Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting information

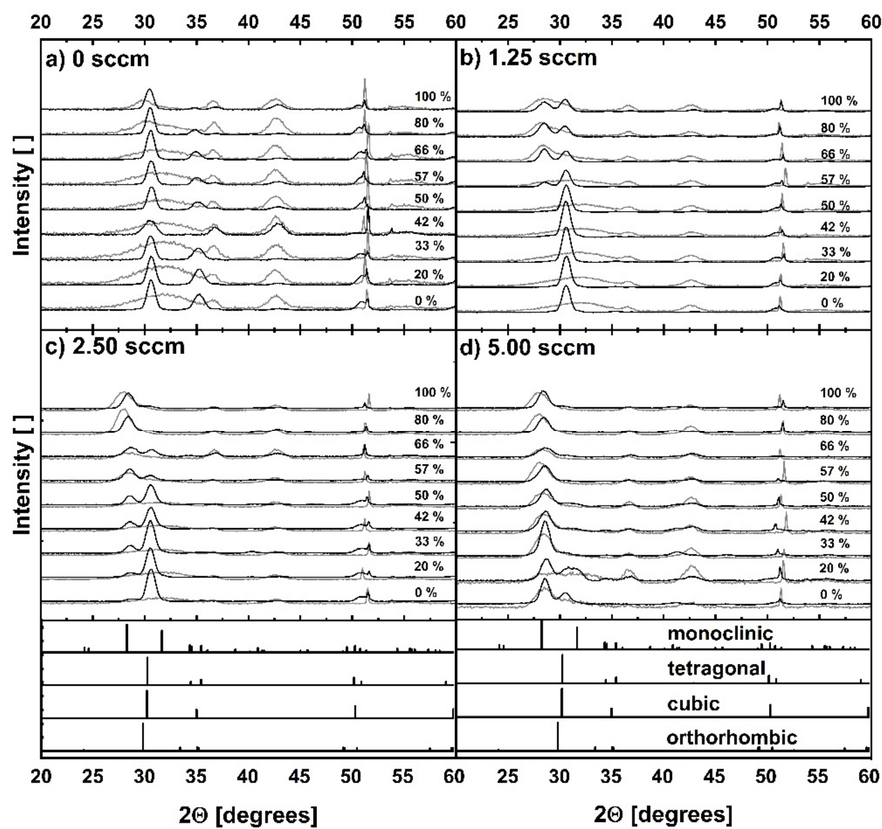

Figure SI 1 Complete set of GIXRD plots of Hf1-xZrxO2 sputtered films under various oxygen ambient as deposited and after 800 °C anneal. The scale of as-deposited and annealed films is not true to scale for a better visibility of the as-deposited films.

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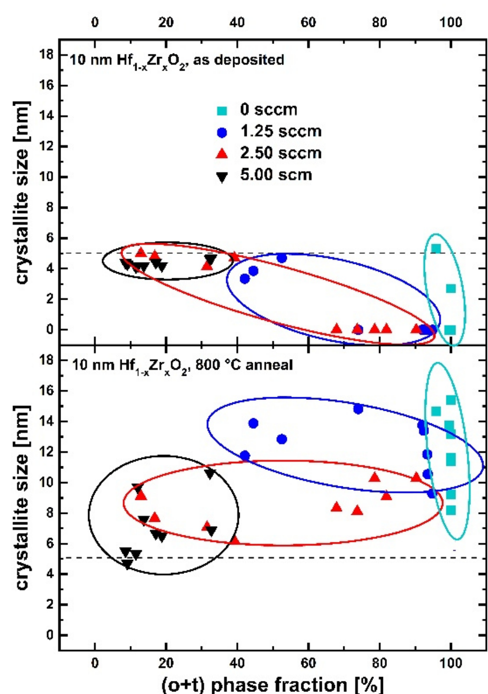

Figure SI 2 With Williams-Hall analysis determined crystallite diameter of the as deposited and 800 °C annealed films for the different (o+t)-phase fraction. Depending on oxygen concentration the dominant phase is used, 0 sccm flow and 1.25 sccm the 30.5 ° o(111) diffraction peaks.

The biaxial film stress Figure 9 b) is calculated by the $\sin^2(\Psi)$ method using the o(111) peak.[31,32] Young's modulus of 284 GPa and a Poisson ratio of 0.6 is used. [33] Since with increasing oxygen amount the o(111) signal becomes lower, the intensity is strongly decreasing when Ψ (angle between the surface normal and scattering vector) is increased. Therefore stress measurements became complicated and inaccurate. Thus the measurement is stopped at 2 sccm oxygen.

The unit cell volume in Figure SI 3 is calculated by using the GIXRD pattern of Figure SI 1 and the o(111) and o(002) peak. The unit cell volume is increasing for increasing oxygen and ZrO_2 concentration. In the ZrO_2 rich regime the unit cell in oxygen rich PVD is much higher than in stoichiometric ALD HZO. This is indicating a compressive stress induced by oxygen interstitials.

