Supplemental Document

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Influence of Temperature and Plasma Parameters on the Properties of PEALD HfO_2: supplemental document

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The thickness and refractive index non-uniformity (NU) of a HfO_2 thin film deposited on a 76 mm Si (100) wafer at 100°C using 80 sccm Ar flow is shown in Fig. S1a, b. The gradient in the thickness is evident as the lower thickness is seen closer to the precursor inlet. The NU in thickness and refractive index is 3.1% and 0.15%, respectively. Figure S1c, d shows thickness and refractive index non-uniformity (NU) of a HfO_2 thin film deposited on a 200 mm Si (100) wafer at 100°C using 160 sccm Ar flow. Due to better distribution of Ar into the reactor, the NU improved to 2.6% on the larger area.

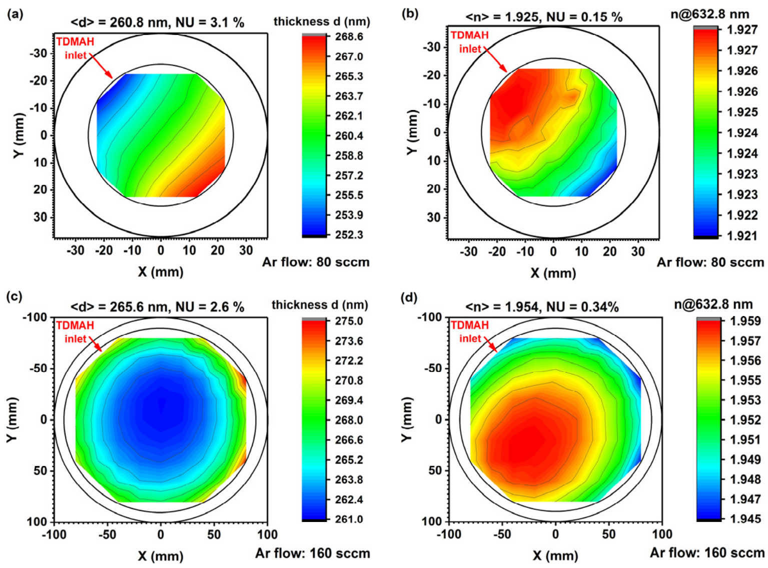

Fig. S1. Thickness and refractive index mapping by spectroscopic ellipsometry of HfO_2 films (ALD sequence: 3.12 s/5s/5s/5s) deposited at 100 °C a) thickness distribution on a 76 mm diameter Si (100) wafer (Ar flow 80 sccm) b) refractive index (at 632.8 nm) distribution on a 76 mm diameter Si (100) wafer (Ar flow 80 sccm), c) thickness distribution on a 200 mm diameter Si (100) wafer (Ar flow 160 sccm), b) refractive index (at 632.8 nm) distribution on a 200 mm diameter Si (100) wafer (Ar flow 160 sccm).

The optical constants of HfO_2 films deposited at 100°C on c-Si substrates were determined using the Tauc-Loretz dispersion model. The measured and fitted ellipsometry data is shown in Fig S2 a,b. The fit quality was determined from the mean square error (MSE). The MSE values is calculated from least square difference between the measured (m) and calculated (th) curves using the equation mentioned below. The fitting was repeated until the lowest MSE value was achieved. A good agreement is realized between the measured and fit spectra. The MSE values of all HfO_2 thin films were less than 2.

$$Least\ squares\ (LSQ) = \frac{1}{N}\sqrt{\sum_{i=1}^{N}\left\{\left(\Psi_i^m - \Psi_i^{th}\right)^2 + \left(\Delta_i^m - \Delta_i^{th}\right)^2\right\}}$$

