Inhibition of Atomic Layer Deposition of Al_2O_3 with Trimethyl Aluminum Precursor by Perfluoroalkylpolyether Thin Layer

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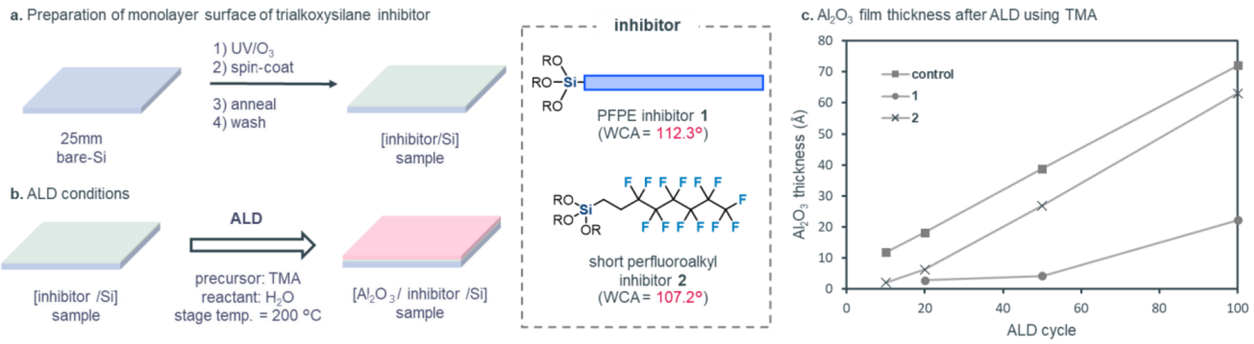
Abstract

Area-selective atomic layer deposition (AS-ALD) is a promising technique for advanced semiconductor manufacturing, capable of replacing conventional processes like photolithography and etching to fabricate complex patterns.[1] Significant efforts have focused on developing highly selective ALD processes through surface pretreatment or process modifications, such as deposition/etching cycles.[2] The use of inhibitors to deactivate non-growth areas against ALD precursors and reactants has proven effective for area-selective deposition. However, the molecular size and chemical reactivity of the ALD precursors strongly affect inhibition performance. Achieving highly selective ALD processes often requires large, less reactive precursors, which exhibit lower growth rates.[3,4] While fluorine-containing surface modification materials can reduce surface energy and suppress molecule deposition, perfluoroalkyl-coated surfaces show limited inhibition performance in Al_2O_3 ALD with trimethylaluminum (TMA), a small and highly reactive precursor.[5]

In this study, a perfluoroalkylpolyether (PFPE)-substituted alkoxysilane inhibitor (inhibitor 1) was developed, exhibiting high inhibition performance for Al_2O_3 ALD using TMA as the precursor. PFPE features a flexible fluorinated structure that differs from perfluoroalkanes due to its ether moieties, which reduce steric hindrance and increase molecular rotation. The inhibitor was evaluated as follows: a monolayer was prepared by spin-coating the compound onto UV/O_3-treated silicon substrates, followed by post-annealing to remove residual solvent. After washing with fluorinated solvent, the ALD process was performed with TMA as the precursor, H_2O as the reactant, at a stage temperature of 200 °C, and a growth-per-cycle (GPC) value of 0.7 Å. The inhibition performance was measured using XPS analysis of the Al2O3 film thickness, specifically evaluating the Al/Si ratio. Inhibitor 1 maintained its performance through 50 ALD cycles. For comparison, a short perfluoroalkyl-substituted trialkoxysilane (inhibitor 2) underwent the same procedure, but its inhibition performance deteriorated after 20 cycles. Water contact angle (WCA) measurements revealed that inhibitor 1-coated surfaces were more hydrophobic (112.3°) than those coated with inhibitor **2** (107.2°). These results suggest that flexible molecular structures and high hydrophobicity are critical for achieving high inhibition performance in ALD processes using highly reactive precursors like TMA. Detailed surface profiles and insights into inhibitor development for AS-ALD processes will be presented.



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