

ALD Fundamentals

Room Hall 3A - Session AF1-WeA

Growth and Characterization: *In-situ* and *in-vacuo* Analysis, Surface Science of ALD I

Moderators: Seán Barry, Carleton University, Canada, Simon D. Elliott, Schrödinger

1:30pm **AF1-WeA-1 Triggering Nucleation of Pt ALD through UV-illumination**, J. Santo Domingo Peñaranda, Jolien Dendooven, Ghent University, Belgium; V. Miikkulainen, Aalto University, Finland; S. Klejna, AGH University of Science and Technology, Poland; E. Solano, ALBA synchrotron, Spain; M. Rosenthal, ESRF, Grenoble, France; Z. Hens, C. Detavernier, Ghent University, Belgium

ALD of noble metals on oxides is marked by the growth of 3D islands rather than a uniform 2D layer in the initial growth stages. A relatively large number of ALD cycles is often required to achieve coalescence of the growing islands into a continuous layer, posing limits to the deposition of thin metal films. To obtain layer closure at lower thicknesses, a larger density of nuclei formed on the substrate surface (#nuclei/cm²) is desired.

For MeCpPtMe₃-based Pt ALD, strategies to enhance the nucleation include using N₂-plasma as reactant instead of O₂ [1], exposing the substrate to alkylated precursors prior to Pt deposition [2], and using electron excitation of the Pt precursor [3]. Here, we implement UV-illumination as an external trigger during MeCpPtMe₃-O₂ ALD and study the Pt uptake and nucleation process *in situ* via X-ray fluorescence (XRF) and grazing incidence small angle X-ray scattering (GISAXS) at the ESRF synchrotron.

With 365 nm illumination turned on continuously during the ALD process, *in situ* growth curves (Fig. 1) reveal a significant increase in Pt deposition during the incubation period at all temperatures tested. Depositions in which a number of Photo-ALD cycles is followed by thermal ALD (Fig. 2) also show a drastic increase in Pt uptake, even if only few Photo-ALD cycles are carried out, confirming a crucial role for the UV-light in the nucleation. The size and areal density of the nuclei is extracted for samples with the same Pt loading (#Pt atoms/cm²) (Fig. 3). Remarkably, a larger amount of smaller islands is formed with Photo-ALD, indicative of an increased nucleation density.

Next, the timing of the UV-illumination in the ALD cycle is varied to understand the effect of light-assistance during each ALD step. UV-illumination during the MeCpPtMe₃ exposure is required to achieve growth enhancement, suggesting that the precursor is activated in the gas phase prior to adsorption. We hypothesize that the UV-light assists in the dissociation of the Pt-Me bonds [5], enabling a larger Pt uptake on the surface.

In summary, UV-light can trigger the nucleation of Pt ALD, leading to a larger nucleation density and faster layer closure compared to conventional thermal ALD. While this in itself offers great opportunities for ALD of thin metal films, the Photo-ALD approach also holds promises towards selective deposition for micropatterning.

- [1] Dendooven et al. Nat. Commun. 2017, 8, 1074.
- [2] de Paula et al. Chem. Mater. 2020, 32, 315.
- [3] Lien et al. J. Phys. Chem. Letters 2018, 9, 4602.
- [4] Engmann et al. PCCP 2012, 14, 14611. Egger et al. J. Organomet. Chem. 1970, 24, 501.

1:45pm **AF1-WeA-2 Reaction Pathway of Copper Atomic Layer Deposition via Time-of-Flight Mass Spectrometry**, Camilla Minzoni, K. Mackosz, C. Hain, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; C. Frege, TOFWERK AG, Switzerland; I. Utke, P. Hoffmann, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Atomic Layer Deposition (ALD) has emerged as one of the most promising technique for depositing conformal and uniform copper thin film, especially for application in electronic devices [1].

