## ALD for Manufacturing
## Room Auditorium - Session AM1-TuA

### ALD for Manufacturing I

**Moderators:** Hardik Jain, TNO/Holst Center, Maksym Plakhotnyuk, ATLANT 3D Nanosystems

1:30pm **AM1-TuA-1 Atomic Layer Deposition Equipment Used in Industrial Production of More Than Moore Devices*, Taguhi Yeghoyan,*** Yole Développement, France

In semiconductor community, Atomic Layer Deposition (ALD) is often associated with upmost advanced nodes, used for manufacturing of logic and memory devices, so called More Moore (MM) applications. For MM, ALD is used in High Volume Production (HVM) already for 20 years, starting with DRAM capacitor coating and logic transistor node shift from 65 nm to 45 nm. From that time on, ALD played a vital role to enable subsequent nodes and transistor architecture evolution, first to FinFet and currently to Gate-All-Around (GAA).HVM of MM devices is done with 300 mm Si wafers, with ALD equipment tailored to a specific process and high throughput. Thus, only few ALD equipment makers are present in MM HVM, generating highest equipment sales revenue.

On the other side of semiconductor industry, More-than-Moore (MtM) device production flourishes with diversified substrates in terms of material, size and sometimes shape. MtM devices encompass MEMS and sensors, Radiofrequency (RF) devices, power devices, CMOS Image Sensors (CIS), photonic devices and various packaging approaches. Among all MtM devices, CIS are manufactured mostly on 300 mm Si wafers on MM-like production lines and require similar ALD equipment. Other MtM devices are manufactured mostly on up to 200 mm production lines at lower volumes and with varied process flow. This MtM devices need flexible ALD equipment able to deposit often thicker films thermally or with plasma assistance, on various substrate sizes and substrate material, i.e. compound, Si, piezoelectric, dies on frame tape among others. Currently, more MtM ALD equipment providers qualify their equipment for Fab production, driven by several applications, where ALD is indispensable. These are for example: GaN HEMT transistors, mini-LEDs and microLEDs as well as wafer level encapsulation.

This presentation aims to give a market research overview on ALD equipment used in industrial production of MtM devices, with market size estimated to $345M in 2020, which is expected to increase to $680.5M in 2026. Moreover, ALD supply chain is outlined: ALD equipment subparts and inspection, process developers and materials suppliers. Finally, commercial MtM devices with identified ALD use are showed.

1:45pm **AM1-TuA-2 Spatial ALD on Large-Area Porous Substrates: How to Avoid Supply Limitation and Maximize Precursor Efficiency?*, Paul Poodt,*** SALDtech B.V., Netherlands

One of our greatest challenges for the coming decade is the transition to a sustainable way of generating, storing, and converting energy. High performance batteries, fuel cells, electrolyzers and solar cells are part of the solution, but still face many challenges that need to be solved. Efficiencies and capacities need to increase, the use of scarce and expensive materials needs to reduce and the life-time needs to improve. There are many examples where ALD has been used to improve on these aspects. For example, by applying thin and highly conformal films on porous substrates using ALD, the lifetime of Li-ion batteries can be improved, the loading of expensive catalyst materials in fuel cells and electrolyzers can be reduced and new devices such as 3D solid state batteries are enabled.

In order to enable large-scale mass production of these applications, Spatial ALD can be used for high deposition rates on both large substrates (square meters) and roll-to-roll. Scaling-up Spatial ALD processes on large area porous substrates, however, can lead to problems with supply limitation; i.e. when the required precursor flow to cover a high surface area substrate exceeds the amount of precursor that can actually be supplied, e.g. due to a low vapor pressure. Furthermore, in case of very expensive precursors, it is required to maximize the precursor efficiency to minimize costs.

The dependency of the precursor dose on aspect ratio, sticking coefficient and reactor pressure has been studied in great detail. However, for supply limitation, the effective surface area of porous substrates is the most important parameter. Furthermore, transport of precursor from the inlet towards the substrate and exhausts has to be taken into account. We have developed a numerical model to solve the diffusion-convection-reaction equation for porous substrates in a spatial ALD reactor, named 3D-DCR. The model combines parameters such as the porosity and effective area of the substrate with reactor dimensions, gas flow rates and deposition rate requirements to calculate and optimize the required precursor dose, precursor mass flow and utilization efficiency.

We will discuss several important results from this model, such as: 1) increasing the efficiency means decreasing the deposition rate and vice versa, 2) the required precursor dose does not only depend on pore aspect ratio but also on the reactor dimensions and used flows and 3) precursor efficiencies exceeding 80% are possible for porous substrates. Furthermore we will show how the these results can be used to optimize Spatial ALD processes and equipment for large scale manufacturing of high performance energy devices.