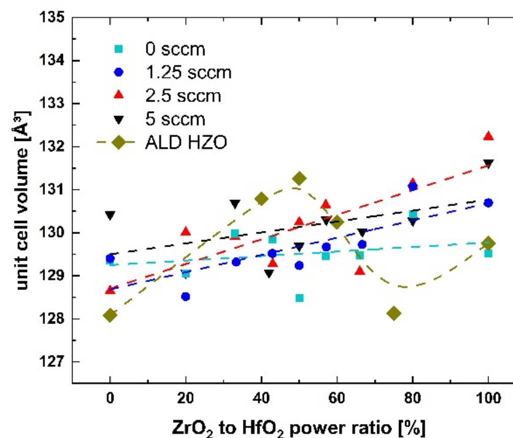

Figure SI 3 Comparison of the unit cell volume extracted from the GIXRD pattern of the sputtered $Hf_{1-x}Zr_xO_2$ films and ALD deposited Hf1-xZrxO2 films

From literature it is known, that increasing anneal temperatures in sputtered HfO_2 and increasing oxygen supply during deposition increase the compressive film stress.[51] The compressive film stress in thin films can cause buckling and finally film delamination as observed in Figure 11 for oxygen and ZrO_2 rich HZO films.[52] The expansion of the unit cell volume for higher oxygen supply shown in Figure SI 3 matches the DFT calculation indicating an incorporation of oxygen interstitials. An ALD reference $Hf_{0.5}Zr_{0.5}O_2$ shows in the ZrO_2 rich regime lower unit cell volumes and no general trend to increase with higher ZrO_2 concentration. The stress effect might be higher in the sputtered films than in the ALD films since they have to be annealed at 800 °C whereas the ALD films are typically annealed at 600 °C. Additionally the density of the thin films is about ~20-30 % higher for the PVD deposited films compared to the ALD deposited films (Table SI 1). Higher film densities are well known to cause compressive strain.[53]

Table SI 1 Density of PVD and ALD deposited HfO_2

	PVD 0 sccm	PVD 2 sccm	ALD 10 s	ALD 60 s
Density [g/cm³]	10.3	12.06	8.5	8.99

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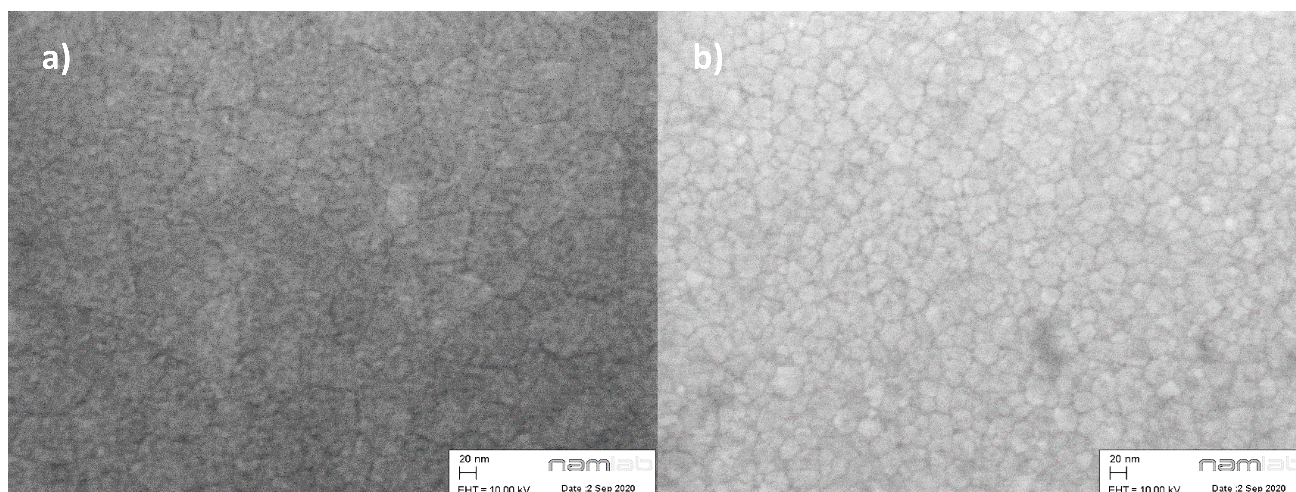

Figure SI 4 As captured top view SEM pictures of the 42 % ZrO_2 ratio and at a) 0 sccm and b) 5 sccm oxygen flow

To measure the grain size of the annealed films residual TiOx from the TiN top layer has to be removed. The samples were etched in 5 % hydrofluoric acid (HF) for 15 min to remove this TiOx. Since the crystalline HfO_2 has low etching rates in HF the HfO_2 should not be affected strongly. The grain diameter was measured by Gwyddion software from the top view SEM pictures (Figure SI 44) after aligning the contrast and brightness.

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