

Computational Design of Metal-Organic Precursors for Controlled Metal Oxide Growth

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The hybrid molecular beam epitaxy (HMBE) technique for oxide growth has opened access to a self-regulated growth regime for complex oxide thin films with a wide range of chemistries, including titanates, vanadates, stannates, and ruthenates. While the favorable growth kinetics is often linked to the volatility of metalorganic (MO) precursors, their thermal decomposition and surface reaction mechanisms remain intricate and not yet fully elucidated. For instance, the widely used metalorganic precursor titanium(IV)-isopropoxide (TTIP), essential for titanate growth via HMBE, is generally believed to decompose thermally through C–O bond dissociation via the β -hydride elimination mechanism. However, alternative reaction pathways may also play a significant role.

We present a hybrid computational framework of quantum mechanics (QM) calculations, ReaxFF reactive force field molecular dynamics (ReaxFF-MD) and metadynamics simulations that challenge this conventionally assumed scenario for thermal pyrolysis of TTIP. Utilizing the newly developed QM-informed ReaxFF force field, this study introduces a complete reaction scheme for TTIP decomposition, along with the statistical analysis and the reaction barriers for the various ligand liberation steps obtained from ReaxFF-MD and metadynamics simulations, respectively. Our combined approach show that the initial organic ligand separation step is spontaneous and occurs pre-dominantly via C-O bond dissociation, albeit not always via β -hydride elimination. Additionally, there is non-negligible contribution from the pathway of Ti-O bond breaking. During the thermal decomposition, the oxidation state of Ti plays a crucial role in directing the reaction pathways, along with other contributing factors; reactants with Ti in its equilibrium oxidation state are prone to undergo β -hydride elimination via H-transfer reactions to stabilize Ti's oxidation state in a degraded molecule, which is also confirmed by the lower activation barriers extracted from Metadynamics. The new MO design strategy presented here constitutes a predictive and cost-effective framework for molecular design of MO precursors with engineered decomposition and tailored reaction pathways, thus affording rapid and cost-effective advancements in the existing and future applications for chemical vapor deposition-based thin film growth and coating processes.