2:00pm **AM1-TuA-3 Atmospheric-Pressure Plasma-Assisted Spatial Atomic Layer Deposition of Silicon Nitride*, Jie Shen,*** TNO-Holst Centre, Netherlands*; F. Roozeboom,* University of Twente, Netherlands*; A. Mameli,* TNO-Holst Centre, Netherlands

Silicon nitride is a ubiquitous material in device fabrication, largely employed as an insulating dielectric layer or a gas permeation barrier layer, for example. Despite the effort that has been devoted to the development of effective $SiN_x$ atomic layer deposition (ALD) processes, reports on novel precursors and processes for $SiN_x$ continue to be regularly published. This highlights that some of the challenges such as low deposition rate and poor conformality, to cite the most common ones, are yet to be completely solved, especially at low deposition temperature.[1]

In this work we investigate the feasibility of $SiN_x$ spatial ALD at atmospheric pressure as a possible method for reaching high-quality and high-throughput $SiN_x$. Deposition temperatures between 150 °C and 250 °C were explored, resulting in growth per cycle (GPC) values between 0.3 Å/cycle and 0.2 Å/cycle, respectively and in a total ALD cycle time of ~2.4 s. The $SiN_x$ films were grown in a dedicated rotary lab-scale spatial ALD reactor,[2] using either a two-step process, employing bisdimethylaminosilane (BDEAS) and $N_2$ plasma from a direct dielectric barrier discharge (DBD);[3] or a three-step process, consisting ofBDEAS, followed by a first plasma exposure to $N_2/H_2$ DBD and a second $N_2$-only DBD plasma step. The influence of $H_2$ and $N_2$ plasma settings, and deposition temperature will be discussed in detail on the basis of the results from X-ray photoelectron spectroscopy (XPS) and Fourier transformed infrared spectroscopy (FTIR).[4] The best results in terms of layer composition and wet etch rate (WER), in 1:100 diluted HF were obtained at a deposition temperature of 250 °C. Here, 10% $O_2$ and 7.4% C contamination levels were detected, for layers with an N/Si ratio of ~ 1.29and a WER of 18 nm/min.

In conclusion we have demonstrated the first atmospheric-pressure spatial ALD process for $SiN_x$. The results presented herein are therefore very encouraging for low-temperature and high-throughput $SiN_x$ spatial ALD in large-area as well as in roll-to-roll mode. Based on the relevant process details explored in this work, we suggest possible next steps for further improving the quality of the spatial ALD deposited $SiN_x$ layers.

This work was supported in part by Semiconductor Research Corporation (SRC).

**References**

[1] X. Meng, *et al.*, *Materials*,**9**, 1007 (2016).

[2] P. Poodt, *et al.*, *Adv. Mater.*, **22**, 3564 - 3567 (2010).

[3] Y. Creyghton, *et al.*, Proc. Int. Conf. on Coatings on Glass and Plastics (ICCG 2016), Braunschweig, Germany, June 12-16, 93-97 (2016).

[4] R. Bosch, *et al.*, *Chemistry of Materials*, **28**, 5864–5871 (2016).

2:15pm **AM1-TuA-4 Recent Development of Large Scale ALD for Non-IC industrial Applications*, Wei-Min Li,*** Jiangsu Leadmicro Nano Technology Co. Ltd., China **INVITED**

Recent advance in ALD technology has shown prospect of HVM applications in several non-IC industry areas. For instance a breakthrough has been achieved during past few years for high efficiency solar cell HVM thanks to the rapid increase of global clean energy demand. ALD offers not only excellent material properties and functions, but also meets the manufacturing throughput and up-time requirements with significantly reduced manufacturing cost. Growing interests is seen for energy storage and flexible electronics applications as well. The great differences in material chemistry and various substrates to be handled however, calls for continuous innovation for different industrial applications. Author

highlights current large scale ALD that are used or with high potential in some of the non-IC industry applications.

In PV industry, both ALD and PEALD have become the enabling technology not only for current mainstream PERC/PERL/PERT, but also finds applications for next generation TOPCon, IBC, HJT, as well as tandem solar cell technology. Batch type ALD and PEALD reactors are exclusively used for wafer based *c*-Si solar cell applications. A record throughput at over 15000 wafers/hour has been achieved with excellent film properties. A typical p-PERC cell efficiency has reached above 23.5%, and novel n-TOPCon solar cell has reached a cell efficiency of above 24.5% in pilot production. While an increase of conversion efficiency can be achieved for ALD enabled high efficiency solar cell manufacturing, the cost-of-ownership is also significantly reduced. With continuous improvement of materials and process integration, further enhancement for high efficiency solar cells are expected.

