Hafnia and Zirconia Precursors

Calculations Show How To Make Molecules Stable

New thin film dielectrics based on hafnium and zirconium oxides are being developed to increase the performance of insulating layers in nanoelectronic transistor and memory devices.

Plots of the electrons (highest occupied molecular orbitals of reactant, transition state and product along decomposition pathway ML2Me2→ML2(CH2) + CH4 for L = Cp, M = Zr.

Atomic layer deposition (ALD) is the process of choice for fabricating these films and the success of this method depends crucially on the chemical properties of the precursor molecules. Designing new precursors
requires molecular engineering and chemical tailoring to obtain specific physical properties and performance capabilities.

A successful ALD precursor should be volatile, stable in the gas-phase, but reactive on the substrate and growing surface, leading to inert by-products. We use density functional theory (DFT) to study the thermal stability in the gas phase of Zr and Hf precursors that contain cyclopentadienyl (C\textsubscript{5}H\textsubscript{5}-xR\textsubscript{x}) and alkyl (Me=CH\textsubscript{3}) ligands. We probe the non-ALD decomposition pathway and find a mechanism via intramolecular beta-H transfer that produces an alkylidene complex. This model of the decomposition pathway can be very helpful in proposing chemical modifications to enhance thermal stability, illustrating how the ALD process window can be widened by rational molecular design based on mechanistic understanding.

**Contact** enquiry (at) tyndall (dot) ie for all Business Development enquiries

**Contact**

- [Simon Elliott](mailto:Simon.Elliott@tyndall.ie)
  MNS (Materials and Devices) - Materials Modelling for Devices
  +353-21-2346392
  simon.elliott (at) tyndall (dot) ie

**Related Publications**

- [Thermal Stability of Precursors for Atomic Layer Deposition of TiO\textsubscript{2}, ZrO\textsubscript{2}, and HfO\textsubscript{2}: An Ab Initio Study of \textalpha-Hydrogen Abstraction in Bis-cyclopentadienyl Dimethyl Complexes](https://doi.org/10.1021/jp9939349) **The Journal of Physical Chemistry A** volume 114 issue 4 pages 1879 to 1886 (2010)
  Authors: Aleksandra Zydor, Simon D. Elliott

- [Deposition of ZrO\textsubscript{2} and HfO\textsubscript{2} thin films by liquid injection MOCVD and ALD using ansa-metallocene zirconium and hafnium precursors](https://doi.org/10.1039/b706529k) **Journal of Materials Chemistry** volume 18 issue 38 page 4561 (2008)
  Authors: Kate Black, Helen C. Aspinall, Anthony C. Jones, Katarzyna Przybylak, John Bacsa, Paul R. Chalker, Stephen Taylor, Ce Zhou Zhao, Simon D. Elliott, Aleksandra Zydor, Peter N. Heys


- [First principles simulation of reaction steps in the atomic layer deposition of titania: dependence of growth on Lewis acidity of titanocene precursor](https://doi.org/10.1021/pc203068y) **Physical Chemistry Chemical Physics** volume 14 issue 22 page 7954 (2012)
  Authors: Aleksandra Zydor, Vadim G. Kessler, Simon D. Elliott