

## ALD for Manufacturing

### Room Event Hall - Session AM-MoP

#### ALD for Manufacturing Poster Session

**AM-MoP-2 Assessing the Potential of Non-Pyrophoric Zn(DMP)<sub>2</sub> for the Fast Deposition of ZnO Functional Coatings by Spatial Atomic Layer Deposition**, David Muñoz-Rojas, CNRS, France; Liam Johnston, LMGP, France; Jorit Obenluneschloß, RUB, Germany; Anjana Devi, IFW, Dresden, Germany; Daniel Bellet, Grenoble INP, France

Spatial atomic layer deposition (SALD) is a promising thin film deposition technique that enables fast, large-scale deposition and nanoscale thickness control by utilizing spatially separated precursor vapors and a substrate-specimen relative motion, while being feasible in atmospheric pressure conditions. This study explores the use of a non-pyrophoric precursor, Zn(DMP)<sub>2</sub>, in open-air SALD to produce ZnO, and compares the SALD processing speed, and thin film properties, as well as the environmental impact of using this precursor *versus* the more conventional diethylzinc (DEZ), whose pyrophoricity discourages open-air processing. For this purpose, a life cycle analysis (LCA) study was carried out. Our investigation shows that Zn(DMP)<sub>2</sub> open-air SALD can yield ZnO films faster than conventional ALD using DEZ, producing high purity ZnO films with a growth per cycle of 0.7 Å at 180 °C, which corresponds to 184 Å min<sup>-1</sup> maximal growth rate. Emphasizing practical applications, the conformality of the ZnO coating produced around silver nanowire (AgNW) networks by Zn(DMP)<sub>2</sub> open-air SALD and the functionality of these protective coatings has also been demonstrated. The resulting transparent conductive nanocomposites had a substantially improved durability on par with their DEZ-synthesized counterparts.

reference

Assessing the Potential of Non-pyrophoric Zn(DMP)<sub>2</sub> for the Fast Deposition of ZnO Functional Coatings by Spatial Atomic Layer Deposition

Liam Johnston, Jorit Obenluneschloß, Muhammad Farooq Khan Niazi, Matthieu Weber, Clément Lausecker, Laetitia Rapenne, Hervé Roussel, Camilo Velasquez Sanchez, Daniel Bellet, Anjana Devi, David Muñoz-Rojas\*.

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**AM-MoP-3 A Novel Microwave ECR Plasma System for Damage-Free PEALD**, Paul Dreher, Dominik Hartmann, Evatec AG, Switzerland; Julian Pilz, Silicon Austria Labs, Austria; Jörg Patscheider, Evatec AG, Switzerland

While most materials will not suffer radiation damage at ion energies below ~20 eV, some crucial compounds do show deterioration already at lower energies. Examples for ion irradiation-sensitive materials are many group III nitrides such as GaN, InN etc., but also sputter-sensitive oxides, e.g. ITO, MoO<sub>3</sub> and other transition metal oxides, as well as sulfides like MoS<sub>2</sub> and other 2D materials [1] [2]. Microwave-excited plasmas can reach these favorable conditions due to low sheath voltages. Such a microwave-excited electron cyclotron resonance (ECR) plasma has been successfully integrated into a novel plasma-enhanced atomic layer deposition (PEALD) system. In this study, we investigate the electronic and structural properties of the produced Al<sub>2</sub>O<sub>3</sub> and AlN films *in-situ* as well as *ex-situ* with Ellipsometry, AFM, FIB-SEM, XRR and XPS.

*In-situ* diagnostics, including optical emission spectroscopy (OES), residual gas analysis (RGA) and retarding field energy analysis (RFEA) were employed to study the deposition processes of Al<sub>2</sub>O<sub>3</sub> and AlN films. These studies provided central information on precursor decomposition and reaction kinetics during the different process steps, which can be used to optimize the materials properties. At 250°C a growth-per-cycle (GPC) of 1.3 Å/cycle was achieved for alumina films, with thickness non-uniformity below 0.5% on 200 mm silicon wafers (see Fig. 1). The 60 nm thick alumina films have a refractive index of 1.65 at 633 nm (see Fig. 2). XPS measurements showed carbon contents below 1 atomic percent.

