## ALD Fundamentals: Growth and Characterization
## Room HB Plant Ballroom - Session AF1-TuA

### ALD Metrology/Characterization I

**Moderators: Dennis Hausmann**, Lam Research, **Ruud van Ommen**, Delft University of Technology

1:30pm **AF1-TuA-1 Low Energy Ion Scattering Surface Analysis of ALD Coated Ti-Based Porous Transport Layers*, Philipp Brüner,*** *Thomas Grehl,* IONTOF GmbH, Germany*; Athina Tzavara-Roussi, Rens Kamphorst, Ruud van Ommen,* TU Delft, Netherlands **INVITED**

Porous transport layers (PTLs) play a crucial role in enabling efficient electrochemical reactions in water electrolyzers. Positioned between the electrodes and the current collectors, PTLs provide structural support, help transport reactants by allowing gas diffusion and moving water from the reaction sites, provide electrical conductivity between electrode and current collector, and aid in heat dissipation for thermal management.

Titanium-based PTLs are a common choice due to good conductivity, corrosion resistance, and mechanical strength, but long-term degradation effects occur under the harsh chemical conditions encountered in an electrolyzer cell. Protective coatings help mitigate these effects and improve PTL performance by improving the chemical stability of the PTL surface and modifying surface properties.

Atomic layer deposition (ALD) is an attractive method for applying the protective coating, as it is ideally suited to porous substrates, and its conformality and precision allows fine-tuning of the thin film properties. Here, we report on low energy ion scattering (LEIS) analyses of ALD-coated Ti-based PTLs, using various coating materials.

The extreme surface sensitivity of LEIS allows quantification of the surface coverage of the ALD film, providing crucial information about film growth and layer closure. At the same time, the film thickness is evaluated to provide insight into the ALD growth mode and growth per cycle. We discuss analytical challenges associated with the highly three-dimensional nature of the deposition substrate, which affect surface quantification and film thickness measurements.

2:00pm **AF1-TuA-3 In vacuo LEIS studies on cleaning and functionalizing substrate surfaces for ALD***, Heta-Elisa Nieminen, Johanna Majlund, Marko Vehkamäki, Mykhailo Chundak, Sakari Kettunen, Matti Putkonen,* ***Mikko Ritala,*** University of Helsinki, Finland

Starting surfaces play a critical role for the success of ALD processes. When loaded from air to the ALD reactor, substrate surfaces have adsorbed airborne hydrocarbon molecules. While some ALD processes may be robust little affected, some others may be blocked by the hydrocarbons or products from their reactions with precursors. For example, we showed that the $Ir(acac)_3 – O_2$ ALD process deposits Ir on fresh, *in situ* deposited $Al_2O_3$ but not on air exposed *ex situ* $Al_2O_3$. On air exposed $SiO_2$ the Ir was deposited, however [1].

While cleaning the surfaces before loading to the ALD reactor may decrease the amount of hydrocarbons on the surface, they may be hard to completely avoid this way. Therefore, it is important to clean the surfaces in the ALD reactor and study the cleaning processes *in situ* or *in vacuo*. In this work we have used the unique ALD cluster tool where a genuine flow type ALD reactor is connected in vacuo to low energy ion scattering (LEIS), X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD). With LEIS and TPD we studied $Al_2O_3$ and $SiO_2$ surfaces (i) directly after loading (*ex situ*), (ii) after heating at 300 °C, (iii) after exposing to ozone for 500 s in the ALD reactor at 300 °C, and (iv) after exposing to atomic oxygen at room temperature. *In situ* deposited $Al_2O_3$ served as a reference. Upon only heating to 300 °C, the hydrocarbons stay better bonded to $Al_2O_3$ than to $SiO_2$, but both the ozone and oxygen treatment clean the surfaces to a level comparable to the *in situ* $Al_2O_3$. We also used time-of-flight secondary ion mass spectrometry (TOF-SIMS) option of the LEIS instrument to compare hydrogen amounts on the $Al_2O_3$ surfaces.

$SiN_x$ surface was studied directly after loading and after heating at 300 °C. This surface was found to have much less hydrocarbons than the two oxide surfaces. We also studied the $SiO_2$ and $SiN_x$ surfaces after treatment with dilute 0.05 % HF and benzaldehyde vapor, aiming for passivation of the surfaces for area-selective deposition.

1. H.-E. Nieminen, M. Putkonen and M. Ritala, Chem. Mater. 2025, 37, 7251

2:15pm **AF1-TuA-4 ALD Outstanding Presentation Award Finalist: Operando Studies of Nitride ALD Using Ambient Pressure XPS*, Henrik Pedersen,*** Linköpings Universitet, Sweden*; Pamburayi Mpofu, Alaa Malekshahineia, Peggy Bagherzadeh Tabrizi,* Linköping University, Sweden*; Esko Kokkonen,* Max IV Laboratory, Sweden*; Joachim Schnadt,* Lund University, Sweden

Studies of the surface chemistry of the first few cycles of ALD using *in situ* and time-resolved *operando* techniques are attractive for realizing, understanding and obtaining mechanistic information during the deposition. We will present surface-chemistry investigations through time-resolved ambient pressure X-ray photoelectron spectroscopy (APXPS) using a dedicated ALD cell[1] at the MAX IV Laboratory to study of the initial growth of TiN, AlN and GaN. While this setup has been used for oxides[2,3] and metals[4], we can here show the first results on nitrides using TDMAT, TMA and TMG/TEG with $NH_3$ in thermal ALD processes.