Significant progress has been achieved as well for ALD industry applications with flexible substrates that requires high permeation barriers properties. A commercial "roll-to-roll" ALD can now handle an effective web width of 1500 mm of PET substrate and achieve WVTR of $10^{-4}$ mg/day/m$^2$ at a maximum coating speed of >5 m/min. Large volume powder coating for lithium ion battery and catalyst applications at hundreds kilogram scale is seen approaching commercialization. Nevertheless, novel material and precursor chemistry and innovative reactor design combined with "intelligent manufacturing" to further improve the performance, enhance the productivity as well as reduce the production cost are highly desired.

Recent advances of ALD technology and contribution to some of the key industry areas shows that with continuous innovation and efforts, large scale ALD is becoming a generic and prospective technology for novel non-IC industrial applications.

2:45pm **AM1-TuA-6 An Innovative Method for in Situ Calorimetry of ALD/ALE Surface Reactions***, **Anil Mane**, J. Elam,* Argonne National Laboratory

Calorimetry is an essential analytical technique for determining the thermodynamics of chemical reactions. In situ calorimetry during atomic layer deposition and etching (ALD/ALE) would be a valuable tool to probe the surface chemical reactions that yield self-terminating growth and removal of material at the atomic scale. Additionally, in situ calorimetry would reveal the partitioning of chemical energy between the individual half-reactions that constitute the ALD or ALE cycle. In this study we present an alternative strategy that exploits temperature-induced resistance changes in ALD thin films. Our approach utilizes a thin film ALD nanocomposite resistive layer deposited conformally on the inner surfaces of a borosilicate capillary glass array (CGA) [1]. The ALD nanocomposite has a high resistivity and a well-defined thermal coefficient of resistance (TCR), both of which can be tuned by adjusting the resistive layer composition. In practice, the resistive CGA (RCGA) calorimeter is installed in the ALD system and electrically biased to produce a current in the microamp range that is recorded in real time. During the ALD/ALE surface reactions, heat exchanged with the coating produces transient current features due to the non-zero TCR of the nanocomposite film. These transient features are highly reproducible and can be used to calculate the reaction enthalpies of the individual surface reactions based on the TCR value and the thermos-physical properties of the CGA. Moreover, the RCGA can be calibrated by subjecting the device to well-defined voltage pulses and measuring the resistance changes induced by Joule heating. The RCGA is highly sensitive due to the high surface area of the CGA, the rapid response of the nm-scale resistive coating, and the tunable TCR value. In addition, the device is relatively low cost and easily integrated into ALD/ALE systems. To demonstrate the RCGA calorimetry method, we performed in-situ calorimetry measurements for a range of ALD processes including $Al_2O_3$, $AlF_3$, $Al_xO_yF_z$, ZnO, MgO, $TiO_2$, and $ZrO_2$. We also studied the nucleation behavior when transitioning between ALD materials and the use of alternative precursors for ALD $Al_2O_3$, $TiO_2$, and $AlF_3$ ALD. We find good agreement between reported enthalpy changes for ALD reactions and the values measured by in situ RCGA calorimetry. We believe that RCGA calorimetry is a versatile in situ method to study the thermodynamics of ALD/ALE surface reactions and a convenient diagnostic for real-time ALD/ALE process monitoring in a manufacturing environment.

1) A. U. Mane et. al., Chem. Vap. Deposition, **19**, 186–193, (2013).

3:00pm **AM1-TuA-7 Production-Suitable 200 Mm Batch ALD/MLD Thin Film Encapsulation Toward Flexible OLED Manufacturing***, **Jesse Kalliomäki**, E. Rimpilä, R. Ritasalo, T. Sarnet,* Picosun Oy, Finland

Organic electronics (OE) have rapidly become a mainstream technology due to their desired properties like low weight, high energy efficiency, flexibility and low manufacturing costs [1]. These advantages can be traced back to the fact that components can be routinely printed on plastics in huge roll-to-roll manufacturing lines. What has changed in the last decade or so is the introduction of thin film encapsulation solutions (TFEs) as a key enabling technology. TFEs can mitigate one of the biggest downsides of OEs - their susceptibility to oxidation by moisture [2]. TFEs allow the devices to stay light, transparent and flexible and help them to achieve their full potential.

TFEs rely heavily on vacuum-based thin film deposition techniques like ALD and MLD, which are not as straightforward to scale to roll-to-roll. Indeed, most of the research on TFEs are carried out on chip-scale and focuses on improving already excellent barrier properties [3]. To avoid bottlenecks in manufacturing, scaling up these TFE processes must be realized. Previously we have reported an industrially viable ALD/MLD process [4], which we have continued to scale with serious production in mind.

