Volatile Cerium and Ytterbium Precursors for Atomic Layer Deposition: Synthesis, DFT and Application

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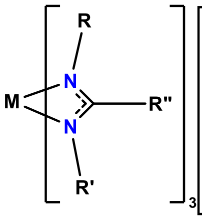
Cerium-containing thin films find a broad range of applications in diverse areas such as catalysis, sensors, solid oxide fuel cells, water splitting, possible high-*k* gate dielectric material to name a few. Ytterbium-containing films have attracted increasing attention for the advancement of semiconductor devices such as Ytterbium-doped optical fibers that are useful for high power laser applications. Atomic layer deposition (ALD) is an appealing technique to grow high quality thin films with precise thickness control and large area homogeneity. However, there are a limited number of suitable ALD precursors for Ce and Yb and thus new metalorganic precursors are much sought after.

Herein, we report a systematic study on the rational development of homoleptic tris-guanidinate [Ln(guan)$_3$] and tris-amidinate [Ln(amd)$_3$] where the lanthanide Ln = Ce and Yb.[2] The C on the N-C-N backbone is functionalised with Me, NMe_2, NEt_2; (Me=methyl, Et=ethyl) and N is functionalised with symmetrical iso-propyl (^{i}Pr) and asymmetrical tertiary-butyl (^{t}Bu) and Et groups (Figure 1) to study their influence on the physicochemical properties. The compounds are analyzed for their structure, spectroscopic purity and composition. The solid-state structures obtained for guanidinates of Ce and Yb reveal the monomeric nature of the compounds and the reactive M-N bonds present could be favourable for ALD. Thermogravimetric (TG) studies show that the complexes are volatile, and the symmetrical complexes are thermally more stable than asymmetrical ones. Density functional theory (DFT) modelling is performed to study the reactivity of the complexes with water and molecular oxygen. It is found that in the presence of water, tris-guanidinates are more reactive than tris-amidinates and the Ce complexes are even reactive with molecular oxygen. As a representative precursor for ALD, [Ce(dpdmg)$_3$] is used for the deposition of CeO_2 using water as the co-reactant. The process yielded polycrystalline CeO_2 films on Si(100) substrates at 160 °C deposition temperature and thin-film analysis is done using XRR, GIXRD, XPS, UV-Vis spectroscopy. While the GIXRD analysis revealed no other peaks except those for the CeO_2 phase, the XPS analysis indicated beside the Ce^{4+} features, an evidence of co-existence of some Ce^{3+} features in the films. (Figure 2). This study further confirms that the nitrogen coordinated lanthanide complexes are very appealing for ALD applications.

1. https://www.atomiclimits.com/alddatabase/

2. P. Kaur, L. Mai, A. Muriqi, D. Zanders, R. Ghiyasi, M. Safdar, N. Boysen, M. Winter, M. Nolan, M. Karppinen, A. Devi, *Chem. Eur. J.* **2021**, *27*, 1–15. DOI: 10.1002/chem.202005268

Supplementary file:



1 [Ce(dpdmg)$_3$] R = R' = ^{i}Pr; R" = NMe$_2$
2 [Ce(bedmg)$_3$] R = ^{t}Bu; R' = Et; R" = NMe$_2$
3 [Ce(dpdeg)$_3$] R = R' = ^{i}Pr; R" = NEt$_2$
4 [Ce(dpamd)$_3$] R = R' = ^{i}Pr; R" = Me
5 [Ce(beamd)$_3$] R = ^{t}Bu; R' = Et; R" = Me
6 [Yb(dpdmg)$_3$] R = R' = ^{i}Pr; R" = NMe$_2$
7 [Yb(dpamd)$_3$] R = R' = ^{i}Pr; R" = Me

Figure 1: List of Cerium and Ytterbium complexes synthesised and characterized.

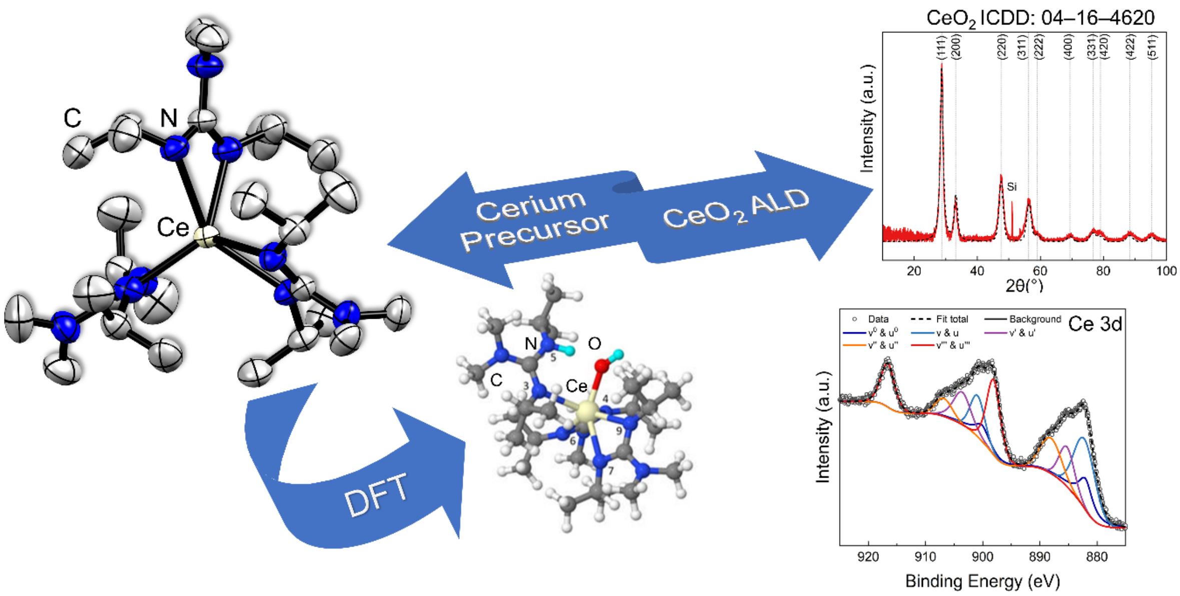


Figure 2: An overview of Ce precursor, DFT modelling and CeO_2 ALD.