Wednesday Afternoon, July 26, 2023

Late-breaking Abstracts
Room Grand Ballroom A-C - Session LB2-WeA

Late Breaking Computational Modeling
Moderator: Benjamin Greenberg, Naval Research Laboratory

4:00pm **LB2-WeA-11 Exploring the Blocking Mechanism of Small Molecule Inhibitors by Density Functional Theory***, **Fabian Pieck**, R. Tonner-Zech,* Wilhelm-Ostwald-Institut Physikalische und Theoretische Chemie, Germany

Within area-selective atomic layer deposition selectivity is achieved by various approaches. A common strategy is to block growth on the non-growth surface by the deposition of small molecule inhibitors (SMI) prior to the ALD process. However, to obtain selectivity the properties of those SMIs, especially their reactivity, has to be tuned with respect to the surface and ALD process. Here, a sound knowledge of the actual blocking mechanism of the SMIs can guide their selection and tuning.

We use ab initio modelling by density functional theory to explore the blocking mechanism of SMIs by investigating their on-surface reactivity. Here, alkoxysilanes like trimethoxypropylsilane (TMPS) [1] and methanesulfonic acid (MSA) are studied as SMIs for the area-selective ALD of Al_2O_3 whereby SiO_2 and Cu(111) are targeted as non-growth surface, respectively. Reaction paths are calculated with the nudged elastic band method to identify the most likely reaction steps while the most stable structures are identified based on Gibbs free energies. The observed reaction paths show that both SMIs behave fundamentally different on the SiO_2 and Cu(111) surface resulting in different blocking mechanisms. Consequently, these SMIs can be used to target different non-growth surfaces within the area-selective ALD of Al_2O_3.

[1] J. Yarbrough, F. Pieck, D. Grigjanis, I.-K. Oh, P. Maue, R. Tonner-Zech, S. F. Bent, *Chem. Mater.* **2022**, *34*, 4646 – 4659.

4:15pm **LB2-WeA-12 Reaction Mechanism of Atomic Layer Deposition of Pt from First Principles***, **Sylwia Klejna**,* AGH University of Krakow, Poland

Atomic layer deposition of Pt is one of the best studied deposition processes of noble metals. Yet, the reaction mechanism is still unknown. In this study, we use density functional theory (DFT) to investigate reaction steps involved in the ALD of Pt from $MeCpPtMe_3$ (MeCp – methylcyclopenthadienyl ligand, $CH_3C_5H_4$; Me – methyl group, CH_3) and O_2. In this process transient metal oxide may be generated and that can greatly facilitate noble metal ALD[1]. Adsorption, decomposition and dehydrogenation pathways during metal precursor pulse are computed. Surface bound species as well as possible volatile by-products are identified. The most abounded surface intermediates after the saturation with metal precursor are: MeCp-surf and Me-surf. The temperature influence on the stability of these species is investigated. Next, we model the O_2 co-reactant pulse to evaluate whether the nuclei of the transient oxide surface can form. We discuss the possibility of production of transient surface bound OH groups predicted in the previous study[2] and other by-products, *e.g*. CH_4 identified in the experiment[3]. The factors that facilitate nucleation are examined. This will allow to propose appropriate conditions, reagents and chemical processes to control and improve efficiency of the atomic layer deposition of other noble metals.

1. *The Journal of Chemical Physics*, 2017, **146**, 052822
2. *Langmuir*, 2010, **26**, 9179-9182
3. *Physical Chemistry Chemical Physics*, 2018, **20**, 25343-25356

4:45pm **LB2-WeA-14 Closing Remarks in Grand Ballroom H-K***,*

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