Electronic Supplementary Material (ESI) for Dalton Transactions.

Growth Behavior of Atomic Layer Deposition HfO_2 by Switching H_2O and O_3 Reactants

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Supporting figures.

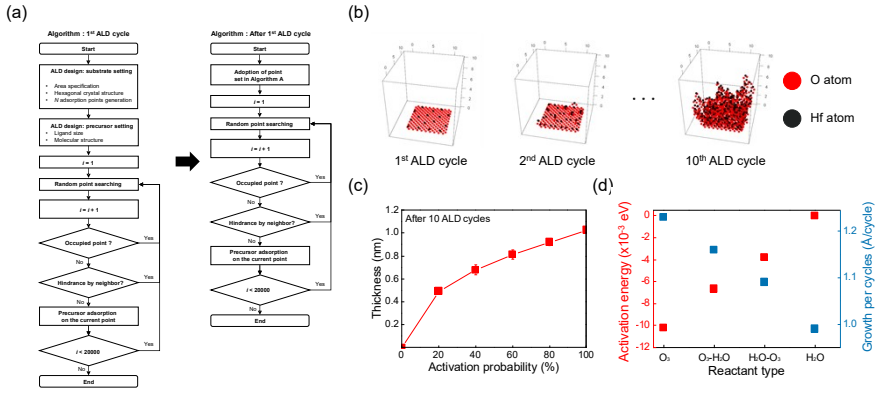

Figure S1. (a) Flow-chart of algorithm for simulation of multilayer HfO_2, (b) MC simulation of HfO_2 ALD process, (c) activation probability—simulated thickness graph, (d) activation energy (red points) of each reactant relative to H_2O compared to GPC trend (blue points).

The rate of the reactions with O_3, H_2O, O_3-H_2O, and H_2O-O_3 pulses was defined by multiplying the probability of TDMAH adsorption on the O- or OH-terminated sites by the oxidizing power of the reactants:

$$Rate \propto k_{O-}^{TDMAH} * k_{TDMAH}^{O_3} = k^{O_3} \quad (1)$$

$$Rate \propto k_{OH-}^{TDMAH} * k_{TDMAH}^{H_2O} = k^{H_2O} \quad (2)$$

$$Rate \propto k_{OH-}^{TDMAH} * k_{TDMAH}^{O_3} = k^{O_3-H_2O} \quad (3)$$

$$Rate \propto k_{O-}^{TDMAH} * k_{TDMAH}^{H_2O} = k^{H_2O-O_3} \quad (4)$$

Here, k_{O-}^{TDMAH} is the probability of adsorption of TDMAH on the O-terminated site, k_{OH-}^{TDMAH} is the probability of adsorption of TDMAH on the OH-terminated site, $k_{TDMAH}^{O_3}$ is the oxidizing power of the O_3 reactant on the adsorbed TDMAH, and $k_{TDMAH}^{H_2O}$ is the oxidizing power of H_2O on the adsorbed TDMAH surface.

The relationship between the reaction rate constant and the activation energy was developed by Arrhenius:

$$k^{reactant} = Ae^{-\frac{E_a^{reactant}}{RT}} \quad (5)$$

where $k^{reactant}$ is the reaction rate constant for each reactant system, A is the pre-exponential factor, $E_a^{reactant}$ is is the activation energy in each reactant system, R is the molar gas constant (8.314 J/mol K), and T is the temperature. Therefore, the activation energy was calculated using the Boltzmann distribution [1]:

$$\frac{k^{reactant}}{k^{H_2O}} = \exp\left(\frac{E_a^{H_2O} - E_a^{reactant}}{K_B T}\right) \quad (6)$$

The Boltzmann constant, K_B, is defined as 1.380649×10^{-23} J/K. In this calculation, $E_a^{H_2O}$ was set to 0 as the fixed value, and the relative activation energy for each reactant type was calculated as:

$$K_B T \ ln\left(\frac{k^{reactant}}{k^{H_2O}}\right) = E_a^{reactant} \quad (7)$$

Simulation of the reaction with different reaction rate constants showed a similar trend for the four reactant systems over ten HfO_2 ALD cycles. The variation of the relative activation energy was compared with the variation of the experimentally determined GPC. The reaction probability decreases exponentially with increasing activation energy, and the low GPC is due to the high activation energy [2,3].

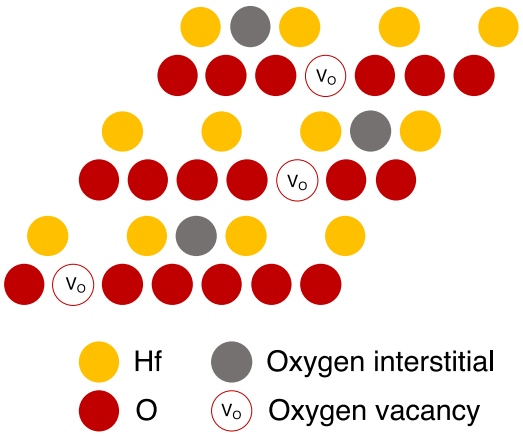

Figure S2. Illustration of HfO_2 structure with oxygen vacancies and interstitial oxygen.

