

ALD for Manufacturing

Room Event Hall - Session AM-MoP

ALD for Manufacturing Poster Session

AM-MoP-1 Low-Temperature Atomic Layer Deposition of Silicon Nitride Films Using Space-Division Equipment, Jae-Min Park, Taeho Jeon, Sung-Eun Lee, Hojin Nam, Hyeong Wook Kim, Hyunsik Hwang, Changhee Han, Heonhyeong Lim, Sangjoon Park, WONIK IPS Co., Ltd., Republic of Korea

Silicon nitride (SiN) films have been widely applied in microelectronics, optoelectronics and other fields due to their excellent dielectric properties, chemical inertness and mechanical strength. The increasing demand for low-temperature SiN deposition is driven by the need for reduced thermal budgets in advanced device fabrication. Atomic layer deposition (ALD) offers precise thin film deposition with excellent film quality and uniformity, even at low temperatures. This study investigates low-temperature SiN ALD using CORBIT NITRAD, a space-division equipment capable of rotation and revolution that uses a microwave plasma source. We designed multi-step plasma enhanced atomic layer deposition process using CORBIT NITRAD. The sequence of the multi-step PEALD process consists of the Dichlorosilane feeding step, the H₂/Ar plasma step, the NH₃/Ar plasma step, Thermal NH₃ step and N₂/Ar plasma step. The H radicals in H₂ plasma and NH₃ plasma efficiently remove the ligands from the precursor, and the N₂ plasma removes the surface hydrogen atoms to activate the adsorption of the precursor. This multi-step PEALD approach is a major advantage of space-division ALD system, allowing the deposition of highly uniform, high quality SiN films at low temperatures while maintaining high throughput. The SiN film deposited at 430°C showed a step coverage of about 98% and a growth rate of ~0.7 Å/cycle, and showed excellent wet etching resistance especially in the low sidewall region.

AM-MoP-2 Assessing the Potential of Non-Pyrophoric Zn(DMP)₂ for the Fast Deposition of ZnO Functionalcoatings 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)₂, 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)₂ 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⁻¹ maximal growth rate. Emphasizing practical applications, the conformality of the ZnO coating produced around silver nanowire (AgNW) networks by Zn(DMP)₂ 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)₂ 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*.

RSC Applied Interfaces, 2024, 1, 1371-1381

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, MoO₃ and other transition metal oxides, as well as sulfides like MoS₂ 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 Al₂O₃ 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 Al₂O₃ 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, Seungheon Lee, Dongkun Song, Gyeongwon Min, Doyoung Jung, Jungeon Park, Jeongmin Han, Dahye Geum, Hyeondo Han, Seungwan Bae, Hyeon 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 Al₂O₃ was simulated. All simulations were performed under same conditions to check uniformities of Al₂O₃ 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_x), 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_x) was deposited using VHF PE-ALD process shown in Fig. 2 at low temperatures (≤200°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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AM-MoP-6 Pneumatic Optimization Utilizing Predictive Analytics Within Embedded Systems for Dose Control of Fast Pulsing Valves., Frank Horvat, Swagelok Company

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, 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.¹ 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,² SiC Power,³ GaN RF and microLEDs⁵. 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.^{6,7}

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-8 Non-Destructive Characterization of Alumina Film Thickness and Fractional Coverage Utilizing XPS and StrataPHI Modeling, Amy Ferryman, Norb Biderman, Kateryna Artyushkova, Physical Electronics

Atomic layer deposition (ALD) is widely used due to its precise deposition capabilities, allowing for the creation of very thin, conformal, and high-quality films on the nanometer scale. These films are ideal for applications requiring precise barrier layers, passivation layers, or protective coatings in complex geometries, particularly in microelectronics, sensors, and medical devices. ALD deposition of alumina offers several advantages, including uniform coating on complex 3D structures, precise thickness control, high purity, and suitability for sensitive substrates due to its low deposition temperature. The self-limiting behavior of ALD cycles allows for controllable film growth in which a homogenous film can be achieved at the lowest film thickness. To control the thickness in a range of few nanometers, it is important to understand the interaction between the reactants and substrate during the nucleation period, or the first few cycles. X-ray photoelectron spectroscopy (XPS) is a well-established technique for non-destructive analysis of the chemical composition of thin layers and interfaces. By analyzing a material at varying takeoff angles between the sample and analyzer, angle dependent XPS (ADXPS) can be utilized to probe the thickness and chemical composition of thin films without creating ion beam-induced damage associated with destructive sputter profiling. The spectral results obtained by ADXPS can be furthered evaluated by *StrataPHI*, a software product designed by Physical Electronics, to calculate not only the thickness of thin films but also provide an estimate of fractional coverage, which is of great importance for high-throughput metrology of thin-film structures. This presentation will highlight the benefits of utilizing angle dependent XPS in combination with *StrataPHI* modeling software to non-destructively characterize and simultaneously calculate the layer thickness and fractional coverage of a series of aluminum oxide films deposited on glass substrates throughout the nucleation period by the ALD process.