We present characterization and scale up results of single-chamber TFEs (Fig 1.). The moisture barrier properties were analysed with tuneable diode laser absorption spectroscopy (Sempa HiBarSense 2.0), delivering excellent results from a very large area (3320 mm$^2$). Bending properties were analysed by applying tensile stress by bending films deposited on polycarbonate and determining the crack-onset-strain with an optical microscope. Confirming TFEs can resist defects up to 2% tensile stress. All films were deposited using a Picosun P-300B batch ALD tool with batch sizes up to 27 pcs of 200 mm wafers. The process scales to larger chambers and achieves several Å/min growth rates and 2% chip-2-chip uniformities over full wafer batches.

In this work, we have demonstrated that ultra-barrier level TFEs can be coated on surfaces areas meaningfully measured in m$^2$. The barrier properties are also confirmed from a large enough area, to reflect the performance of the final product.

[1] Chang et al. (2017), doi:10.1109/JETCAS.2017.2673863
[2] Steinmann et al. (2018), doi:10.1557/jmr.2018.194
[3] Li et al. (2019),doi:10.1557/jmr.2019.331
[4] Kalliomäki et al. (2021), ALD2021, conference presentation

3:15pm **AM1-TuA-8 Roll-to-Roll ALD Coatings for Battery Cell Interfaces at Production Scale***, **Andrew Cook**,* Beneq, Finland

ALD is an enabling technology, which has been shown to improve battery performance, through the introduction of thin film coatings to modify interface surfaces on cathodes, anodes and separators. ALD can help to improve thermal stability, stabilise SEI layer, suppress dendrite, inhibit transition metal dissolution, and increase interfacial contact between layers, all of which are current issues facing lithium ion battery technology. This presentation will demonstrate how Beneq use ALD technology to solve these issues and show how this can be scaled to production levels within a Gigafactory environment.

Atomic Layer Deposition (ALD) is an advanced coating technique, which has been extensively studied for more than 10 years for uses in battery applications on small scale batch systems. ALD coatings have been applied to cathode, anode, and separator materials to modify the surface interfaces, and improve battery performance. This presentation will describe the current R2R ALD system, Beneq has developed for high throughput production.

## 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.

## ALD for Manufacturing
## Room Arteveldeforum & Pedro de Gante - Session AM-TuP
## ALD for Manufacturing Poster Session

**AM-TuP-1 Atmospheric Pressure Plasma Enhanced Spatial ALD for Energy Applications**, ***Corne Frijters***, *V. Tielen, R. Pals, J. Smeltink, K. Driessen, H. Heezen, P. Poodt,* SALDtech B.V., Netherlands

One of our greatest challenges for the coming decade is the transition to a sustainable way of generating, storing, and converting energy. High performance batteries, fuel cells, electrolyzers and solar cells are part of the solution, but still face many challenges that need to be solved. Efficiencies and capacities need to increase, the use of scarce and expensive materials needs to reduce and the life-time needs to improve. There are many examples where ALD has been used to improve on these aspects. For example, by applying thin and highly conformal films on porous substrates using ALD, the lifetime of Li-ion batteries can be improved, the loading of expensive catalyst materials in fuel cells and electrolyzers can be reduced and new devices such as 3D solid state batteries are enabled. In order to enable large-scale mass production of these applications, Spatial ALD can be used for high deposition rates on both large substrates (square meters) and roll-to-roll.

Precise control of film thickness uniformity is essential for a reliable performance of energy devices. We will show that we have used CFD modeling to develop a remote atmospheric pressure plasma source that is integrated in our Spatial ALD tool, demonstrating excellent uniformity of plasma gas flows towards the surface, leading to thickness non-uniformities of less than 2% over more than 30 cm widths.

This plasma source also allows to do maskless patterned deposition, in combination with stripe coating, to only deposit films on targeted active areas and not in between. Not only does maskless patterned deposition mean that no masks are required, it also leads to a significant decrease in precursor use, as precursors are only dosed where and when required. Especially in the case of expensive materials, like platinum-group metals, this is essential to minimize cost. Additionally, there is the option to reclaim unreacted precursor from the Spatial ALD reactor for recycling purposes, further decreasing the overall process costs.

Finally we will show how these components have been integrated in a 300 mm Spatial ALD R&D tool, that can be used to deposit a range of different materials on substrates of various shapes and sizes. This tool can be used to develop and optimize Spatial ALD processes for energy applications, in preparation for future large-area or roll-to-roll manufacturing.