Despite a comprehensive understanding of ALD mechanisms in metal oxides, limited theoretical and *in situ* experimental work has been dedicated to unraveling the reaction mechanisms of copper and related metals. The extension of ALD to elemental metals presents distinctive challenges, primarily attributed to the lack of the mechanistic understanding of the ongoing surface reactions [2].

Time-of-Flight Mass Spectrometry (ToFMS) has become a powerful tool for addressing these issues, providing unique advantages in terms of high

sensitivity and resolving power, rapid data acquisition, ability to detect species over a wide mass range and real-time tracking of surface reactions and volatile byproducts.

This study presents *in situ* ToFMS monitoring to investigate the gas-phase mechanism involved in the ALD process of copper through transmetalation, using dehydrated Cu(hfac)₂ (CuC10H2F12O4) with diethylzinc DEZ (Et₂Zn) being the reducing agent.

Lee et al. [3] previously proposed a transmetalation reaction mechanism using an analogous copper complex and DEZ. The mechanism involves a ligand exchange step between the copper complex and DEZ, leading to the formation of the volatile byproduct Zn(hfac)₂ (ZnC10H2F12O4), along with the generation of copper alkyl surface species. These copper alkyl species rapidly undergo reductive elimination, producing copper metal and butane (C₄H₁₀) [4] (Fig. 1).

During the monitoring of the ALD cycles with ToFMS, the theoretically anticipated byproducts from the transmetalation reaction were detected (Fig. 2). The results identifying these byproducts are the first of their kind under vacuum ALD conditions, supporting also the theoretical calculations and solution-based of analogous reactions [5-6].

The combination of ALD and ToFMS is therefore proving to be a powerful method for a depth understanding of complex ALD reaction mechanisms at molecular level that would be challenging by other means.

References

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2:00pm **AF1-WeA-3 *in vacuo* Cluster Tool for Studying Reaction Mechanisms in ALD and ALE Processes**, Marko Vehkamäki, M. Chundak, H. Nieminen, M. Putkonen, M. Ritala, University of Helsinki, Finland

ALD and ALE processes are solely dependent on the chemical reactions occurring on the substrate surface. These surface reactions define the outcome of each process and can set critical challenges on the process development and integration. Studying the chemical reactions is hence of utmost importance to fully understand the growth and etch processes and exploit the advantages ALD and ALE have to offer.

The best ways to study reaction mechanisms in ALD and ALE processes is to do the measurements without exposing the film to air, that is, either *in situ* or *in vacuo*. A cluster tool which allows a variety of ways to study reaction mechanisms in nearly all kinds of process chemistries has been set up in HelsinkiALD laboratory. In this tool, a commercial flow-type ALD reactor is connected directly to a set of ultra-high vacuum analysis chambers. After interrupting the process at selected point the substrate can be transferred *in vacuo* straight from the ALD reactor to surface analysis. The chemical composition of the surface, including also reaction intermediates on the film, can be investigated after each precursor pulse individually. With this information, the overall film growth mechanism can be resolved.

The newest addition to the cluster tool is a low-energy ion scattering (LEIS) instrument. LEIS has the ultimate surface sensitivity as it distinguishes the outermost atom layer from the others. This resolution is important in distinguishing reaction intermediates from the rest of the surface and in analyzing the closure of the thinnest films. X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD) and *in situ* quartz crystal microbalance (QCM) have already been utilized effectively in reaction mechanism studies on ALD of Al₂O₃, noble metals Pt and Ru, and ALE of Ta and Mo. Additionally, the cluster tool contains *in vacuo* ion scattering spectroscopy (ISS), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), low-energy electron diffraction (LEED), and ultraviolet photoelectron spectroscopy (UPS). There is also an ellipsometer for *quasi in situ* measurements in the ALD chamber. As the system contains genuine flow-type ALD reactor, reaction mechanisms can be solved without compromising true ALD conditions.