AM-MoP-9 Optimization of Liquid Fluidization Design for Temperature Control on the Showerhead, Eunsun Jung, Tae S Cho, Eungseo Kim, Bonuk Koo, WONIK IPS, Republic of Korea

Additive manufacturing(AM) is well-suited for creating complex functional parts that cannot be realized through traditional machining technology, and

its applications have been rapidly increasing across various industries. It is expected to play a significant role in enhancing the performance of key components in semiconductor equipment. Specifically, the showerhead, which uniformly sprays process gases onto the wafer surface, requires a highly complex structure to prevent performance degradation caused by structural deformation from heat and uneven temperature. However, due to the limitations of traditional machining processes, its design is constrained. To optimize the showerhead design, we implemented the following structure. The process gas flows through a cylindrical hole inside the showerhead, while a temperature compensation channel is added to the outer wall of the cylinder. A cooling gas or liquid can flow through the multi-stage baffle from a single supply port through nozzles branched out toward the center and outward of the showerhead. For efficient cooling and heat exchange, the gap and shape of the baffles were adjusted, such as circular, elliptical, and curved baffles. The cooling channel was added only to the exact location that need to be cooled. Finite element analysis was performed using Ansys Fluent to analyze the showerhead. A reference endplate was divided into triangular meshes, resulting in an analysis model consisting of a total of 4,467,043 nodes and 25,799,364 elements. To reflect actual process conditions, 630°C radiative heat was applied to the lower part of the endplate, and 155°C radiative heat was applied to the upper part to set the internal surface temperature to 225°C. To analyze the effect of the cooling fluid, Solvay Galden HT 200 fluid provided by Ansys Fluent was used. The physical properties of this fluid are density 1790 kg/m³, specific heat 960 J/(kg·K), thermal conductivity 0.065 W/(m·K), and viscosity 0.0043 kg/(m·s). The inlet temperature of the cooling fluid was fixed at 175°C through a heat exchanger, and the flow rate was changed to 10 LPM, 2 LPM, and 1 LPM, respectively, to analyze the temperature change inside the showerhead. When there was no cooling fluid (reference), the average temperature inside the showerhead was 227.1°C with a range of about 15°C. On the other hand, when the flow was set at 10 LPM, 2 LPM, and 1 LPM, the average temperature decreased to 180.9°C, 180.7°C, and 180.8°C, respectively, with a range reduced to 1.2°C, 4.3°C, and 8.97°C. It was confirmed that the temperature uniformity improved significantly as the flow rate of the cooling fluid increased, as clearly shown in the attached figure.

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, Genco 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. TiO₂ was deposited using titanium isopropoxide (TTIP) and water, while Al₂O₃ 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-14 Optical Monitoring of MoCl₅ and MoOCl₄ Vapor Delivery for Atomic Layer Deposition Applications, Berc Kalanyan, James Maslar, NIST-Gaithersburg

Ultrathin Mo is a candidate material for interconnects in advanced logic and gate metallization in flash memory applications. Hydrogen reduction of molybdenum pentachloride (MoCl₅) is one of several ALD routes for preparing metallic Mo films¹. While MoCl₅ is an attractive precursor, it presents challenges for manufacturing due to its low volatility, its tendency

Monday Evening, June 23, 2025

to form oxychlorides, and self-etching³. Solids are especially problematic for high-volume manufacturing because their delivery characteristics can depend on vessel design, operating conditions, and packaging. Further, volatile oxychlorides are also precursors for film deposition². Therefore, a detailed understanding of MoCl₅ delivery and subsequent deposition behavior requires quantitative metrology to measure the partial pressures and flow rates of MoCl₅ and reactive impurities such as MoOCl₄.

To address this need, we have demonstrated direct absorption measurements in the visible and UV wavelengths to monitor the partial pressures and delivery rates of MoCl₅ and MoOCl₄ under ALD conditions. Using spectral signatures⁴ of MoCl₅ and MoOCl₄, we designed high-speed in-line gas analyzers to simultaneously detect both species during flow. Calculations using the spectral response of the analyzers show detection limits of 0.35 Pa and 0.90 Pa for MoCl₅ and MoOCl₄, respectively⁵. However, spectral overlap between MoCl₅ and MoOCl₄ in the UV wavelengths makes quantitative determination of each species difficult. We have recently expanded upon this work by independently measuring MoOCl₄ species using a non-dispersive IR analyzer installed on the ALD chamber. In addition to the gas analyzers, the measurement system also incorporates a high-speed UV-vis spectrometer to monitor gas phase spectral changes over time.

