ALD for Manufacturing
Room Auditorium - Session AM2-TuA
ALD for Manufacturing II

Moderators: Rong Chen, Huazhong University of Science and Technology, Ruud van Ommen, Delft University of Technology

4:00pm **AM2-TuA-11 High-Throughput Nanocoating Technology for Energy Applications*, Dmitrii Osadchii,*** Delft IMP B.V., Netherlands

In order to decarbonize the automotive sector, increased adoption of electric vehicles (EVs) is necessary. Two technologies are seen as a major driver for this development: Li-ion batteries (LIBs) and fuel cells (FCs). Many challenges still exist to enhance the performance of these power sources, such as the stability, cost, and environmental impact.

At the heart of these challenges are the active materials. For example with LIBs, much research is focused on the substitution of cobalt with nickel in the cathode. Not only does this enable a reduction of the battery cost, but it also enhances the capacity. Unfortunately, these benefits come at a cost, and significant stability issues still remain. A solution to enhance the stability can be found by protecting the surface of cathode powders. As such, there is a large body of literature showing that Atomic Layer Deposition (ALD) is well-suited to enhance the stability of low-cobalt cathode materials.

To capitalize on the benefits that ALD can bring, there is a growing need to bring powder ALD from lab to fab. For that, several challenges need to be overcome. Delft IMP tackles these challenges by developing high-throughput technology based on powder ALD. By combining pneumatic transport with ALD a continuous stream of nanocoated powder can be produced. In this talk we will showhow Delft IMP's unique technology allows to increase the cycle life of cathode materials up to 100% at up to 40% lower costs compared to traditional wet coating technologies.

4:15pm **AM2-TuA-12 Optimizing Vapor Delivery of Transition-Metal Diazadienyl Complexes for ALD Processes*, James Maslar*,** *B. Kalanyan,* NIST-Gaithersburg*; V. Dwivedi,* NASA Goddard Space Flight Center*; D. Moser,* EMD Electronics

Metal ALD processes have potential applications in many areas, including microelectronics and heterogeneous catalysis. However, such processes have not been widely demonstrated for many of the transition metals. Transition-metal diazadienyl complexes represent a class of precursors that has been used for metal ALD, including deposition of cobalt and nickel films. Furthermore, these precursors have been shown to deposit metal films at low temperatures and with substrate selectivity, making them suitable for many microelectronics applications. In this investigation, the delivery of bis(1,4-di-*tert*-butyl-1,3-diazadienyl)nickel [$Ni(DAD)_2$] was studied for ALD of nickel metal. $Ni(DAD)_2$ is a solid at typical delivery temperatures and, in general, delivering a constant flux of a solid precursor can be difficult. However, this may not be an issue for an ideal ALD process unless the total precursor dose is insufficient to saturate all surface reactive sites. Unfortunately, under some conditions the dose of $Ni(DAD)_2$ has been observed to decrease significantly after storage for nominally identical delivery conditions, complicating subsequent ALD. The primary goal of this investigation is to elucidate the factors impacting $Ni(DAD)_2$ delivery, including any conditions resulting in irreproducible delivery. To achieve this goal, both $Ni(DAD)_2$ and the DAD ligand (the primary decomposition product under the conditions of this study) were monitored as a function of delivery conditions using direct absorbance measurements. Measurements were performed with an ultraviolet-visible spectrometer and a two-channel gas analyzer. The gas analyzer employed broadband ultraviolet-visible sources, a beam splitter, bandpass filters for wavelength isolation, and avalanche photodiode detectors. The results from this investigation should provide more insight into conditions to optimize the delivery of transition-metal diazadienyl complexes.

4:30pm **AM2-TuA-13 Inherently Selective Atomic Layer Process Based on Spatial Micronozzles: Microreactor Selective Area Direct Atomic Processing (µSADALP)*, Maksym Plakhotnyuk,*** ATLANT 3D Nanosystems, Denmark*; I. Kundrata,* ATLANT 3D Nanosystems, Germany*; J. Bachmann,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), ATLANT 3D Nanosystems, Germany **INVITED**

In parallel to additive manufacturing leading the revolution in traditional manufacturing, by supplementing the weaknesses of substractive machining, so can additive manufacturing supplement the weaknesses of traditional thin film deposition techniques. Where lithography struggles, for example with rapid iterations for prototyping or incompatibility with the used chemistry, additive manufacturing can shine. Indeed, several approaches are in development for 3D nanopriting[1,2,3].

