. With increasing annealing temperature, the tetragonal phase is transforming to the orthorhombic phase.

In ALD-manufactured HfO$_2$ films, it could be observed that the initial phase of formed nanocrystallites during the film deposition strongly impacts the later polymorphism.[15,34] The diffuse GIXRD pattern of the as-deposited sputtered 10 nm HfO$_2$ shown in the bottom of Figure 4 indicates mainly an amorphous structure with 1 nm crystallites. In contrast to ALD films, the GIXRD pattern after annealing at 500 °C for 20 s still indicates a mostly amorphous film with discontinuous nanocrystallites. One possible conclusion from this result would be a higher nucleation energy in PVD compared to ALD films. Since ALD films are deposited at higher deposition temperatures (260–300 °C) compared to the PVD films (room temperature), the higher thermal energy enhances the mobility and conglomeration of atoms during film growth. This lowers the subsequent activation energy for nucleation causing crystallization to proceed with less thermal energy input during the annealing process.[35] In addition, a possible difference in the nucleation energy could be caused by a lower number of impurities observed in PVD films because of direct sputtering from nominally HfO$_2$ targets. In particular, ALD often has a higher carbon incorporation owing to the organic-based precursors. For the comparison of the carbon content of ALD- and PVD-manufactured films, time-of-flight secondary ion mass spectrometry (ToF-SIMS) is used in this study. Independent of the annealing temperature, PVD films contain ten times lower carbon concentration (~0.1 at%) compared to ALD films (~1 at%) (Figure S7, Supporting Information). Larger grain sizes of 20 nm in PVD films, compared to grain sizes of 8 nm observed in ALD films (Figure S6, Supporting Information), support this assumption, since a higher carbon concentration would lead to a larger number of grains as well as a suppressed grain growth.[16,36] In addition, different concentrations of oxygen in ALD versus PVD films as discussed in the later part of the text could impact the crystallization behavior.

It is already known from ALD undoped HfO$_2$ films that oxygen vacancies can be a driving force or at least an important factor in the stabilization of the metastable ferroelectric orthorhombic phase.[24,37] Due to film deposition by sputtering from an oxide target, an unbalanced sputtering and deposition of Hf and O can occur which results in sub-stoichiometric films with a higher amount of oxygen vacancies. To check this assumption, HfO$_2$ films with an additional oxygen flow from 0.25 to 2 sccm at the substrate were deposited.

**Figure 6** shows the remanent polarization $2P_r$ as a function of the oxygen flow during deposition of HfO$_2$ films.
2\(P\) is correlated with an increase of the monoclinic phase portion and a decrease of the orthorhombic phase as can be seen in the \(o/(o+m)\) ratio in Figure 7. In addition, \(2P\) versus oxygen flow and annealing temperature might also be impacted by other factors like film texture, additional vacancy formation at TiN/HfO\(_2\) interface, pinning of domains due to changes of the interface stoichiometry, and oxidation of the TiN bottom electrode with different oxygen partial pressure. The \(o/(o+m)\) ratio is calculated by using the peak areas of the \(o\)(111), \(m\)(−111), and \(m\)(111) diffraction peaks at 30.5°, 28.5°, and 31.6° as described for the m-phase fraction in ref. [6].

Figure 7. \(o/m\)-ratio calculated from peak areas of GIXRD pattern of sputtered HfO\(_2\) films with different oxygen ambient during deposition.