This presentation will discuss precursor delivery and composition data obtained from both non-dispersive and spectroscopic measurements performed during MoCl₅ injections. We will show that it is possible to simultaneously obtain high-speed quantitative measurements of MoCl₅ and MoOCl₄ partial pressures and flow rates. We will compare the sensitivity and selectivity of different analyzer designs toward MoCl₅ and MoOCl₄. Further, we will apply the measurements to characterize MoCl₅ delivery and MoOCl₄ generation from a small diameter 300 mL vessel and a wider 1.2 L vessel suitable for HVM.

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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, Jong Hyun Choi, Hyeongkeun 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.

ALD for Manufacturing

Room Samda Hall AB - Session AM1-WeA

ALD Equipment I

Moderators: Eun-Hyoung Cho, 2D Device TU(SAIT)/Samsung Electronics, Woo Jae Lee, KNU

1:30pm AM1-WeA-1 Spatial Atomic Layer Deposition of Cu-Based Thin Films, *David Muñoz-Rojas*, CNRS, France **INVITED**

Spatial Atomic Layer Deposition (SALD) is an emerging variant of ALD that enables rapid processing, even at atmospheric pressure, while retaining the key advantages of ALD: precise nanometer-scale thickness control, high-quality films at low temperatures, and exceptional conformality. These features make SALD particularly well-suited for high-throughput, cost-effective applications, such as next-generation photovoltaics, LEDs, and packaging.

A key strength of SALD, especially when utilizing close-proximity deposition heads, lies in its versatility. The design of these deposition heads can be easily customized, and since the process takes place in open air, no deposition chamber is required, further simplifying scalability.

To fully leverage the benefits of SALD, however, new processes must be developed to deposit functional materials with optimized properties using mild conditions and stable precursors. In this talk, I will introduce our close-proximity SALD approach and highlight our recent work in developing innovative SALD processes. Specifically, I will present a novel SALD method for depositing Cu₂O thin films with record-high transport properties, achieved despite low-temperature processing. I will also explore the critical role of precursors and process conditions in determining the final film properties. Lastly, I will demonstrate that, even in an open-air environment, it is possible to selectively deposit Cu, Cu₂O, or CuO from the same precursor simply by adjusting the coreactant.

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

L. Johnston, et al. *RSC Applied Interfaces*, 2024, 1, 1371-1381

2:00pm AM1-WeA-3 Visualization of Precursor Transport in Vapor Deposition Systems: Measurements and Simulations, *James Maslar, Vladimir Khromchenko, Berc Kalanyan*, NIST-Gaithersburg

Advanced models for semiconductor fabrication unit processes are needed for improved process control, defect reduction, and ultimately yield improvement. Development of such models is limited by a general lack of non-proprietary process data. The goal of this work is to aid in vapor deposition process model development by 1) generating measurement data sets and 2) evaluating the utility of these data sets by using them to validate simulations of precursor flow in our ALD chambers. Central to achieving this goal is absorption imaging of precursor flow as a function of process conditions, e.g., gas flow rate, chamber pressure, and temperature. Two precursors were selected for investigation: molybdenum pentachloride (MoCl₅) and tetrakis(dimethylamido)titanium (TDMAT). MoCl₅ flow was visualized at about 100 images per second in the ultraviolet-visible spectral region using a 7.1-megapixel complementary metal oxide semiconductor camera and a light emitting diode source. TDMAT flow was visualized at about 30 images per second in the mid-infrared spectral region using an

uncooled microbolometer thermal imaging camera and a blackbody source. Simulations of flow in this chamber were performed using a commercial computational fluid dynamics (CFD) package. CFD simulations of low-volatility precursors in a carrier gas are simplified since the precursor is dilute and the gas properties are that of the carrier gas, properties that are well known for typical deposition conditions. Simulations were validated using the time-dependent, pathlength-integrated precursor concentration obtained from the absorption imaging measurements and the time-dependent total pressure measured at selected locations in the deposition system. In this talk, aspects of both the measurements and simulations will be discussed, including the choice of parameters included in the data set.

2:15pm AM1-WeA-4 Atomic Layer Deposition on Highly Cohesive Granular Material in Fluidized Beds, *Rens Kamphorst*, Delft University of Technology, Netherlands; *Kaiqiao Wu*, Delft University of Technology, China; *Saeed Saedy, Gabrie M.H. Meesters, J. Ruud van Ommen*, Delft University of Technology, Netherlands

Atomic layer deposition (ALD) on granular materials is gaining increasing attention due to its potential applications in pharmaceuticals, nanocatalysts, and colloidal stabilization. Powders with smaller particle sizes have higher specific surface areas, which can be utilized, however, they pose significant challenges for processing, especially when particle sizes are <30µm. At these scales, van der Waals forces dominate making particles cohesive. In conventional fluidized beds, ALD is challenged by precursor gas escaping via cracks in the powder bed, having little interaction with the particles. Furthermore, particle clusters appear frequently, resulting in parts of individual particles being inaccessible to be coated, leading to non-uniform deposition. These complications necessitate dedicated systems that can overcome the inherent cohesiveness of such powders.