In further investigations the influence of substrate biasing with RF power and its influence on the materials roughness and density, as measured with AFM and XRR, were studied. The ion energies and flux were monitored with an RFEA system during the process. As the ion energy in microwave discharges is typically small, the energy range can be modified from a few eV without RF power up to >200 eV ion energy using an RF bias.

The findings show that microwave ECR plasma is indeed a versatile type of plasma source, which can be beneficial for high quality PEALD processes to deposit for damage-free films. The possibility to combine this new PEALD

module in an Evatec cluster system with separate modules for PECVD, sputter deposition and etching opens up new paths to investigate and develop innovative processes and devices.

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**AM-MoP-4 Optimization of the showerhead for Atomic Layer Deposition by Computational Fluid Dynamics**, Seunghoon Lee, Dongkun Song, Gyeongwon Min, Doyoung Jung, Jungeon Park, Jeongmin Han, Dahye Geum, Hyeondo Han, Seungwan Bae, Hyoeun Lee, Guyoung Cho, Dankook University, Republic of Korea

Atomic Layer Deposition (ALD) is widely used in many fields that require high-quality thin films, such as semiconductor and display. These industries also need precise controlled thin film thickness. The ALD generally satisfies these requirements – defect free thin film, impurity free thin film, superior uniformity, angstrom level thickness control and such on. However, the ALD process generally has the disadvantage of slow process speeds and difficulty in controlling the proper process conditions. The superior uniformity and the high-quality thin films which are powerful strong points of ALD are significantly related with the optimized shape of process chamber.

In this study, we focused on improving the uniformity of the deposition by modifying the flow distribution inside the process chamber. Computational fluid dynamics (CFD) was carried out at a fixed working pressure of 1 Torr and a fixed temperature of 250 °C. Gas flows inside the reactor were assumed as the continuum flow during all process steps. Simulations were performed for various showerheads to obtain optimized internal flow distributions. And the optimized showerhead geometry was selected using an approximation method in the commercial program.

For each flow direction obtained, the deposition on Al<sub>2</sub>O<sub>3</sub> was simulated. All simulations were performed under same conditions to check uniformities of Al<sub>2</sub>O<sub>3</sub> thin films. The result allowed us to determine which direction of flow should be changed to improve the uniformity of the thin film. In addition, the distribution of flow and chemical species along with the direction were investigated to confirm the influence of each distribution on the deposition.

#### Acknowledgements

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**AM-MoP-5 Very High Frequency Plasma-Enhanced ALD: System Configuration and Thin Film Property Analysis**, Jae Yeon Han, Hyung Min Kim, Da Eun Bae, Jae Ho Choi, Jae Hack Jeong, CN1 Co., Ltd, Republic of Korea

The atomic layer deposition (ALD) process is required in semiconductor manufacturing due to its advantages, such as high step coverage, atomic-level thickness control, and uniform film deposition. Additionally, a high temperature (>400°C) process is required for high-quality properties when the thermal ALD is used for the deposition of nitride films such as silicon nitride (SiN<sub>x</sub>), aluminum nitride (AlN), titanium nitride (TiN), and tantalum nitride (TaN), leading to active development of the plasma-enhanced ALD (PE-ALD) processes.

However, depositing thin films at high temperatures can cause damage to the substrate. To solve this problem, a technology is needed that can maintain the quality of thin films while reducing damage to the substrate at low temperature. Currently, extensive research is being conducted on very high frequency (VHF) plasma as a method to mitigate damage to the substrate. VHF plasma shows significantly higher plasma density and lower substrate damage at the same plasma power as radio frequency (RF)

We developed a PE-ALD system capable of uniformly applying VHF plasma and analyzed the characteristics of thin films according to plasma frequency. A multi-contact matcher system was applied to the VHF plasma PE-ALD system, enabling the application of plasma from RF to VHF. Additionally, a B-matcher system was implemented in the VHF plasma PE-

ALD system to maintain process reproducibility, as shown in Fig. 1. The silicon nitride (SiN<sub>x</sub>) was deposited using VHF PE-ALD process shown in Fig. 2 at low temperatures ( $\leq 200^\circ\text{C}$ ) and varying the plasma frequency according to the B-matcher position. Thickness and refractive index were measured using ellipsometry. Impurity content was measured through X-ray photoelectron spectroscopy (XPS) depth profiling. Thin film density and interface roughness were measured by X-ray reflectivity (XRR).