According to the \(o/(o+m)\) ratio from the diffraction peak areas, a decrease of the orthorhombic phase portion and an increase of the monoclinic phase with increasing oxygen flow can be observed. Less oxygen during deposition may lead to more oxygen vacancies in the HfO\(_2\) films. Similar to the discussion above, the different oxygen concentrations in HfO\(_2\) are leading to different nucleation behaviors which impact the formation of the crystal phase and according polarization values. Comparing the GIXRD results of as-deposited PVD HfO\(_2\) films (Figure 8) and the case after 800 °C annealing (Figure 9), nuclei of certain phases are already present after deposition that determine the later predominant phase of the film. HfO\(_2\) films with low O\(_2\) flow show broad \(o/m\)-phase diffraction peaks as expected for mainly amorphous films in contrast to m-phase nuclei for the highest O\(_2\) flow. In parallel, the peak width of the m-phase peak is reduced, indicating larger m-phase grain nuclei for higher O\(_2\) flow. The crystallite size in the as-sputtered films, determined by Scherrer’s equation, remains roughly constant at about 1 nm until an O\(_2\) flow of 2 sccm is used which causes larger 4 nm monoclinic crystallites to nucleate (Figure S18, Supporting Information). Similar to these results, ALD-based HfO\(_2\) films also exhibit an improvement in FE for lower oxygen content during deposition\([24]\) caused by shorter O\(_3\) precursor pulse times, although the predominant phases are shown only after high-temperature annealing and the nucleating phase is not clear. To prove the assumption of different oxygen vacancy levels, leakage current measurements were performed (Figure S11, Supporting Information). For ALD HfO\(_2\) films, Pal et al. reported a strong change in the leakage current for different ozone dose times and ascribed this to a change in the oxygen vacancy level.\([24]\) Sputtered HfO\(_2\) films deposited under different oxygen ambient do not show this behavior. The leakage current is fluctuating around \(10^{-5}\) A cm\(^{-2}\) with no clear influence of the oxygen ambient. Either the concentration is too low to appear in the leakage current or other effects such as grain boundary leakage superimpose the influence of oxygen deficiencies. For this reason, hard X-ray photoelectron spectroscopy (HAXPES) was applied as a method to clearly determine the oxygen vacancy concentration difference between samples with 2 sccm additional oxygen flow and without oxygen (Figure 10). In the layers without additional oxygen, a shift of the Hf 4f and the O 1s peaks towards higher binding energy was observed, while the Ti 2p levels remain unaffected for both
samples (not shown here). With regard to the literature,\textsuperscript{38–40} this peak shift is related to a downward band bending caused by an increasing amount of oxygen vacancies at the HfO\textsubscript{2}/Ti electrode interface. Here one has to take into account that the O 1s peak can be superimposed with other peaks and the Hf 4f peaks are separated from other features. Both peaks of the PVD samples are in between the peak positions determined by Sowinska et al. for ALD as-deposited HfO\textsubscript{2} films and after forming a low resistive state with high amount of oxygen vacancies.\textsuperscript{39} From thermally stimulated depolarization currents (TSDC), it is known that the amount of oxygen vacancies is in a range from 0.1 to 0.25\% after annealing.\textsuperscript{41} This low-concentration difference correlates with the small peak position shift in Figure 10. The strong shift in the peak position of the amorphous films stems from the fact that in the virgin state, almost no oxygen vacancies are present and, after electroforming, a high amount of oxygen vacancies concentrate at the TiN/HfO\textsubscript{2} interface.\textsuperscript{40} Since no additional interstitial O feature at 528 eV is observed in the O 1s peak for PVD HfO\textsubscript{2} films with additional oxygen flow, this interstitial oxygen amount is expected to be low for crystalline HfO\textsubscript{2} (see Figures S8 and S9, Supporting Information).\textsuperscript{42} For amorphous HfO\textsubscript{2} (not shown), interstitial O is difficult to be detected and, accordingly, it is expected that no feature is present. Overall, this confirms that the number of oxygen vacancies in the HfO\textsubscript{2} can be influenced by additional oxygen flow during sputter deposition.

Independent of the deposition method, nucleation can be described by the Ostwald’s rule, which states that not the most but the least stable polymorph crystallizes first.\textsuperscript{43} Following the free energy as calculated by DFT (Figure S17, Supporting Information), nucleation would start in the phase with the highest free energy (cubic phase) and transform to phase with lower free energy depending on the grain size (cubic to tetragonal to orthorhombic to monoclinic transition). This approach follows the same explanation path as discussed by Materlik et al. using a surface/interface model. Again, a grain size–dependent phase formation is expected which can be experimentally shown in temperature-dependent GIXRD measurements (see Figure S16, Supporting Information). Since a high activation barrier is reported between the o-phase and m-phase as described by Park et al., a metastable ferroelectric o-phase can be formed under certain process conditions (e.g., thermal budget). The amount of oxygen within the HfO\textsubscript{2} layer can impact the nucleation and grain growth behavior.