Wednesday Afternoon, August 7, 2024

2:15pm **AF1-WeA-4 Understanding the Dual-Source Behavior of LiHMDS for Si-Free Li-Containing Films**, *Meike Pieters, L. Bartel, C. van Helvoirt, M. Creature*, Eindhoven University of Technology, The Netherlands

The electrochemical stability of interfaces is key to long-lasting and safe Li-ion batteries. To study these interface processes, ALD can deliver thin film model systems of electrodes. For example, the behavior of Ni-rich $\text{LiNi}_x\text{Mn}_y\text{CO}_{1-x-y}\text{O}_2$ cathodes can be understood by investigating LiNiO_2 thin films due to the similar electrochemical properties. Moreover, the control that ALD provides over film composition and crystal orientation allows to study how those material properties influence the interface stability. To grow LiNiO_2 by ALD, lithium hexamethyldisilazide (LiHMDS) is preferred over the widely-used LiO^tBu because of its lower melting point of 70°C , but the presence of silyl groups can result in the undesired incorporation of Si. Previous work proposes that Si is incorporated during both precursor and O_2 plasma steps in the ALD cycle [1]. However, processes in which the LiHMDS dose is followed by a H_2O pulse can yield Si-free films [2,3], indicating that the co-reactant plays a major role in the Si incorporation.

To shed light on the reaction mechanisms of LiHMDS and the two co-reactants, we carry out in-situ growth studies by spectroscopic ellipsometry and mass spectrometry (QMS) [4]. The O_2 plasma process shows linear growth and the film contains 16 at.% Si according to XPS, but the H_2O process results in bulk-driven growth and Si-free films. QMS shows that the difference between the processes lies in the reaction products during the co-reactant step: H_2O removes the HMDS ligands of physisorbed LiHMDS via a proton exchange reaction, whereas the O_2 plasma combusts HMDS. The redeposition of Si-containing combustion products during the plasma step is presumably the origin of the dual-source behavior of LiHMDS.

We also include a H_2 plasma step following the O_2 plasma step, with the hypothesis that H radicals can etch the incorporated Si. This process exhibits bulk-driven growth and the grown films are, as expected, Si-free and have a Li_2O composition. QMS confirms the release of SiH_x -species during the H_2 plasma step. Interestingly, the growth behavior and film composition remain the same when the order of the O_2 and H_2 plasmas is reversed. The QMS results in this case indicate that H_2 plasma removes the HMDS ligands and thereby prevents Si incorporation in the subsequent O_2 plasma step.

Overall, this work shows that the co-reactant controls the reaction mechanism, and therefore the dual-source behavior, of LiHMDS. These insights can aid the fabrication of Si-free LiNiO_2 films.

- [1] Werbrouck et al., J. Phys. Chem. C, 2020, 124
- [2] Østreng et al., RSC Adv., 2012, 2
- [3] Østreng et al., J. Mater. Chem. C, 2013, 1
- [4] Pieters et al., to be submitted

2:30pm **AF1-WeA-5 ALD of Two-Dimensional Gallium Sulfide: Understanding the Nucleation and Strain Evolution During Growth**, *O. Massmeyer, R. Günkel, S. Kachel*, Philipps Universität, Germany; *P. Klement*, Justus Liebig University Giessen, Germany; *J. Belz*, Philipps Universität, Germany; *S. Chatterjee*, Justus Liebig University Giessen, Germany; *M. Gottfried, Kerstin Volz*, Philipps Universität, Germany

Two-dimensional (2D) materials are gaining great attention due to their extraordinary thickness-dependent properties. The layered III-VI semiconductors such as GaS and GaSe show a unique band structure. Furthermore, 2D GaS and GaSe have a bandgap in the UV region, which makes them candidates for several LED and detector concepts. Moreover, the composition tuning of multilayer $\text{GaS}_x\text{Se}_{1-x}$ alloys allows for establishing bandgaps between 2.0 and 2.5 eV.

