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

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

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