**AM-TuP-2 Computational Fluid Dynamics Analysis of Cyclone-Type Vaporizer for Atomic Layer Deposition**, *D. Shin,* ***Cha-Hee Kim***, Sejong University, Korea (Republic of)*; S. Seo, Y. Lee, K. Jeong, D. Kim,* GO Element Co. Ltd., Korea (Republic of)*; W. Lee,* Sejong University, Korea (Republic of)

Due to the three-dimensionalization of semiconductor devices, the substrate surface area for atomic layer deposition (ALD) increases, requiring high-capacity precursor delivery systems. The commercial liquid delivery system (LDS) has a vaporizer with complicated pathways to secure a sufficient vaporization area. However, since it is difficult to control the inner wall temperature of the vaporizer precisely, there are concerns about line clogging and particle generations due to the condensation or decomposition of the precursor [1]. The development of vaporizers has relied heavily on experimental trial-and-error methods. Computational fluid dynamics (CFD) can analyze the gas flow and temperature distribution inside the vaporizer, which enables the prediction of potential issues and the optimization of the vaporizer structure. In this study, we proposed a cyclone-type vaporizer structure for a high-capacity LDS. We performed CFD analysis for cyclone-type vaporizers with different design parameters, such as inlet guide pipe diameter, outlet length, cylinder length, and total length. The optimized model that maximizes the gas flow path and minimizes the temperature nonuniformity was selected based on the CFD results. The optimized model showed better characteristics than the conventional Lapple-type cyclone structure [2].

[1]K. Erickson et al, Advanced Semiconductor Manufacturing Conference, (2019)

[2] C. E. Lapple, Chemical Engineering, (1951)

**AM-TuP-3 Lightweight, Modular Model for Multizone Spatial ALD**, ***Angel Yanguas-Gil***, *J. Elam,* Argonne National Laboratory

Spatial ALD is a promising route for transitioning ALD processes into manufacturing that has long been explored by the research community and that is compatible with a wide range of applications, from photovoltaics to energy storage and separations membranes. As part of our development of an atmospheric pressure spatial ALD tool, we developed a simple model to explore the evolution of surface coverage and film thickness as a moving web or substrate passes through a series of spatially-separated precursor zones. Our simulation approach solves the reactive transport and surface reaction of ALD precursors under realistic conditions all the way from the precursor insertion point to the upstream and downstream exhaust regions, tracking the evolution of surface coverage and precursor concentration at each point on the substrate surface. By coupling multiple zones, we were able to simulate experimental configurations involving multiple ALD cycles in a single pass.

To benchmark this simple model, we compared the model results with those of 2D computational fluid dynamic (CFD) simulations that computed the reactive transport of precursor and the evolution of surface coverage as the substrate moves through a single ALD zone. The agreement between the simple model and the CFD simulation is excellent under conditions where precursor transport is efficient and the gap above the substrate is small enough to prevent the formation of significant mass boundary layers. We then applied these simulations to model the evolution of surface coverage and film thickness over multiple precursor/co-reactant zones. Our results show that after two cycles the growth per cycle achieved by passing through a single zone reaches a steady state value. Depending on the web velocity, substantial growth can take place in the inert gas purge regions upstream and downstream of the precursor insertion point.

This research was funded through Argonne's LDRD program.

**AM-TuP-4 Effect of Surface Treatment of Tan for Rapid Nucleation and Growth of ALD Ru Films**, ***Corbin Feit***, *U. Kumar, L. Tomar, Z. Caribe, N. Berriel , S. Seal , P. Banerjee,* University of Central Florida

Ruthenium (Ru) is a promising alternative to copper interconnects due to its improved electromigration with reducing line width and excludes the need for diffusion barriers compared to copper interconnects. Atomic layer deposition (ALD) is the industry standard for ultra-thin film deposition. However, the challenges of depositing ultra-thin films of Ru remain. Current Ru ALD processes proceed through island-like growth as a result of poor nucleation, especially on industrially relevant tantalum nitride (TaN) surfaces. This growth behavior hinders coalescence in the ultra-thin (i.e., < 10 nm) regime, which ultimately leads to increased surface roughness, resistance, and diffusion. Through surface engineering of TaN surfaces, improved nucleation and growth can be achieved.

This work investigates the effect of pretreatments on TaN surfaces on inducing Ru nucleation and growth to achieve early coalescence of ultra-thin films using Ru-dimethyl butadiene tri-carbonyl ($Ru(DMBD)(CO)_3$) and $H_2O$ (growth rate = 0.1 nm/cy).Pretreatments include UV-ozone, hydrogen plasma, and strong reducing agents such as trimethyl aluminum. The film nucleation and roughness are monitored by atomic force microscopy. The Ru thickness is measured by spectroscopic ellipsometry. The interface chemistry is probed by X-ray photoelectron spectroscopy (XPS) and water contact angle measurements. Finally, electrical probing elucidates the film coalescence via conductivity.

