Nucleation and growth reactions in atomic layer deposition (ALD) using trimethylaluminum (TMA):

TMA-monomer vs. -dimer reactions

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Introduction

The ALD of Al\textsubscript{2}O\textsubscript{3} using TMA is one of the most widely studied ALD reactions; both experimentally and computationally. Although TMA-ALD processes are considered well understood, details of the fundamental chemistry involved in the elementary reactions have not been fully established. There have been a significant number of reports using Density Functional Theory (DFT) to gain insight into the mechanism, energetics and atomic details of reactions in TMA-ALD processes. Despite experimental and computational evidence for TMA-dimer formation in the vapor-phase, all previous computational ALD investigations have represented the TMA precursor as a monomer co-reactant. TMA dimerizes through formation of three-centered, two-electron bonds with a binding energy of ca. 20 kcal/mol. In this work, the effect of the TMA-dimer precursor is elucidated. The TMA-ALD half-reactions for homopropagation and heterodeposition of Al\textsubscript{2}O\textsubscript{3} are reinvestigated for both monomer and dimer precursor states using DFT.

Relative Reactivity: TMA vs H\textsubscript{2}O

The initial deposition of Al\textsubscript{2}O\textsubscript{3} on hydrogen-terminated silicon by ALD could require nucleation through exposure to either the Al- or O-precursor (TMA or H\textsubscript{2}O, respectively). To determine the differential reactivity for Al\textsubscript{2}O\textsubscript{3} nucleation on H\textsubscript{2}O, the kinetic barrier for initial reaction between TMA and H\textsubscript{2}O with H\textsubscript{2}O was calculated with DFT using Jaguar. The calculated kinetic barriers for TMA and H\textsubscript{2}O with H\textsubscript{2}O(100) indicate significant preference for TMA. The ∆G\textsubscript{‡} for the Al-precursor reaction is predicted to be lower than the O-precursor reaction by 9.1 kcal/mol. The kinetic selectivity for the Al-precursor reaction is predicted to be lower than the O-precursor reaction by 9.1 kcal/mol. The kinetic selectivity for the Al-precursor reaction is predicted to be lower than the O-precursor reaction by 9.1 kcal/mol.

TMA vs DTMA

DFT correctly predicts both the enthalpic binding energy of ca. 20 kcal/mol and IR vibrational spectra of the TMA-dimer (DTMA). Additionally, the free energy of TMA dimerization was computed at 1.0, 0.1, 0.01 and 0.001 atm. For all pressures the vibrational spectra of the TMA-dimer (DTMA). Additionally, the free energy of TMA on the termination of the silicon surface. For hydrogen terminated Si(100), TMA experimental and computational evidence for TMA-dimer formation in the vapor-phase are reinvestigated for both monomer and dimer precursor states using DFT.

TMA – H-Si(100)

\[ \Delta G^\ddagger = 37.8 \text{ kcal/mol} \]

TMTA – H-Si(100)

\[ \Delta G^\ddagger = 47.8 \text{ kcal/mol} \]

TMA/DTMA Al\textsubscript{2}O\textsubscript{3} Growth

After nucleation all subsequent steps are growth of the Al\textsubscript{2}O\textsubscript{3} film. The kinetic barriers between TMA with Al\textsubscript{2}O\textsubscript{3} (Al growth) and H\textsubscript{2}O with H\textsubscript{2}O(AlMe\textsubscript{3}) (O growth) were calculated. The calculated Al growth kinetic barriers show significant preference for DTMA over TMA, with a predicted ∆G\ddagger preference of 14.0 kcal/mol. Additionally, both O growth steps have a similar kinetic barrier at 22.9 and 25.2 kcal/mol.

References

3. All geometries and energies calculated with B3LYP/LACVP**/M06-2X/LACVP**.
4. Si bonded H removed for clarity.