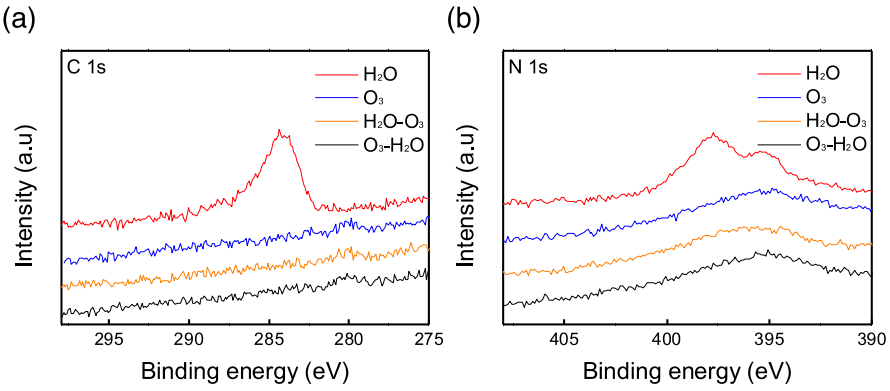

Figure S3. Content of (a) C and (b) N impurities in HfO_2 film, determined from XPS data.

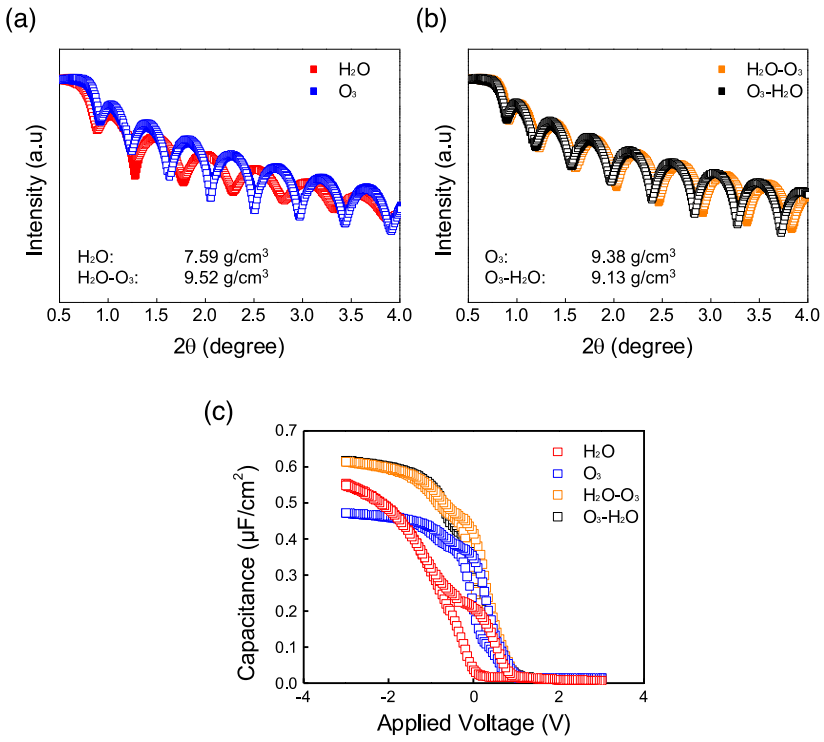

Figure S4. XRR data for HfO_2 films formed by using each reactant process: (a) H_2O and H_2O-O_3, (b) O_3 and O_3-H_2O, (c) capacitance values of MOS capacitors using 18 nm ALD HfO_2 deposited at 275 °C.

Reference

[1] L. Huang and L. Wang, Accelerated Monte Carlo simulations with restricted Boltzmann machines, Phys. Rev. B, 2017, 95, 3, 1–6, DOI: 10.1103/PhysRevB.95.035105.

[2] S. Park, B. E. Park, H. Yoon, S. Lee, T. Nam and T. Cheon, et al., Comparative study on atomic layer deposition of HfO2: Via substitution of ligand structure with cyclopentadiene, J. Mater. Chem. C, 2020, 8, 1344–1352, DOI: 10.1039/c9tc05778a.

[3] S. Kinnunen, M. Lahtinen, K. Arstila and T. Sajavaara, Hydrogen and Deuterium Incorporation in ZnO Films Grown by Atomic Layer Deposition, Coatings, 2021, 11, 5, 542, DOI: 10.3390/coatings11050542.