## Acknowledgments

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This work was supported by the Korea Institute of Energy Technology Evaluation and Planning(KETEP) and the Ministry of Trade, Industry & Energy(MOTIE) of the Republic of Korea (All-inorganic thermally deposited perovskite solar cells and advanced materials, RS-2023-00236664).

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### AM-MoP-6 Pneumatic Optimization Utilizing Predictive Analytics Within Embedded Systems for Dose Control of Fast Pulsing Valves., *Frank Horvat*, Swagelok Company; *Masroor Malik*, *Benjamin Olechnowicz*, Swagelok

Precision valve timing is a necessary need for proper chemical dosing within the Atomic Layer Deposition (ALD) process. The affect of dosing has a direct influence on the consistency and overall wafer yield in high volume manufacturing. There are various elements within a pneumatic system which if not properly addressed can affect the overall actuation time of a process valve, therefore directly influencing chemical dosing. Investigation into identifying these various elements within a pneumatic system and its overall influence on valve timing is performed. Additionally, research utilizing time based predictive algorithms were employed to specifically designed embedded hardware to allow for the mitigation of these pneumatic inefficiencies. The adaption of an embedded architecture has allowed for seamless integration within pneumatic systems. The use of real time, process information from valves has allowed for improved valve timing, valve to valve repeatability and hence more control of chemical dosing.

### AM-MoP-7 Fast Deposition of High-Quality ALD Materials Using the PlasmaPro ASP System, *Yi Shu*, *Arpita Saha*, *Dmytro Besprozvanny*, *Besprozvanny*, *Michael Powell*, *Powell*, *Agnieszka Kurek*, Oxford Instruments Plasma Technology, UK; *Harm Knoops*, Oxford Instruments Plasma Technology, UK, Eindhoven University of Technology, Netherland, UK

With the fast evolution of device design and fabrication, the ability of manipulating materials and layers at atomic scale has become more important.<sup>1</sup> Due to its ability to deposit high-quality materials layer-by-layer, Atomic Layer Deposition (ALD) has been started to utilise in novel fabrications for the latest applications including CMOS gates,<sup>2</sup> SiC Power,<sup>3</sup> GaN RF and microLEDs<sup>5</sup>. One of the main challenges in integrating ALD processes with these applications is the relatively high cost of development time due to the slow growth rates and long cycle times. This limits R&D cycles to focusing on ALD chemistries that deliver high growth rates or can be thin (<10 nm) for the application, as the time required to deposit the material becomes a significant bottleneck to device development.

To enable ALD techniques for a wider range of applications, it is fundamental to deposit ALD layers at a higher dep rate, whilst maintaining the desired high-quality of the deposited materials. To this end, we have designed an ALD platform, PlasmaPro ASP (PPASP), for research and development customers. The novel remote capacitively coupled plasma (CCP) source and compact chamber design enable fast deposition rates for a variety of ALD chemistries, whilst maintaining control over plasma conditions to deliver low damage.<sup>6,7</sup>

Here, we show how the PPASP can deposit dielectric oxides and nitrides films with significant improvements in deposition rates, whilst maintaining excellent material properties and conformality. We also illustrate the ability to run super-cycles for doping/ternary material deposition. These improvements can therefore enable fast development of ALD processes for devices by rapid comparisons of different recipe conditions, which would open an entire new space for ALD exploration to realise the ambition of utilising ALD across a wider range of devices and research space.

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### AM-MoP-10 XPS Metrology for Area Selective Deposition Applications in Semiconductor Manufacturing, *Kangwon Kim*, *Hyung Keun Yoo*, Samsung Electronics, Republic of Korea; *Heechang Yang*, *Sunho Kim*, Nova Measuring Instruments Korea, Ltd., Republic of Korea; *Wei Ti Lee*, *Torsten Stoll*, Nova Measuring Instruments, Inc.

Propelled by the relentless miniaturization of integrated circuits, area selective deposition (ASD) process has emerged as an important enabling deposition technique in the semiconductor industry. Traditional processing methods are sometimes being hampered by shrinking design rules in 2D features, as well as the challenges of three-dimensional architectural designs. As in every deposition step in the semiconductor manufacturing process, ability to do process control is essential to maintain stability and to maximize yield. Over the past decade, through adoption in high volume manufacturing fabs across the globe, X-ray Photoelectron Spectroscopy (XPS) has established itself as a reliable metrology of choice for ultra-thin films measurements.