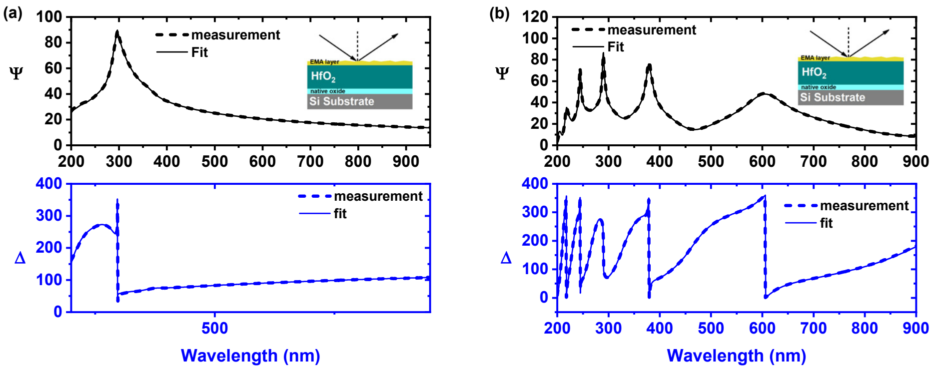

Fig. S2. Measured and fitted spectra of psi (Ψ) and delta (Δ) obtained from ellipsometry measurement of HfO_2 thin films deposited at 100°C on c-Si substrate. The thickness (d) and mean square error (MSE) are given for HfO_2 a) d = 35 nm, MSE = 0.5 and b) d = 272 nm, MSE = 1.2. A Tauc-Lorentz dispersion model (see inset image) with 3-oscilattors was used to fit the data. The measurement and fitting were performed in the wavelength range from 200 - 980 nm. There is a good agreement between the measured and fitted curves using 3-oscilattors. The ALD sequence was 3.12/5/3/5.

The optical constant of HfO_2 films deposited on fused silica substrates were determined from transmittance and reflectance measurement. The spectra were fitted using Lorentz oscillator model in LCalc software. A good fit was achieved by using 7-9 oscillators. The model consists of fused silica substrate, HfO_2 thin film, roughness layer consisting of 50% air and 50% HfO_2 and air. Fig S3 shows good agreement between measured and fit spectra (using 8 oscillators) of HfO_2 film deposited at 100°C using 3.12/5/3/5 ALD sequence. The calculated thickness from this method was 272 nm, which is similar to the thickness obtained from ellipsometry measurement (Fig S2 b).

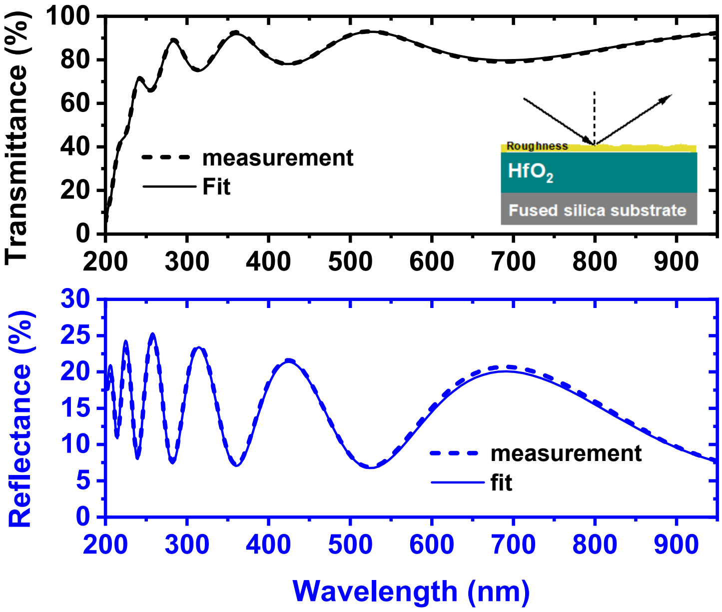

Fig. S3. Measured and fitted spectra of transmittance and reflectance obtained from spectrophotometry measurement of HfO_2 thin films deposited at 100°C on fused silica substrate. The thickness of the film was 272 nm. A Lorentz oscillator model (see inset image) with 8 oscillators was used to fit these data. The ALD sequence was 3.12/5/3/5.

Influence of the plasma parameters

The variation in surface morphology for different plasma conditions is shown in Fig. S4 a-d, where the surface of HfO_2 films deposited using 3s plasma pulse (S4 a) and 20 sccm O_2 gas flow (S4 b) appears to be smooth. The HfO_2 film deposited using 7 s plasma pulse shows a slightly rougher surface compare to 3 s plasma pulse. It may be due to the onset of crystallization due to more prolonged exposure of plasma species (oxygen radicals and ions). The HfO_2 thin film deposited using 500 W ICP power shows larger grain sizes (Fig. S4 c). The high ICP power increases ion flux at the surface, thereby induces crystallization of the film. Increased surface roughness is observed by AFM (see Fig. S5) in correlation to the SEM images. The change in film morphology is also reflected in the XRD diffractogram shown in Fig S6.

