

# The thermal decomposition process of metalorganic precursors used in hybrid molecular beam epitaxy

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The hybrid molecular beam epitaxy approach for the growth of oxides – i.e. the co-supply of atomic and molecular species in their elemental and metalorganic form – has allowed accessing a self-regulated growth window for complex oxides thin films with a range of chemistries, including titanates, vanadates, stannates, and ruthenates [1,2]. While it is widely accepted that the favorable growth kinetics is enabled by the volatility of the metalorganic molecules supplied, their thermal decomposition and surface reaction kinetics is complex and far from understood. For example, while it is generally assumed that the thermal decomposition of the widely employed metalorganic molecule titanium(IV)-isopropoxide (TTIP) used for the growth of titanates by hybrid MBE takes place by dissociating C-O bonds via the  $\beta$ -hydride elimination process, alternative reaction pathways, in particular in proximity of solid surface with different chemistries, such as SrO and TiO<sub>2</sub> terminated growth fronts, might be relevant as well.

We present reactive force field molecular dynamics (ReaxFF-MD) and density functional theoretical calculation along with metadynamics simulations to shed light on the reaction kinetics of TTIP at the atomic scale. The initial organic ligand pyrolysis step was found to be spontaneous and occurred primarily by breaking a C-O bond, albeit not always via  $\beta$ -hydride elimination. Bond dissociation in subsequent thermal decomposition stages typically occurred with partial hydration of the remaining Ti-containing fragment. The complete reaction scheme for the thermal decomposition of TTIP will be presented along with the reaction barriers and thermodynamic driving force for the different bond dissociation events. The computational approach provides a predictive and computationally inexpensive framework to identify chemical reaction pathways relevant to hybrid MBE film growth processes at the atomic scale under realistic, while experimentally relevant conditions.

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[2] W. Nunn, S. Nair, H. Yun, A.K. Manjeshwar, A. Rajapitamahuni, D. Lee, A.K. Mkhoyan, B. Jalan, *APL Mater.* **9**, 091112 (2021).

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