In this paper, we will describe the use of XPS as a versatile yet sensitive metrology technique for developing, measuring, and monitoring the ASD deposition process. Due to its specificity to elements or species of interest, and combining with its surface sensitivity, XPS is a powerful metrology for ASD thin film applications. Examples of ASD applications will be presented.

One traditional ASD process is via self-assembled monolayer (SAM), where SAM is selectively adsorbed on the nongrowth area before deposition of the desired material [1]. XPS is shown to be able measure the selectivity of SAM and its effectiveness to enable a defect-free ASD process. Selectivity of SAM is also evaluated as a function of linewidth. Another example is the selective deposition process aiming for a bottom-up growth in trenches or vias. XPS is demonstrated to measure thicknesses of selectively deposited material at the bottom via. Excellent repeatability and consistency of XPS ASD thin film measurements on a full 300mm wafer will also be presented.

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### AM-MoP-12 A Remote Plasma Spectroscopy Diagnostic for Monitoring of Atomic Layer Deposition Processes, *Marcus Law*, Gencoa Ltd., UK

Effective and robust monitoring of individual gas concentrations during ALD processes offer a unique insight into the condition of the process. Analysis of the gaseous environment can be used to assess reaction saturation and help to quickly establish optimum cycle and purge times. In addition, precursor delivery can be monitored and quantification of vacuum quality in terms of leaks and contamination is imperative to achieve optimum and repeatable results.

Conventional quadrupole residual gas analysers have difficulty monitoring ALD processes due to the high process pressures and the presence of contaminating hydrocarbons contained within many ALD precursors. In this work, a compact remote plasma optical emission spectroscopy (RPOES) gas sensor that operates over a wide pressure range (0.5 – 1 E-7 mbar) without filaments or the need for differential pumping was employed, providing robust, fast measurement of gaseous species.

In this contribution, we report on the real-time monitoring of by-product release and precursor consumption determined using this method. Examples of this sensing technique's practical uses for ALD processes are discussed; this includes detection of contaminants, optimising purge cycle length and monitoring the reaction dynamics in terms of precursor gas intake. Furthermore, the use of RPOES for measurement of vacuum quality and leak detection prior to process start is discussed in combination with analysis of ALD reaction dynamics and optimisation and control of the full ALD cycle.

**AM-MoP-13 Early Detection of Process Window Shifts in ALD Processes by PillarHall Lateral High Aspect Ratio Test Structures,** *Jani Karttunen*, Chipmetrics Oy, Finland; *Anish Philip*, Aalto University, Finland; *Jussi Kinnunen*, *Kalle Eskelinen*, **Feng Gao**, *Mikko Utriainen*, Chipmetrics Oy, Finland

The increasing complexity of 3D DRAM and 3D NAND demands precise control over atomic layer deposition (ALD) to ensure high yield and reliability. Ultra-high aspect ratio (AR >100) structures pose challenges for thin film conformality, making early detection of process shifts crucial. ALD tool qualification is particularly complex for ultra-thin dielectric films, widely used in 3D memory channel holes, where process deviations are difficult to detect using blanket monitor wafers, requiring more sensitive qualification methods.

This study evaluates whether the PillarHall® Lateral High Aspect Ratio (LHAR) test chip can serve as a high-sensitivity ALD monitoring tool, capable of detecting precursor decomposition, temperature drift, pressure fluctuations, and other process instabilities before they impact device production.

ALD process evaluations were conducted using PillarHall® LHAR5 test chips (Chipmetrics) with 500 nm and 100 nm gap heights, enabling analysis of cavity aspect ratios >1000. TiO<sub>2</sub> was deposited using titanium isopropoxide (TTIP) and water, while Al<sub>2</sub>O<sub>3</sub> was grown from trimethylaluminum (TMA) with water and ozone. The LHAR method provides film penetration depth profiles, offering direct insight into step coverage and deposition behavior across ultra-high aspect ratio cavities.