As mentioned above for PVD films, oxygen-deficient HfO\textsubscript{2} films are almost amorphous with some small nuclei within the layer likely positioned at defects (see Figure 11). For heterogeneous nucleation, these defect sites are likely at film interfaces. During polymorphic crystallization at 800 °C, the amorphous and crystalline phase are of the same composition and the oxygen content in the layer is kept. The nucleation is following the abovementioned grain size–dependent phase formation. For smaller grains, the higher surface and interface energy causes the formation of the t-phase at 800 °C, since a high activation barrier is inhibiting a phase transformation to the m-phase. During cool down, the t-phase is transformed to the o-phase below Curie temperature.

In contrast, for oxygen-rich PVD HfO\textsubscript{2} films, more oxygen is available leading to a lower energy required for nucleation. Hence, a lower incubation time reduces the crystallization temperature and larger nuclei are already present in the as-deposited HfO\textsubscript{2} at room temperature (Figure S18, Supporting Information).\textsuperscript{44,45} According to DFT calculations the t-phase formation is suppressed for higher oxygen concentrations in HfO\textsubscript{2} (Figure S17, Supporting Information) and m-phase

![Figure 10](image1.png)

**Figure 10.** Binding energies of the O 1s and Hf 4d 5/2 peak for ALD and PVD films fabricated under different oxygen conditions. Closed symbols: this work; open symbols: Sowinska et al. and Bertaud et al.\textsuperscript{39,40}

![Figure 11](image2.png)

**Figure 11.** a) Phase formation during cooling: depending on the grain size, a different phase is formed. b) The grain size can be impacted by the layer thickness or the defect/oxygen vacancy level in the film.\textsuperscript{44,45}
nuclei are formed. These m-phase nuclei are determining the dominate phase of the crystallized layer during 800 °C anneal.

This work highlights the impact of oxygen in ferroelectric HfO₂. In the literature, other factors like dopants, stress, and surface/interface energy are discussed to impact the phase formation.[12] All these factors can also be related to vacancies since the amount of dopants can influence vacancy levels in a HfO₂ layer, and stress caused during electrode deposition can also change vacancy amounts due to different deposition times and interface reactions. Furthermore, the ferroelectric properties in HfO₂ were related to grain size and varying grain sizes would have a different surface/interface energy, but the grain boundaries are also preferred sites for vacancies which could impact the phase. Overall, the amount of oxygen vacancies play an important role in the stabilization of the ferroelectric phase.

3. Conclusion

In conclusion, sputtering HfO₂ from ceramic HfO₂ targets is an effective way to produce stable ferroelectric films over a wide thickness range with high remanent polarization Pₑ of 18–20 μC cm⁻² without using additional doping. Ferroelectric properties are confirmed on macroscopic capacitor structures and by PFM on the nanometer scale. The results indicate that the defect structure in thin films is extremely important for the stabilization of the orthorhombic phase. The concentration of oxygen within the HfO₂ film can be directly or indirectly responsible for the stabilization of the orthorhombic phase. With increasing oxygen flow during the sputter deposition of undoped HfO₂, it was possible to vary the amount of oxygen vacancies incorporated in the HfO₂ films as confirmed by HAXPES. The concentration of oxygen determines the nucleating phase of nanocrystallites in the as-deposited films, which impacts the later phase transitions during annealing and cooling to room temperature in the HfO₂ films. Here, the ferroelectric orthorhombic phase is preferred in oxygen-deficient layers, whereas oxygen-rich films could initiate larger monoclinic grains. The observation of a very low monoclinic phase fraction in combination with high remanent polarization values make undoped sputtered HfO₂ an excellent candidate for applications where doping needs to be avoided. Moreover, the obtained results help to further clarify the factors influencing the stabilization of the metastable orthorhombic phase in hafnium thin films.

4. Experimental Section

MIM capacitor structures were fabricated on silicon substrates for electrical and structural characterization. The MIM capacitors were deposited in a BESTEC ultra-high vacuum (UHV) sputter cluster equipped with three chambers. Using one chamber for metal deposition and two for dielectrics, it is possible to build the film stack without breaking vacuum. TiN top and bottom electrodes were deposited at room temperature from a 3 in. target in 20 sccm Ar and 4 sccm N₂ flow at 1.2 × 10⁻² mbar. A 3 in. ceramic HfO₂ target with 99.9% purity bonded on a copper back plate was used for the deposition of HfO₂ films with various thicknesses between 8 and 40 nm using 20 sccm Ar.

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.
Keywords
ferroelectricity, hafnia, orthorhombic phase, oxygen vacancies, sputtering

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