Supplemental Information

As described in the main text, the sticking probability of TMA was evaluated by molecular dynamics (MD) simulations. As shown in **Fig. 1**, the MD-derived value is in close agreement with that obtained from adsorption-rate measurements by quartz-crystal microbalance (QCM), within the expected experimental and computational uncertainties. To account for steric hindrance during TMA adsorption, we introduced a local coordination-based descriptor to impose adsorption-site restrictions. As shown in **Fig. 2**, a total of **283 TMA molecules adsorbed** on a **20 × 20** surface (**400 adsorption sites**). Based on this surface coverage, the calculated mass gain is **36.8 ng cm^{-2} cycle^{-1}**, which is in good agreement with the QCM-measured value. In addition, our KMC model reproduces the step-resolved mass evolution during an ALD cycle (**Fig. 3**). Specifically, it captures not only the mass increase associated with the conversion of **–CH_3** ligands to **–OH** groups upon **H_2O** exposure, but also the subsequent mass decrease due to **H_2O** desorption formed from two neighboring **–OH** groups.

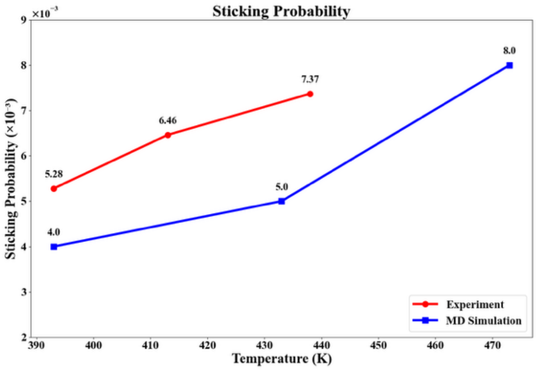

Figure 1. Comparison of TMA sticking probabilities obtained from NNP-MD collision simulations and ALD experiments using QCM over the temperature range **393–473 K**.

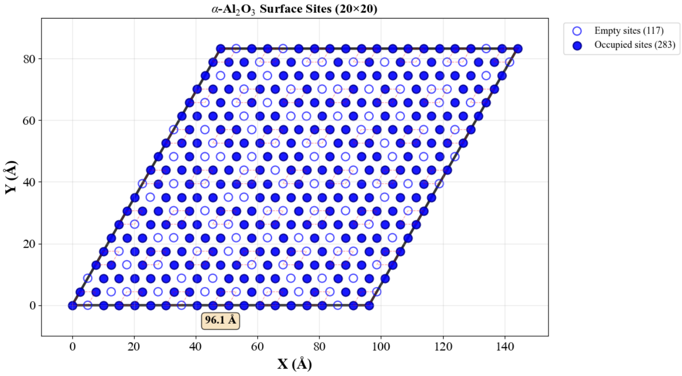

Figure 2. Spatial distribution of TMA adsorption on the α-Al_2O_3(0001) surface after the first TMA pulse in the KMC simulation. The **20 × 20** surface grid contains **400** adsorption sites, of which **283** are occupied (blue filled circles) and **117** remain empty (open circles).

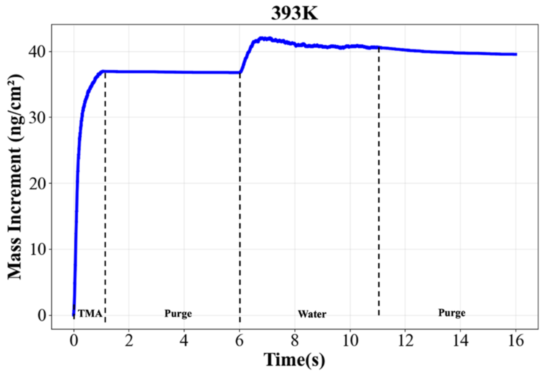

Figure 3. Averaged mass increment within a single ALD cycle at **393 K**, obtained by excluding the initial transient cycles and averaging over the steady-state regime of the KMC simulation.