The as-deposited TaN surfaces induced a significant nucleation delay and roughness of Ru ALD (> 0.5 nm). Alternatively, UV-ozone pretreatment on TaN shows no indication of island-like growth and no marked increase in film roughness of Ru ALD (< 0.3nm). The enhanced nucleation and growth of Ru ALD on UV-ozone treated TaN is attributed to increased wettability. The role of TaN oxidation states on nucleation is understood through XPS. We provide evidence that UV-ozone treatment enhances nucleation and growth of Ru films on TaN without effecting the overall sheet resistance. Ultra-smooth, 2 nm Ru films on UV-ozone treated TaN can be achieved. In addition, the effect of strong reducing agents on inducing nucleation and growth of Ru ALD on TaN surfaces will be discussed.

**AM-TuP-5 How to Improve ALD Process Consistency with Optimized Process Valves and Pneumatic Control Systems**, ***Masroor Malik***, *J. Butler,* Swagelok Company

Atomic layer processes (ALD/ALE) generally rely on specialized high-purity valves for precise chemical dosing. Fast and consistent valve actuation performance is critical for efficient, accurate, and reliable atomic layer processes. Pneumatically actuated high-purity valves offer response times

under 10ms with better than 1ms consistency and remain the most effective solution for atomic layer process chemical delivery systems. The performance of these high-performance atomic layer process valves is highly dependent on the pneumatic system that drives them.

The performance and characteristics of pneumatic systems used to operate atomic layer process valves will be analyzed and reviewed. Performance data and design guidelines for optimizing a pneumatic system for fast and reliable chemical dosing will be provided. A poster that highlights the relationship between the many pneumatic system parameters and the process dose output will be submitted.

**AM-TuP-6 Spatial Atomic Layer Deposition for the Coating of Tubular Membranes**, *F. Toldra-Reig,* Laboratoire des Matériaux et du Génie Physique, LMGP-CNRS, France; ***Clément Lausecker,*** Institut Européen des Membranes, IEM-CNRS / Laboratoire des Matériaux et du Génie Physique, LMGP-CNRS , France; *M. Weber,* Laboratoire des Matériaux et du Génie Physique, LMGP-CNRS, France; *M. Bechelany,* Institut Européen des Membranes, IEM-CNRS, France; *D. Muñoz-Rojas,* Laboratoire des Matériaux et du Génie Physique, LMGP-CNRS, France

Highly efficient gas separation membranes represent a promising prospect for the energy sector and the chemical industry, as they are able to significantly reduce cost, energy, and environmental impact of many processes while also being considered as a key element for process intensification. Tubular-shaped membranes are particularly appealing since they offer stronger adaptability, more convenient cleaning, easier sealing, higher pressure resistance, and higher modularity than their planar counterparts. Furthermore, the membrane surface properties has to be precisely controlled during the fabrication process in order to enhance gas selectivity and permeability. In this context, atomic layer deposition (ALD) has become a valuable technique for membrane surface preparation. Recently, spatial ALD (SALD) has gained increasing interest as it enables the possibility to form high quality thin films under atmospheric pressure faster than conventional ALD while keeping high uniformity, excellent conformality, and good thickness control on substrates with high aspect ratios. Moreover, SALD presents the unique asset of being compatible with the use of 3D printed gas manifolds to readily customize the system to different deposition configurations. Therefore, the SALD technique is particularly suited for the preparation and optimization of membrane surfaces, although it has been limited so far to planar substrates.

In this work, we present a novel approach to perform thin film deposition by SALD on tubular surfaces such as tubular membrane supports. A dedicated custom close-proximity SALD gas manifold was designed, where polymer 3D printing was advantageously used for rapid prototyping and optimization. By implementing the 3D printed gas manifold in the SALD system, various materials such as ZnO were successfully deposited on different tubular surfaces including porous $Al_2O_3$ membrane supports. Furthermore, by optimizing the material and design used to fabricate the 3D printed gas manifold, this approach can be applied to a broad range of chemical precursors and non-planar surfaces. These results thus reveal the great potential of this new versatile approach for membrane applications, and also extends the capability of SALD for the coating of complex substrates with functional materials which could be of high interest for a variety of other applications including electrolyzers and fuel cells.

**AM-TuP-7 Hybrid PEALD/PECVD Reactor Design for Depositing Thick GaN Films on Si**, ***Birol Kuyel,*** *J. Marshall, A. Alphonse,* NANO-MASTER, Inc.

Depositing thick GaN on Si wafer using PECVD or CVD will require a thin buffer layer on sapphire wafers. We have presented results showingALD deposited GaN on Si wafer could possibly be a buffer layer for growing thick GaN layer on Si because of Si/GaN interlayer mixing* during ALD deposition. Now we want to show results of depositing a thick GaN film in a PECVD system on a Si wafer having ALD GaN. Furthermore we will show that our new "Hybrid PEALD/PECVD reactor"** can deposit both thin ALD buffer layer and thick PECVD GaN on Si wafer in same chamber without changing the hardware and breaking the vacuum.