Hence, group III-chalcogenides are promising materials for next-generation optoelectronic applications, as they even reach these properties with comparably little use of material. Typical preparation routine for 2D materials, however, is the mechanical exfoliation, which is no suitable technique when applications are aimed for. Hence, we establish a pulsed growth regime using metal organic precursors to find suitable growth routines for 2D materials using a well-accepted growth technique. The samples are characterized by means of Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Raman spectroscopy, X-ray reflectometry (XRR), X-ray photoelectron spectroscopy (XPS) and

Transmission Electron Microscopy (TEM) as well as several optical spectroscopy techniques.

The ALD (Atomic Layer Deposition) scheme is needed due to prereactions of the di-*tert*-butyl-sulphide (DTBS) and tri-*tert*-butyl-gallium (TTBGa) precursors on the surface. This results in the formation of 2D, closed films instead of 3D structures containing liquid Ga on the surface. The growth of a 2D film is enabled by a specific interface reconstruction between the sapphire and the GaS.

The presentation will summarize our current understanding of the nucleation and ALD growth of group III-chalcogenides by systematic variation of different growth parameters such as temperature, chalcogen/group III gas phase ratio and deposition sequences and correlate the findings to optoelectronic properties of the layers.

2:45pm **AF1-WeA-6 Self-Limiting Deposition of Copper from Copper Beta-Diketonates and Plasma Electrons**, *Premrudee Promdet, P. Niiranen, A. Haridas Choolakkal, D. Lundin, H. Pedersen*, Linköping University, IFM, Sweden

We have recently demonstrated how films of elemental metals can be deposited using free electrons from a plasma discharge as reducing agents.¹ We refer to this process as electron CVD (e-CVD). We will here demonstrate e-CVD of Cu using plasma electrons and copper beta-diketonates precursor; we will also show that the deposition chemistry appears to be self-limiting. Hence, we suggest that this might be an e-ALD process.

In this study, a positive bias is applied to the substrates to attract plasma electrons to the surface. The copper precursors and the plasma electrons were supplied in pulses separated by argon purge steps. The deposition was monitored *in situ* by a QCM sensor specially developed for e-CVD². Self-limiting deposition was found from the mass gain per deposition cycle for the time of precursor pulse, plasma exposure and purge. X-ray photoelectron spectroscopy show the formation of fluorinated copper species, suggesting some level of redeposition of ligand fluorine to the copper surface. We found that the residual fluorine could be removed by further plasma exposure. A plausible explanation supported by optical emission spectroscopy and mass spectroscopy is offered on the formation of volatile compounds as byproducts from the longer plasma exposure. Based on these results, a possible surface chemical mechanism will be discussed.

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2. P. Niiranen et al. Rev. Sci. Instrum. 2023, 94 023902.

3:00pm **AF1-WeA-7 Exploration of Nucleation Phenomena in Ultra-Thin ALD Films on NMC 811 Substrates: An in Situ Quartz Crystal Microbalance Study**, *Léo Lapeyre, L. Pethö, J. Michler*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *P. Raynaud*, LAPLACE, France; *I. Utke*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Ultra-thin films deposited by ALD have emerged as essential components in improving the performance and stability of Li-ion battery systems. Particularly, the utilisation of ultra-thin films as artificial solid electrolyte interfaces (SEIs) holds significant promise for enhancing battery efficiency and lifespan. However, the accurate characterisation of these films by ex situ methods presents significant challenges, primarily due to their low thicknesses which provides low signal-to-noise ratios and potential contamination from air exposure. Additionally, the substrate's influence on film properties remains a critical but often overlooked factor. Many studies rely on silicon substrates for process development and film characterization, yet the disparities between silicon and actual battery substrates, such as NMC 811, can significantly impact film growth and characteristics. Among others aspects, unsaturated surface coverage, non-linear growth per cycle (GPC), or compositional variations during early stage growth may result from an ALD process not specifically optimized for the particular substrate in use. Consequently, these variations can adversely affect battery performances.

