The Role of Precursor Design on Area-Selective Atomic Layer Deposition

Area selective atomic layer deposition (AS-ALD) is a highly sought-after strategy for the fabrication of next-generation electronics. This work reveals how key precursor design parameters strongly influence the efficacy of AS-ALD by comparing a series of precursors possessing the same metal center but different ligands. By changing the number of methyl and chloride groups in $Al(CH_3)_xCl_{3-x}$ (x = 0, 2, and 3) and the chain length of alkyl ligands in AlC_yH_{2y+1} (y = 1 and 2), the effect of precursor chemistry (reactivity and molecular size) on selectivity is elucidated. The results show that optimized parameters for the Al_2O_3 ALD processes on a self-assembled monolayer (SAM)-terminated substrate, which serves as the non-growth surface, differ significantly from those on a Si substrate. Chlorine-containing precursors need much longer purging time on the SAMs due to stronger Lewis acidity than alkyl precursors. With reoptimized conditions, ALD of Al_2O_3 using the $Al(C_2H_5)_3$ precursor is blocked most effectively by SAM inhibitors, whereas the widely employed $Al(CH_3)_3$ precursor is blocked least effectively among the precursors tested. Finally, this study shows that a selectivity exceeding 0.98 is achieved for up to 75 ALD cycles with $Al(C_2H_5)_3$, for which 6 nm of Al_2O_3 film grows selectively on Si–OH. Quantum chemical calculations show significant differences in the energetics of dimer formation across the Al precursors, with only ~1% of $AlCl_3$ and $Al(CH_3)_2Cl$ precursors but 99% of the alkyl precursors, $Al(CH_3)_3$ and $Al(C_2H_5)_3$, existing as monomers at 200 °C. This work proposes that a combination of precursor reactivity and effective molecular size affects the blocking of the different precursors, explaining why $Al(C_2H_5)_3$, with weaker Lewis acidity and relatively large size, exhibits the best blocking results.