To evaluate industrial applicability, LHAR test structures were integrated into FEOL-compatible pocket wafers, allowing wafer-level ALD tool qualification and comparison across different reactor systems.

Our results demonstrate that LHAR test structures effectively detect process deviations across multiple ALD chemistries and tool configurations, proving invaluable for process development, optimization, and industrial tool qualification. Ultra-thin dielectric films in HAR structures require advanced qualification methodologies, as blanket wafers fail to capture critical process shifts.

By integrating LHAR test chips into ALD qualification workflows, fabs and tool manufacturers can benchmark ALD reactors, enhance process control, and accelerate tool qualification, ensuring optimized ALD performance for next-generation semiconductor architectures.

**AM-MoP-15 Process Monitoring via Time-of-Flight Mass Spectrometry based on Isotopic Patterns,** *Hye-Young Kim*, **Sung Kyu Jang**, *Seul-Gi Kim*, *Yoonjeong Shin*, Korea Electronics Technology Institute, Republic of Korea; *Il Hwi Lee*, *Nam Young Kim*, SurplusGLOBAL Inc., Republic of Korea; *Jong Hyun Choi*, *Hyeonkeun Kim*, Korea Electronics Technology Institute, Republic of Korea

Although Time-of-Flight Mass Spectrometry (ToF-MS) is widely used to monitor semiconductor processes such as Atomic Layer Deposition (ALD) and Etching (ALE) in real time, there always remains uncertainty in naming byproducts and their quantities due to a number of candidate chemical compounds with the same masses. This, accordingly, leads to the difficulty in making use of resultant mass spectra for practical applications such as fault detection and classification.

To ensure reliability of ToF-MS analysis, we have devised a method based on isotopic patterns, which mainly consists of the following two steps: constructing basis matrices given stable isotopes and their relative abundances, and finding a non-negative weight vector associated with each basis matrix by solving a Non-Negative Least Squares (NNLS) problem.

To be concrete, at first, basis matrices are roughly formulated by listing chemical elements expected to appear during processes provided materials in use together with process parameters and performing convolution of the distributions of their isotopes. A following filtering, which excludes unreasonable combinations of atoms and singles out representative patterns of atoms, increases confidence in the matrices.

At the next step, an original MS data is split into time intervals to closely track the dynamics of elements in consideration. By solving a series of corresponding NNLS problems, which take the basis matrices and the mass spectra split into time intervals as input, weight vectors at each interval are obtained. It stands to reason that these vectors would coincide with relative composition ratios of chemical compounds and therefore act as indicators to determine process abnormality. The weight vectors are then optimized by taking their statistical properties into account and solving a set of modified NNLS problems. Here, in order to alleviate high

computational demands of dealing with NNLS problems, distributed GPU computing is adopted.

In conclusion, this analysis method for ToF-MS based on isotopic patterns opens up a new and reliable way to deal with ToF-MS data and to monitor semiconductor processes. It is, furthermore, expected to facilitate application of ToF-MS to practical purposes to detect process abnormality or to optimize processes.

**AM-MoP-16 Advancing Fast Spatial Atomic Layer Deposition: Optimizing Precursor Control and Atmospheric Effects for Functional Oxide Thin Films,** *Viet Huong Nguyen*, Faculty of Materials Science and Engineering,

Phenikaa University, Viet Nam; **Hao Van Bui**, Phenikaa University, Viet Nam  
Spatial atomic layer deposition (SALD) has emerged as a powerful technique to achieve high deposition rates while maintaining the atomic precision of conventional ALD. However, challenges persist in controlling unwanted chemical vapor deposition (CVD) contributions and optimizing process parameters for large-scale applications. In this work, a comprehensive study on enhancing control in SALD by tuning precursor diffusion, injection head geometry, and deposition conditions will be presented. Using a combination of experimental data and computational modeling, we elucidate the critical role of precursor exposure and deposition gap on growth kinetics, leveraging insights from ZnO and SnO<sub>2</sub> thin films.<sup>1</sup> A refined injection head design is proposed to mitigate CVD-related issues while maximizing throughput. Furthermore, we investigate the impact of atmospheric pressure on the electrical properties of metal oxide semiconductors,<sup>2-4</sup> and suggest a few strategies to enhance control over growth and functionality for optoelectronic and energy applications.<sup>5</sup>

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