Supplemental Information

As described in the main text, NH_3 can function as a small-molecule inhibitor (SMI) in Co-ALD using CCTBA. Figure 1 shows that supplying NH_3 during the CCTBA pulse prolongs the incubation period and reduces the growth-per-cycle (GPC). Figure 2 presents molecular simulations performed with Matlantis (PFP), demonstrating that NH_3 preferentially adsorbs on hydroxyl (–OH) sites on the SiO_2 surface and blocks adsorption of CCTBA at these reactive sites.

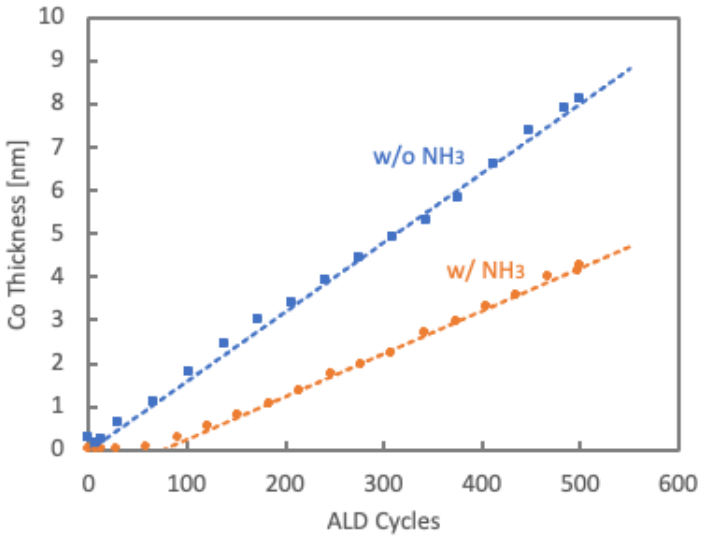

Fig. 1. Co thickness as a function of ALD cycles obtained by in-situ spectroscopic ellipsometry. Filled squares (■) indicate the temporal evolution of Co film thickness on the SiO_2 surface without NH_3 supply, whereas filled circles (●) indicate that obtained with simultaneous NH_3 supply during the CCTBA pulse. The suppression of nucleation by NH_3 leads to a prolonged incubation period and an approximately 40% reduction in GPC.

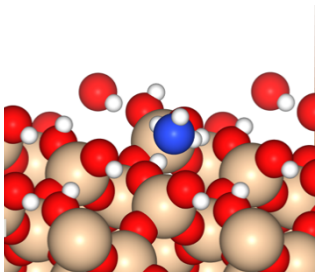

Fig. 2. NH_3 adsorption geometry on OH-terminated SiO_2 and site-blocking concept. Optimized structures illustrate that NH_3 is stabilized at specific surface hydroxyl motifs via directional hydrogen bonding, forming a localized "cap" over the reactive OH site. The annotated contact distances and orientation clarify how this adsorption configuration can sterically and electronically hinder access of the Co-precursor fragment to the same site.