Atomic Layer Deposition, and in more general Atomic Layer Processing, offers a unique opportunity for 3D printing due to its two-step chemical reaction. While simple in theory, due to well-developed examples of Spatial Atomic Layer Deposition (SALD), in practice minimization of SALD requires substantial effort into the creation of suitable micro-nozzles. Uniquely, ATLANT 3D Nanosystem has developed proprietary Spatial ALD micronozzles, naming the process microreactor Selective Area Direct Atomic Processing - µSADALP™.

In general fields such as advanced materials innovation, MEMS & sensors, RF devices (transparent antennas), Optics & Photonics (Optical coatings, surface modifications) and many other can benefit from µSADALP™.

As for now, µSADALP™ is in its development stage, with several standard ALD processes explored, but further research is being done in using it for Atomic Layer Etching and Molecular Layer Deposition, or even Atomic Layer Surface Doping (ALSD) which further opens the door for more processes and thus more applicability for this technology in advanced materials, functional surfaces and electronics design, development and manufacturing.

5:00pm **AM2-TuA-15 Atomic Layer Rastering*, Ivan Kundrata,*** ATLANT 3D Nanosystems ApS, Slovakia

Atomic layer deposition is, due to its inherent separation of reactions, uniquely suitable for adaptation into a 3D printer. In fact, the concept of spatial atomic layer deposition, which can be considered as a precursor for 3D atomic layer printing, goes all the way back to 1974.[1] Despite the many challenges of creation and miniaturization of spatial ALD reactors, atomic layer 3D printing was successfully proved as a concept recently.[2,3]

The Atomic Layer 3D printer, by its nature of exploiting a physical precursor/reactant separation, is in sharp contrast to Area Selective ALD[4,5] which exploits a chemical reaction to achieve localization. Therefore, no pre-patterning or tricks are needed for spatial Atomic Layer 3D printing to produce localized deposition. However, the cost of achieving localization via spatial separation is the difficulty in design and manufacture of micronozzles, which the Area Selective ALD does not need to struggle with. This inherent spatial separation, agnostic of the ALD chemistry used, or the substrate, allows to explore and use techniques normally associated with fused filament printing or plotting, such as sacrificial layer deposition or rastering.

Rasterization is a traditional technique from printing and engraving, where the picture is broken down into line and then “rastered”. Its use so far for nanostructuring has been limited, however using Atomic Layer 3D printing allows us to explore the creation if nanostructures by rastering. Furthermore, there are unique effects created by the nozzle geometry of Atomic Layer 3D printing, that can be exploited in rastering, which for example results in the ability to controllably print gradients.

In this study, we use the Atomic Layer 3D printer to manufacture rastered structures, from simple structure of 2 lines overlapping with various overlaps, to rastered squares in of various complexity, to a set of concentric circles with a 600 nm line overlaps. To show that the technique is not materially dependent rasters were performed both in TiO_2 and Pt. We demonstrate that we can control both the pattern, to the resolution of the kinematic apparatus, and the aspect ratio with ALD resolution.

5:15pm **AM2-TuA-16 Maskless Localized Atomic Layer Deposition: Surface Structuration and Functionalization**, *L. Midani, W. Ben-Yahia, V. Salles,* Université Lyon 1, France*; **Catherine Marichy,*** CNRS-LMI, France

Nowadays, interest in nanotechnologies is strongly expanded in many domains like nanoelectronics, energy, transportation, medicine, and the environment. Precise designs of micro- and nanostructures are sought after for many devices and applications such as thin films transistors, diodes, electrocatalysts, solar cells, sensors, or membranes. Additive and subtractive technologies are thus areas of extensive research. In particular, additive approaches permit the controlled stacking of layers made of different materials. However, they display limitations either in thickness of the deposited material, in lateral resolution, or structuring scale. Combining control of at least one dimension at the nanometer level with large-scale patterning is still challenging in the direct write approach.