The effect of different plasma conditions on the surface morphology of HfO_2 films is also visible in AFM images shown in Fig S5 a-d. The surface roughness for the films deposited using 3s plasma pulse (Fig. S5 a), 20 sccm O_2 flow rate (Fig. S5 b), and 7 s plasma pulse (Fig. S6 d). However, a significant increase in roughness is seen in Fig 5c for the HfO_2 films deposited using 500 W power, indicating crystallization.

The HO_2 films deposited using 3 s plasma pulse (S6 a), and 20 sccm oxygen flow (S6 b) show broad feature around ~32° 2θ indicating amorphous films. Whereas HfO_2 film deposited using 500 W ICP power shows two peaks between 32.5° and 35° (Fig. S6 c). It indicates the transformation of HfO_2 film from amorphous to polycrystalline on increasing ICP power from 100 W to 500 W. A small and broad feature is seen around 35° (Fig S6 d) for HfO_2 deposited using 7 s of plasma pulse, indicating the onset of crystallization.

The residual OH groups in the films deposited at different plasma conditions are visible in Fig. S7. The high amount of OH incorporation is visible for HfO_2 films deposited using 3 s of plasma pulse and low oxygen flow rate. The lowest incorporation of OH groups is observed for

HfO_2 films deposited using high plasma power. It may be attributed to an increase in density and crystallization at high ICP power.

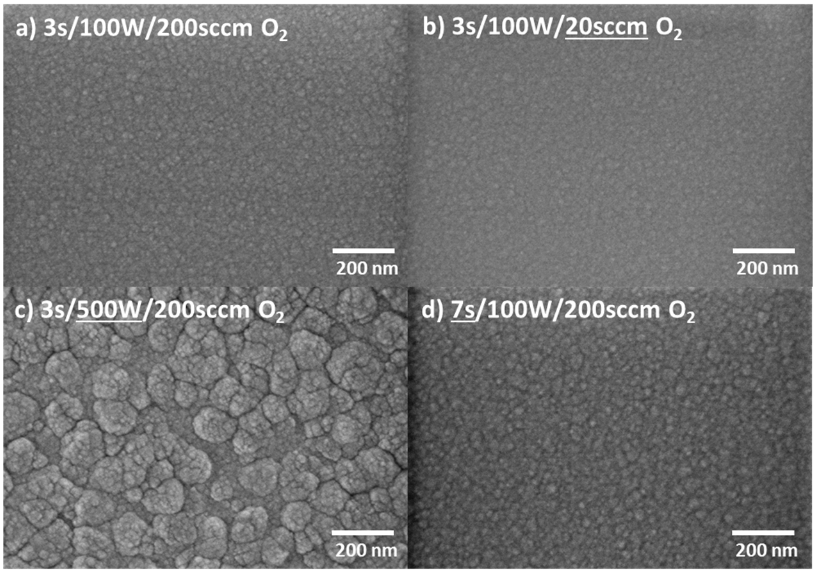

Fig. S4. SEM images of HfO_2 deposited at 100°C and different plasma configurations a) 3s plasma pulse time, 100 W ICP power, 200 sccm O_2 flow b) 3s plasma pulse time, 100 W ICP power, 20 sccm O_2 flow c) 3s plasma pulse time, 500 W ICP power, 200 sccm O_2 flow and d) 7s plasma pulse time, 100 W ICP power, 200 sccm O_2 flow.