*Operando* APXPS is conducted concurrently with the dosing of the precursor, *i.e.*, monitoring the chemical environment of the substrate and film surface while pulsing the ALD precursors.[5] As opposed to the more common *in situ* XPS experiments that are performed after ALD half-cycles and at times under non-realistic conditions (*e.g.*, high vacuum), *operando* APXPS closely mimics or replicates actual processing environments, such as atmospheric or near-pressurized conditions.

Deposition of nitrides is a thermodynamical uphill battle as metals have a stronger driving force to form and oxide than a nitride. This is reflected in our results as an initial formation of the metal oxide, followed by slow nitridation by the ammonia. We speculate that the native oxide on silicon is acting as a source of oxygen for the initial oxidation. We also propose that this initial metal oxide formation explain long nucleation delays seen in thermal ALD of nitrides, *e.g.*, approximately 120 ALD cycles in thermal ALD of AlN.[6]

A delay in nucleation on the TDMAT-terminated surface was also observed during the $NH_3$ pulse. The intensity of the Ti 2p and N 1s core levels began to increase after four ALD cycles, showing that the surface was coated with Ti and N atoms and no Si signals were observed with time. The results show that ligand exchange reactions take place before transamination reactions. This was verified using the periodic changes in the intensity and peak positions of the above-mentioned spectra and complemented by residual gas analysis using mass spectrometry.

References

(1) Kokkonen et al. *Rev. Sci. Instrum.* **2022**, *93*, 013905.

(2) D'Acunto et al. *Chem. Mater.* **2023**, *35*, 529–538.

(3) Jones et al. *J. Vac. Sci. Technol. A* **2024**, *42*.

(4) Kokkonen, et al. *J. Vac. Sci. Technol. A* **2024**, *42*.

(5) Jones et al. *Surf. Sci.* **2025**, *753*.

(6) Mpofu et al. *J. Mater. Chem. C* **2024**, *12*, 12818–12824.

2:45pm **AF1-TuA-6 In-situ XPS Study of Ozone Oxidation of Aminosilane Adsorption Layers on Alumina*, Yuki Tsuchiizu,*** Institute of Fluid Science, Tohoku university, Japan*; Daisuke Ohori,* Institute of Fluid Science, Tohoku University, Japan*; Teruhisa Ohtsuka, Masashi Yamazaki, Hiroshi Arimoto,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*; Kazuhiko Endo,* Institute of Fluid Science, Tohoku university, Japan

We have determined the post-oxidation surface termination of tris(dimethylamino)silane (TDMASi) on alumina under ozone exposure using in situ XPS. Alumina was used as a reproducible hydroxylated oxide model surface for first-cycle adsorption and oxidant-half-cycle studies. A TDMASi adsorption layer on alumina was exposed to ozone for 2-20 s at 200°C. C 1s deconvolution shows that the C-N component decreases, while a high-binding-energy component at 289-290 eV increases up to 5 s. In contrast, the Al 2p-normalized N 1s signal shows no large change over 2–20 s. These results indicate that ozone cleaves C-N bonds and promotes formation of oxidized carbon species, while nitrogen-containing fragments remain on the surface. Overall, the oxidant half-cycle approaches a saturated post-oxidation surface state.

$SiO_2$ spacers in back-end-of-line integration require conformal deposition below 400°C with atomic-layer thickness control on 3D devices. Aminosilane precursors enable low-temperature $SiO_2$ ALD, and ligand variants have been developed to tune growth per cycle (GPC) and impurity behavior. This trend implies that ligand identity governs ligand-fragment incorporation during growth, so the oxidant half-cycle may yield ligand-dependent surface terminations. Because ligand-fragment retention during

early cycles can affect dielectric properties (reliability/leakage) and spacer etch response, the termination chemistry is directly relevant to BEOL $SiO_2$ process design. We previously used in-situ XPS to show that both the ease of initial adsorption and the adsorption structure of aminosilanes on alumina depend on ligand architecture. In this study, we use TDMASi as a case study to identify post-oxidation termination motifs under ozone.

An alumina film was deposited on a Si substrate by ALD using trimethylaluminum and O2 plasma. TDMASi was adsorbed as an initial adsorption layer, followed by exposure to ozone (≧90%) for 2-20 s at 200℃. Samples were loadlock transferred under high vacuum to in situ XPS, where Al 2p, C 1s, and N 1s spectra were acquired.