Atomic Layer Deposition (ALD) is a technique of choice for depositing thin films with a thickness control at the atomic scale. In particular, direct patterning can be realized using spatial ALD (SALD).[(1–3)]

Herein, maskless deposition of uniform and homogenous oxide thin films is successfully demonstrated with a lateral resolution tuned from millimeters to hundred micrometers range while keeping a film thickness in the range of a few to hundreds of nanometers with a control at the nanoscale. A modified open-air SALD head is employed to fabricate complex oxide patterns on various substrates.[(4)] The co-reactant being kept in the surrounding atmosphere *i.e.* water from relative humidity in the present case, a simple injection head that consists of three concentric nozzles with only one precursor outlet has been designed. An easy and reversible modification in the diameter of the metal precursor outlet that permits direct patterning with different lateral sizes is demonstrated. Typical SALD characteristics are observed. Deposition on various planar and structured substrates is also investigated as well as complex and multilayer oxide patterns. This maskless SALD approach also enables controlled surface functionalization. In particular, local tuning of the wetting properties is successfully realized that permits controlling the water dropwise condensation.

1. C. A. Masse de la Huerta *et al.*, *Advanced Materials Technologies*. **5**, 2000657 (2020).
2. P. Poodt, B. Kniknie, A. Branca, H. Winands, F. Roozeboom, *physica status solidi (RRL) – Rapid Research Letters*. **5**, 165–167 (2011).
3. M. Aghaee, J. Verheyen, A. A. E. Stevens, W. M. M. Kessels, M. Creatore, *Plasma Processes and Polymers*. **16**, 1900127 (2019).
4. L. Midani, W. Ben-Yahia, V. Salles, C. Marichy, *ACS Appl. Nano Mater.***4**, 11980–11988 (2021).

5:30pm **AM2-TuA-17 New Spatial ALD/CVD Approaches for Area-Selective Deposition***, **David Muñoz-Rojas**,* CNRS-LMGP, Université Grenoble Alpes, France*; C. Masse de la Huerta,* LMGP, France*; V. Nguyen,* phenikaa University, Viet Nam*; A. Sekkat, C. Crivello, F. Toldrá-Reig, C. Jimenez, O. Graniel, M. Dibenedetto,* LMGP, France

Within the materials deposition techniques, Spatial Atomic Layer Deposition (SALD) is gaining momentum since it is a high throughput and low-cost alternative to conventional ALD. SALD relies on a physical separation (rather than temporal separation, as is the case in conventional ALD) of gas-diluted reactants over the surface of the substrate by a region containing an inert gas.[1] Thus, fluid dynamics play a role in SALD since precursor intermixing must be avoided in order to have surface-limited reactions leading to ALD growth, as opposed to CVD growth. Fluid dynamics in SALD mainly depend on the geometry of the reactor and its components. While care is normally taken to prevent precursor crosstalk when using SALD, we have shown that the spatial separation principle can also be applied to perform CVD reactions (SCVD), i.e. growth not limited to the surface, yielding yet faster deposition rates while maintain the film quality and conformality typical of ALD and SALD. [2,3] We have also shown that selective deposition can be achieved by working in SCVD mode. In this new approach to area-selective deposition (ASD), the depositions are performed in static mode (i.e. no relative movement between the reactor and the substrate), and Computational Fluid Dynamics (CFD) simulations are used to control de effect of the different deposition parameters on the SCVD mode. [4] In this presentation we will show how close-proximity SALD based on a manifold injection head working in the open air can be tuned to deposit custom patterns without the need of pre-patterning steps. This is achieved by using the system in static SCVD mode and by a proper design of the injection head using 3D printing.[5] We will also show other new approaches to ASD developed with our SALD system.

1. Muñoz-Rojas, D., et al. Spatial Atomic Layer Deposition. inIntech open1 (2019). doi:10.5772/32009

2. Musselman KP, et al. Rapid open-air deposition of uniform, nanoscale, functional coatings on nanorod arrays. Nanoscale Horiz. 2017 2(2):110–7.

3. Hoye RLZ, et al. Synthesis and Modeling of Uniform Complex Metal Oxides by Close-Proximity Atmospheric Pressure Chemical Vapor Deposition. ACS Appl Mater Interfaces 2015;7:10684−10694.

4. Masse de la Huerta, C., et al. Influence of the Geometric Parameters on the Deposition Mode in Spatial Atomic Layer Deposition : A Novel Approach to Area- Selective Deposition. Coatings 9, 5 (2018).

5. Masse de la Huerta, et al., Gas-phase 3D printing of functional materials, Advanced Materials Technologies, 5, 2000657 2020.

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