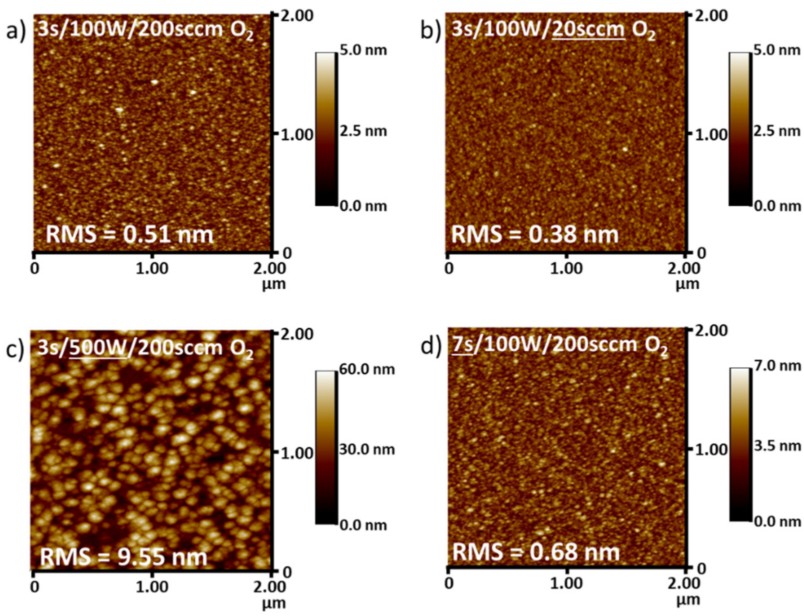

Fig. S5. AFM images of HfO_2 thin films deposited using different plasma conditions a) using an initial condition with 3 s plasma pulse, 200 sccm O_2 gas flow, 100 W ICP power b) 3 s plasma pulse, *20 sccm O_2 gas flow*, 100 W ICP power c) 3 s plasma pulse, 200 sccm O_2 gas flow, *500 W ICP power* d) *7 s plasma pulse*, 200 sccm O_2 gas flow, 100 W ICP power.

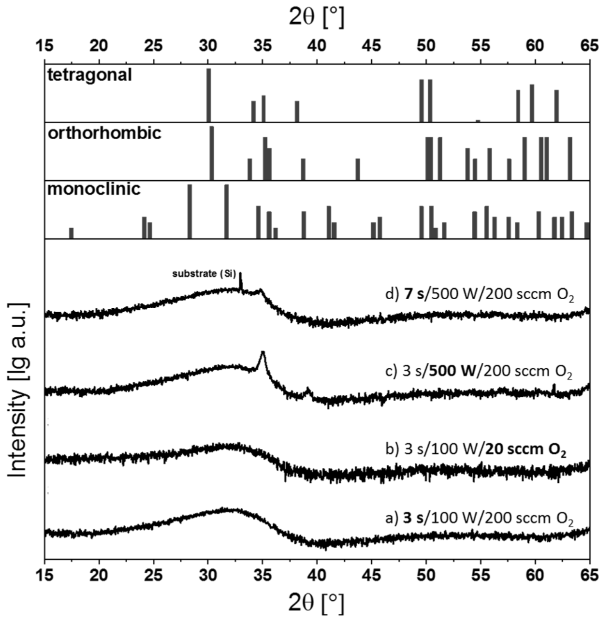

Fig. S6. XRD diffractogram of HfO_2 films deposited at different plasma configurations a) 3s plasma pulse time, 100 W ICP power, 200 sccm O_2 flow b) 3s plasma pulse time, 100 W ICP power, 20 sccm O_2 flow c) 3s plasma pulse time, 500 W ICP power, 200 sccm O_2 flow and d) 7s plasma pulse time, 100 W ICP power, 200 sccm O_2 flow. The peak positions corresponding to tetragonal, orthorhombic, and monoclinic phases are shown at the top as a reference. The peak positions corresponding to tetragonal (ICDD: PDF card No. 08-0342), orthorhombic (ICDD: PDF card No. 21-0904) and monoclinic (ICDD: PDF card No. 43-1017) phase are given as reference.

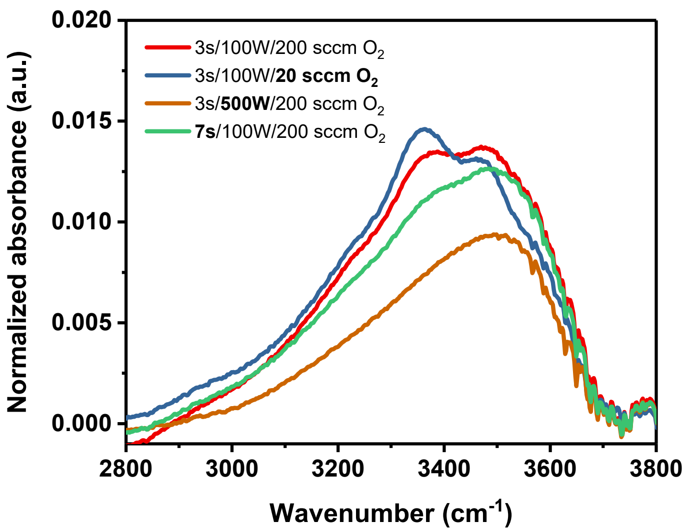

Fig. S7. The FTIR spectra in the wavenumber range corresponding to -OH groups for the films deposited with different plasma conditions.