To address these challenges, we use in situ Quartz Crystal Microbalance (QCM) techniques with NMC 811-coated QCM crystals to achieve closer-to-application conditions and overcome limitations associated with ex situ methods. This approach enables us to investigate nucleation phenomena and growth kinetics of ultra-thin films with fine precision [2], providing a better understanding of the substrate's influence on film properties and facilitating the development of tailored deposition strategies for enhanced battery performance.

Our study encompasses the deposition of various materials, including SnO₂ and LiNbO₃, using both ALD and PE-ALD techniques. We aim to compare the influence of deposition methods (thermal and plasma ALD) on the early-stage growth dynamics of films and explore the effects of deposition parameters (such as temperature, precursor's exposure time and number of cycles) on growth behaviours. Ultimately, we seek to optimize the deposition process to minimize non-linear growth and enhance film quality.

Finally, we will assess the electrochemical performance of NMC 811 electrodes coated with SnO₂ and LiNbO₃ films, investigating their capacity retention, cycling stability, and rate capability. Through this comprehensive analysis, we strive to advance our understanding of ultra-thin film deposition processes and their impact on battery performance, ultimately contributing to the development of high-performance energy storage solutions.

3:15pm **AF1-WeA-8 The Role of the Oxidizing Co-Reactant in Pt Growth by Atomic Layer Deposition Using MeCpPtMe₃ and O₂/O₃/O₂-Plasma**, *Jin Li*, Ghent University, Belgium, China; *S. Klejna*, AGH University of Krakow, Poland; *M. Minjauw*, *J. Dendooven*, *C. Detavernier*, Ghent University, Belgium

Atomic layer deposition (ALD) of Pt using MeCpPtMe₃ and O₂/O₃/O₂-plasma (O₂*) at 300°C is investigated with *in vacuo* X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) to gain a better understanding of the Pt growth mechanism.¹ Most notably, the chemical state of the surface Pt atoms and the role of surface O species in Pt growth are revealed. In the MeCpPtMe₃/O₂ process, the surface Pt atoms remain in a metallic Pt⁰ state throughout the ALD cycle, and the surface O species generated by the O₂ exposure only exist as unstable adatoms, desorbing in vacuum. As for the O₃/O₂* processes, the surface Pt layer is oxidized to a mixture of Pt⁰, Pt²⁺O and Pt⁴⁺O₂ upon O₃/O₂* exposure and then fully reduced to Pt⁰ during the precursor exposure. Surface Pt oxides are stable in vacuum but can be reduced by hydrocarbon vapors. DFT reveals differences in the combustion mechanism for Me vs. Cp species, during the metal precursor and co-reactant pulses. Quantification analysis shows that the O₃/O₂* processes have a much higher surface O species content than the O₂ process after the co-reactant exposure, favoring precursor ligand combustion over dehydrogenation in the next precursor exposure and leading to lower surface C density after the precursor pulse. Regarding the surface C species, apart from common -C_xH_y/-Cp groups, -C_x is recorded as a highly dehydrogenated product only in the MeCpPtMe₃/O₂ process. For all processes, no C-O/C=O or -OH group is identified by *in vacuo* XPS, in line with DFT energetics. Importantly, the differences in the surface O content do not significantly affect the growth per cycle. Moreover, the MeCpPtMe₃/O₂ process with surface O species and a tailored MeCpPtMe₃/O₂ process without surface O species, both at 300°C, yield nearly identical growth rates and as-deposited Pt with the same chemical state. This indicates that surface O species present before the precursor exposure have limited impact on the overall Pt growth, in contrast to previous assumption.

KEYWORDS: *In vacuo* XPS; DFT; ab initio thermodynamics; surface reaction mechanism; Atomic layer deposition; Pt; growth mechanism; combustion of hydrocarbons mechanism

1 J. Li, S. Klejna, M. M. Minjauw, J. Dendooven and C. Detavernier, *J. Phys. Chem. C*, DOI:10.1021/acs.jpcc.3c07568.

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