*Deposition of GaN using $GaCl_3$ with $N_2$ plasma using PAALD, 44th ICMCTF conference at San Deigo, Apr 2015.

**Patent pending

**AM-TuP-8 Deposition of $CeO_{2-\delta}$ Thin Films by Atmospheric-Pressure Spatial Atomic Layer Deposition**, ***Ozden Celikbilek,*** Univ. Grenoble Alpes, CNRS, France; *M. Bianchini,* Catalonia Institute for Energy Research (IREC), Spain; *F. Toldra-Reid,* Univ. Grenoble Alpes, CNRS, Spain; *A. Sekkat ,* Univ. Grenoble Alpes, CNRS, France; *N. Alayo , A. Tarancón ,* Catalonia Institute for Energy Research (IREC), Spain; *D. Muñoz-Rojas ,* Univ. Grenoble Alpes, CNRS, France

With the discovery of nanoscale phenomena in thin films (TFs), such as grain boundary and strain engineering, increases in Solid Oxide Cells (SOCs) performance up to several orders of magnitude have been achieved.(1) Therefore, Thin film Solid Oxide Cells (TF-SOCs) has received considerable attention as alternatives for their thick, powder-based counterparts. In this study, we aim to develop durable and scalable TF-SOC materialsusing Spatial Atomic Layer Deposition (SALD) technique which provides high-quality film growth under atmospheric pressure and at faster deposition rates than Atomic Layer Deposition (ALD).(2) Since our SALD approach works in the open air, i.e. at atmospheric pressure, it is challenging to find sufficiently volatile, reactive and non-toxic precursors. In the case of $CeO_{2-\delta}$ (ceria), this is particularly difficult due to the low volatility and toxicity of standard Ce precursors. In our communication we will show a comparative study of the deposition of ceria films by SALD using non-toxic precursors.

(1)Acosta, M. *et al*. *Adv. Mater. Interfaces*, 1900462, 1–15 (2019).

(2)Muñoz-Rojas, D. *et al.Mater. Today Chem.*,**12**, 96–120 (2019).

**AM-TuP-9 Thermoelectric Performance Improvement by Interface Engineering With Atomic-Layer-Deposited ZnO Thin Films on Snse Powders**, ***Myeong Jun Jung,*** *Y. Weon, J. Park, Y. Yun, J. Byun, B. Choi,* Seoul National University of Science and Technology, Korea (Republic of)

Thermoelectric device, one of energy harvesting is a device that converts thermal energy into electrical energy can recycle wasted thermal energy. However, since improvement of thermoelectric performance is still required, various kinds of research are being conducted. In particular, many studies have been reported on the improvement of thermoelectric performance through the introduction of nanostructures. Atomic layer deposition (ALD) on powder materials is one of them. ALD thin film on powders increases interfaces by preventing the growth of grains during the bulking process. ALD-engineered interface between powders and thin films reduces thermal conductivity through phonon scattering, and the energy filtering effect increases the Seebeck coefficient by generating a potential difference. In this study, SnSe and ZnO were selected as the thermoelectric powder and thin film material, respectively. SnSe shows excellent thermoelectric performance under high temperature (>700K). ZnO thin film has superior electrical properties compared to other oxide films, is easy to deposit, and has a difference in bandgap energy from SnSe, making it possible to introduce an energy filtering effect.

SnSe powders were ground by ball mill (250 RPM, 50hr). ALD coating process on SnSe powders was proceeded with rotary-type ALD reactor (CN-1, Korea). For understanding the thickness effect, 10 , 40, and 100 cycles of ZnO thin films were grown with DEZ (diethylzinc) source and $H_2O$ (water) reactant at 100˚C. Uncoated SnSe powder was also used as a control group. SnSe pellets were produced through Spark plasma sintering at 60MPa, 723K for 6 minutes. Scanning and transmission electron microscopy combined with energy-dispersive spectroscopy (EDS) were used to confirm the uniform growth of thin film and its structural and chemical properties. X-ray photoelectron spectroscopy and X-ray diffraction was used to confirm chemical bonding states and structures. Thermoelectric performance was obtained by measuring thermal conductivity, thermal diffusivity, electrical resistivity, and Seebeck coefficient by laser flash analysis and Seebeck and electrical resistivity measurement system. As a result of calculating zT, figure of merit, through the obtained properties, it was demonstrated that the performance improvement up to about 40% was achieved by ZnO coating on SnSe powders.