Figure 1 shows the C 1s spectra of (a) alumina, (b) before ozone exposure, and (c) after 20 s ozone exposure. The C 1s envelope was deconvoluted into C-C/C-H, C-N, C=O, and carbonate (OCOO) components. Carbonate is already present on alumina (a). Compared with (b), the C-N component decreases in (c), indicating loss of C-N bonds in amino-derived species on alumina. Figure 2 shows Al 2p normalized ozone dose time dependences of the C 1s components and N 1s. C-C/C-H, C=O, and N remain nearly constant, whereas C-N decreases and carbonate increases up to 5 s. Thus, ligand-derived N does not desorb, while ozone cleaves C-N bonds and forms carbonate species, and the reaction approaches saturation with carbonate termination.

This work was partially supported by JSPS KAKENHI 24K0786 and MEXT ARIM (JPMXP1225AT0193).

3:00pm **AF1-TuA-7 In situ and Operando investigation of MLD of Hafnicone Using Ambient Pressure-XPS***, **Hariprasad Parayil Kalappurackal,*** Lund University, Sweden

Molecular Layer Deposition (MLD) extends Atomic Layer Deposition (ALD) by enabling the growth of hybrid organic–inorganic thin films through sequential, self-limiting surface reactions. By incorporating organic precursors into ALD-type processes, MLD (cf. Fig. 1) provides access to materials with tunable chemical functionality while maintaining the precise thickness control, conformality, and scalability of conventional ALD. Such hybrid materials are of growing interest for applications requiring tailored mechanical, electronic, or chemical properties.

Understanding MLD surface chemistry, particularly during nucleation and low-temperature growth, remains a key challenge. Here, MLD processes are studied using a dedicated ALD/MLD reactor cell integrated with ambient pressure x-ray photoelectron spectroscopy (APXPS) at the SPECIES beamline of the MAX IV Laboratory,[1A] Lund, Sweden. The setup mimics ALD reactor conditions and enables time-resolved in situ observation of surface reactions under realistic growth environments.

As a model hybrid system, we demonstrate the MLD of hafnicone[2] on silicon substrates using a deposition sequence in which the inorganic precursor TDMAHf is pulsed before the organic precursor ethylene glycol. The deposition process took place at a substrate temperature of 100℃ and the steps consists of precursor adsorption, nucleation, and saturation, which together define the deposition cycle and can be followed in real time using APXPS. As shown in Fig. 2, presence of the N 1s and Hf 4f signals from the very beginning of the measurement are due to preceding ALD experiments in the same cell: the surface is saturated by adsorbed TDMAHf already before the metal precursor pulse. Following introduction of the organic precursor, the N 1s signal completely disappears, consistent with the expected complete removal of the -$NMe_2$ ligands by ethylene glycol and their replacement by oxygen containing groups from the organic precursor, leading to the formation of Hf-O-C bonds characteristic of hafnicone. The shifts of the Hf 4f and C 1s core levels toward higher binding energy indicate a decrease of electron density on these atoms. The O 1s shifts towards lower binding energy. Both observations are in agreement with the formation of new oxygen bonding environments, consistent with metal organic Hf-O-C film formation. The C 1s binding energy is in line with presence of an intact ethylene linker, as expected for the present MLD process.

Hafnicone type materials are of interest due to their potential functionality, including enhanced mechanical flexibility and tunable dielectric or chemical properties resulting from the incorporation of organic linkers into a hafnium based inorganic framework.

**References:**

[1] Kokkonen, E. et al. Rev. Sci. Instrum. 93, 013905 (2022).

[2] Lee, B. H. et al. ACS Appl. Mater. Interfaces 6, 16880–16887 (2014).

3:15pm **AF1-TuA-8 Pyroelectric Calorimetry of MgO and $ZrO_2$: Untangling Thermodynamics, Kinetics, and Precursor Transport***, **Ashley Bielinski,*** *Cong Liu, Alex Martinson,* Argonne National Laboratory

A detailed understanding of ALD surface reaction mechanisms, thermodynamics, and kinetics is essential for the development of new processes, particularly those that rely on chemical selectivity between different surface sites.While computational modeling, such as DFT can provide valuable insight on the thermodynamically favorable reactions of ALD precursor molecules, this approach is limited to simplified and idealized substrate surfaces and reaction conditions. In situ and operando studies of ALD surface reactions provide necessary information on how ALD reactions proceed on realistic substrates and under typical deposition conditions. ALD pyroelectric calorimetry provides quantitative measurements of reaction heat generation and heat transfer from surface reactions as well as precursor and byproduct flow with sufficient time resolution to measure the dynamics of these processes.

We have investigated ALD processes including the reaction between tetrakis(dimethylamido)zirconium(IV) (TDMAZr) and water to form $ZrO_2$ and the reaction between bis(ethylcyclopentadienyl)magnesium ($Mg(CpEt)_2$) and $H_2O$ to form MgO using pyroelectric calorimetry.These experimental results show how practical processes both agree with and contrast computationally proposed reaction mechanisms.Additionally, we present the design of an ALD reactor customized for pyroelectric calorimetry measurements with improved timing across and array of calorimeters. Combined with reactor-scale modeling, this enhanced experimental platform gives new insight into the interplay between precursor delivery, reaction kinetics, and the role of reaction byproducts.

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