ALD Fundamentals
Room Jan & Hubert Van Eyck - Session AF1-TuM

ALD Mechanisms and Modeling

Moderators: Annelies Delabie, IMEC, Michael Nolan, University College Cork

8:45am **AF1-TuM-2 Automated Design of Thermally Stable Heteroleptic Precursors by Computational Screening**, *Simon D. Elliott*, D Giesen, S Kwak, M Halls, Schrödinger, Inc.

Ligand choice in ALD/CVD precursors is crucial for throughput, stoichiometry, impurities and process temperature. Heteroleptic precursors (containing more than one type of ligand) are one way to compromise between conflicting chemical requirements. However to date we have barely 'scratched the surface' of the vast chemical space of possible heteroleptic precursors. As an example to illustrate the magnitude of the design problem, 8,855 chemically-distinct complexes can be formed by combining four of 20 ligands around a tetravalent metal center. Clearly, an exhaustive experimental analysis is not possible. Instead we look to computational screening to narrow down the search to the most promising options. Here we present a computational approach for screening metal precursors with respect to thermal stability. The computational strategy is illustrated on the example of Zr precursors for zirconium nitride, used as a hard coating to protect industrial parts in corrosive environments.

CVD precursors should decompose unimolecularly at elevated temperature in the reactor and we therefore seek complexes with moderately low energies for homolytic bond dissociation (i.e. into a pair of radical fragments). ALD on the other hand requires the gas-phase stability of precursors to be as high as possible, as this dictates the upper temperature limit for ALD.

We first enumerate over ligands. Even a small ligand library of just six O-free, N-bearing ligands (amines, amidinates, cyano and guanidinate, with various alkyl groups) gives $6^4=1296$ possible complexes, but many are symmetrically equivalent or over-coordinated, leaving 81 for optimization with density functional theory (DFT). To study thermal stability requires a second phase of enumeration, over the 1280 different bonds that can be broken in these complexes, yielding a set of radical fragments that are also computed at the DFT level. It is clear that every step in this computational workflow requires robust and efficient automation.

DFT reveals that the lowest bond dissociation energies are obtained for cleaving intact ligands from the metal. The least thermally stable complexes are found to be zirconium amides with bidentate amidinates/guanidinates, and so we predict that these would be the best CVD precursors. We observe very little steric effect when replacing methyl groups with ethyl groups. By contrast, cyano groups have a stabilizing influence, suggesting that similar electron-withdrawing groups would be useful as spectator ligands in heteroleptic precursors for ALD. On the basis of this sample system, we discuss the general requirements for chemical enumeration software and the limits faced by automation.

9:30am **AF1-TuM-5 Unravelling the Reaction Mechanisms of Trimethyl Borate for the Atomic Layer Deposition Boron- and Hydrogen-Doped Alumina Films with Non-uniform Transversal Doping Profiles**, *F Mattelaer, Véronique Cremers, M Van Daele, M Minjauw, M Nisula,* Ghent University, Belgium*; S Elliott,* Schrödinger, Inc.*; T Sajavaara,* University of Jyväskylä, Finland*; J Dendooven, C Detavernier,* Ghent University, Belgium

Atomic layer deposition (ALD) of boron-containing films has been mainly studied for use in 2D materials, B-doping of Si and towards lithium-containing borates as solid electrolyte coatings for enhanced energy storage. A series of precursors have been studied as boron-containing precursors, including B_2H_6, BBr_3, BCl_3, $B(OEt)_3$, $B(OMe)_3$, $B(OiPr)_3$ and more complex bi-metallic molecules. Trimethyl borate ($B(OMe)^3$, or TMB) and triethyl borate ($B(OEt)_3$, or TEB) are considered as ideal candidates based on limited safety issues (not pyrophoric and limited toxicity) and high vapor pressure.

In this work, we examine TMB and triethyl borate TEB in combination with O_2 plasma as precursors for ALD of B-containing films, targeting the growth of B_2O_3. It is found that films grown from TEB contain no boron. With TMB as a boron-containing precursor, films growth was found on a SiO_2 or Al_2O_3 surface, but a rapid decrease of the growth rate to a near zero-growth mode during subsequent ALD cycles indicated surface inhibition during continued growth. DFT cluster calculations in combination with in-situ FTIR demonstrated that because of its weak Lewis acidity, the TMB molecule is found to adsorb via hydrogen-bonding to B-OH covered surfaces, without elimination of ligands, so that it is subsequently removed in the plasma pulse and does not contribute to growth. The initial growth is possible because this is not the case for adsorption of TMB on for example Al-OH sites on which TMB chemisorption is energetically more favourable and typical ligand exchange reactions are expected. Knowing this, the growth could be maintained in a mixed process, by re-activating the surface through single exposures to trimethyl aluminium (TMA) and oxygen plasma and thus resetting the surface to Al-OH.

Surprisingly, this process did not result in B_2O_3 (or Al-doped B_2O_3) films, but instead in B- and H-doped Al_2O_3 films. Moreover, rather than uniform boron doping, the Al_2O_3 films grown from this process contain a large amount of hydrogen, up to 17at%, and displayed non-uniform transversal distributions of boron and hydrogen. The depth distribution is found to rely primarily on the deposition conditions. Using in-situ FTIR, - ellipsometry and DFT, this anomalous behaviour was attributed to sub-surface reactions of the TMA with the formed B-OH films deposited. This makes the process an interesting, albeit atypical, ALD process that allows for a quasi-continuous tuning of the B-concentration in the top region of high-purity Al_2O_3 films.

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