

## Atomistic Simulations of Surface Chemical Reactions for Growing High-K Gate Stacks

Possibly the most severe technical issue facing the semiconductor industry is finding a replacement for  $\text{SiO}_2$  as a gate dielectric in MOSFET integrated circuits. We have used density functional theory to predict detailed atomistic mechanisms and associated kinetics of atomic layer deposition processes to deposit the candidate high-K dielectrics  $\text{ZrO}_2$ ,  $\text{HfO}_2$ , and  $\text{Al}_2\text{O}_3$ . These mechanisms had not previously been investigated theoretically and our results lead to insight into the details of the surface chemistry and an explanation of several unanswered questions regarding the deposition of these materials. We find that in the ALD of these materials surface and precursor OH groups play a critical role as hydroxyls form dative bonded complexes with metal atoms. The strength of this interaction determines the adsorption energy and also affects the kinetics of ligand exchange. The competition between surface reaction and desorption results in desorption of precursors under ALD conditions in many cases. This explains the observation that ALD of these materials often leads to submonolayer coverage.

Keywords: Atomistic simulations, surface chemistry, quantum chemistry, atomic layer deposition,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{Al}_2\text{O}_3$  nanolaminates, chemical mechanisms, density functional theory, MOSFET, film growth, high- $\kappa$  dielectrics.