**AM-TuP-10 Mechanical Properties of Atomic-Layer-Deposited $Al_2O_3/Y_2O_3$ Nanolaminate Films on Aluminum Towards Protective Coatings**, ***Barbara Putz,*** *J. Niemelä,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *G. Mata-Osoro,* INFICON Ltd., Liechtenstein, Switzerland; *C. Guerra-Nunez,* SwissCluster, Switzerland; *K. Mackosz, I. Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Atomic layer deposition is an appealing deposition technology for the fabrication of protective coatings for various applications, including semiconductor manufacturing chambers and related metallic parts with

complex 3D topographies, where a key requirement is (thermo) mechanical robustness of the coatings. Here we study the mechanical properties of atomic layer deposited $Al_2O_3$, $Y_2O_3$ and their nanolaminate coatings on Al metal substrate. Tensile straining experiments accompanied with in-situ optical and scanning electron microscopy indicate that the fragmentation onset of 100-nm thick coatings can be tailored in the strain range of 1.3 – 2.1 % by controlling the layer structure and composition of the nanolaminates, such that a higher $Al_2O_3$ content, denser layer spacing and amorphisation favor higher crack onset strain. Although the fracture toughness of $Al_2O_3$ and $Y_2O_3$ are found to be similar, $K_{IC}$ = 1.3 MPa·$m^{1/2}$, the (substantially tensile) intrinsic residual stress for $Y_2O_3$ is a disadvantage for applications where tensile applied stresses are to be expected. The films adhere well to the Al substrate as significant delamination of the films is not observed in the tensile experiments; the analysis of the fragmentation patterns indicates that insertion of an $Al_2O_3$ layer at the film/substrate interface can enhance interface toughness. High-temperature (425 °C) tensile experiments for the $Al_2O_3$ films indicate good temperature tolerance for the coatings, and in comparison to the room-temperature data, a significant difference is seen in the increase of saturation crack spacing. Moreover, structure and composition of the films are studied in detail through X-ray reflection and diffraction, transmission electron microscopy, Rutherford backscattering spectrometry, and elastic recoil detection analysis. The results are particularly interesting for protective coating applications.

**AM-TuP-11 How to Improve Control of Plasma-Assisted Ald/Ale Processes by Accurate Measurement of Ion Flux, Ion Energy Distributions, and Ion-Neutral Ratios in Commercial Plasma Tools Using RFEAs***, A. Rawat, C. Linnane,* ***Sean Knott****, T. Gilmore,* Impedans Ltd, Ireland

Plasma assisted ALD/ALE processes have demonstrated potential advantages for next-generation semiconductor processes including high-k, multi-patterning and fin doping. However, with more spatially demanding structures and ever-shrinking device dimensions, the need for controllable and optimized plasma processes has never been greater. To fulfill this need, Impedans automated advanced Retarding Field Energy Analyzers (RFEAs) offers researchers, scientists, and engineers a versatile means to measure the ion energies and ion flux measurements [1, 2] at the substrate position, thereby providing deep insight into what happens at the wafer surfaces. *RFEAs* measure the uniformity of ion energies and ion flux hitting a surface, negative ions, and bias voltage at multiple locations inside a plasma chamber using an array of integrated sensors. A novel RFEA, that combines energy retarding grids with an integrated quartz crystal microbalance (QCM) allows measurements of the ion energy and flux properties as well as the ion-neutral ratio and deposition rate. The ion-neutral ratio is a critical control knob for optimizing film properties. A brief theory of operation will be described.

Measurements reported emphasize how the ion energy distribution of the ions impinging on the wafer can be adjusted with a broad range of plasma processing conditions. The data from various Oxford Instruments tools such as FlexAL, AtomFab, PlasmaPro, PlasmaLab will be presented [3, 4]. Some other major contributions to be showcased in this work include the evidence for low-energy ions influencing plasma-assisted ALD of $SiO_2$ [5], adjustment of the Argon ion energy in controlling an ALE process [6] and the influence of ions and photons during ALD of metal oxides [7] *etc.*, highlighting a few of the many possibilities that exist to gain more control over ALD/ALE processes.

**References**

[1] Impedans Ltd, Dublin, Ireland [www.impedans.com]

[2] S. Sharma *et al.*, Ph.D. Thesis, Dublin City University (2016)

[3] J. Buiter, Master's Thesis, Eindhoven University of Technology (2018)

[4] H. C. M. Knoops *et al.*, J. Vac. Sci. Technol. A 39, 062403 (2021)

[5] K. Arts *et al.*, Appl. Phys. Lett. 117, 031602 (2020)

[6] S. Dallorto, Ph.D. Thesis, Ilmenau University of Technology (2019)

[7] H. B. Profijt *et al*., *ECS Trans.*33 61 (2010)

# Author Index

## Bold page numbers indicate presenter