In our work, we set out to coat cohesive particles in an ALD fluidized bed reactor. We employed X-ray imaging to evaluate methods for improving fluidization of cohesive powders, including mechanical vibration, pulsed flow, and mechanical agitation. These methods are designed to break up structures within the powder, improving gas-solid interaction.

Our findings demonstrate that assistance methods initiate smooth fluidization, significantly enhancing gas-solid contact. We visualize the dynamics within powder beds subjected to various assistance methods and propose scalable methods to fluidize cohesive powders in order to perform ALD. We also show successful deposition of SiO₂ layers on otherwise unfluidizable particles. These results open pathways for functionalizing fine powders for advanced technological applications.

2:30pm AM1-WeA-5 From the Research Lab to the Fab: Comparison of Vapor Generation by Bubbler and Direct Liquid Injection Vapor Delivery Systems, *David Curran*, 5910 Rice Creek Parkway Suite 300

As the semiconductor industry is moving to smaller nodes, the need for high-quality and high-throughput vapor delivery is paramount. As the geometry and structures of the depositions evolve, research institutions and chemical manufacturers are developing new precursors offering superior reaction mechanisms for selective surface depositions and other difficult reactions. Initial testing of these precursors in chemical vapor deposition or atomic layer deposition processes are typically conducted by supplying the vapor by means of a bubbler or a flow over vessel. Bubblers in conjunction with a downstream ALD valve can be a straightforward solution; however mass delivery accuracy, adjustability and stability are known issues, which can create thin film irregularity and wafer-to-wafer variability. Additionally, if precursors are thermally sensitive, there can be issues with the liquid decaying in the heated ampoule over time leading to long deposition times and/or wasted material. To meet the industry needs, a solution is needed to improve vapor delivery to scale up from development to production.

Direct liquid injection (DLI) vaporizing systems present an attractive solution to the scale-up problem. DLI systems allow the throughput of the vapor delivery system to be increased by generating nanometer to micron sized droplets of the precursors, improving the heat transfer to the liquid. Coupled with a liquid flow controller, DLI systems can provide fast, high-throughput, consistent, known concentrations of vapor to deposition chambers.

The work presented in this presentation will directly compare the vapor concentration and quality delivered by a bubbler and a DLI vaporizer for several difficult to vaporize precursors. To compare the delivery systems, a method using Fourier Transform Infrared (FTIR) spectroscopy to conduct real-time measurement of vapor concentration and droplet content of the vapor stream will be employed. This presentation will briefly detail

Wednesday Afternoon, June 25, 2025

hardware and experimental setup used, key control criteria, and advantages and disadvantages will be discussed.

2:45pm AM1-WeA-6 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, Hanoi 12116, Viet Nam., 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 SnO₂ thin films.¹ 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,²⁻⁴ and suggest a few strategies to enhance control over growth and functionality for optoelectronic and energy applications.⁵

1T. T. Nguyen, D. Nguyen Thi Kieu, H. V. Bui, L. Le Thi Ngoc and V. H. Nguyen, *Nanotechnology*, 2024, 35, 205601.2H. T. T. My, N. L. Nguyen, T. K. Mac, D. A. Duong, T. T. Nguyen, A.-T. Duong, H. V. Bui and V. H. Nguyen, *Journal of Physics D: Applied Physics*, 2023, 57, 025303.3V. H. Nguyen, U. Gottlieb, A. Valla, D. Muñoz, D. Bellet and D. Muñoz-Rojas, *Materials Horizons*, 2018, 5, 715–726.4V. H. Nguyen, H. T. T. My, H. T. T. Ta, K. A. Vuong, H. H. Nguyen, T. T. Nguyen, N. L. Nguyen and H. V. Bui, *Adv. Nat. Sci. Nanosci. Nanotechnol.*, 2023, 14, 045008.5H.-A. Tran Vu, D.-T. Pham, H. Tran Thi My, D. A. Duong, A. H. Alshehri, V. T. Tran, T. M. H. Nguyen, D. Pham-Cong and V. H. Nguyen, *Dalton Transactions*, 2025, 10.1039.D4DT02689F

3:00pm AM1-WeA-7 High Deposition Rate TiO PEALD Process for Semiconductor Industry, Sungbae Kim, Yeahyun Gu, Hyunchul Kim, Hyungjoo Shin, ASM, Republic of Korea

TiO thin films are increasingly used in the semiconductor industry due to their excellent physical and chemical properties. Due to their high etching selectivity for the Si base materials and pattern fidelity, they have been mainly used for patterning applications such as hard-mask and spacers. Recently, however, due to the material's unique optical property (High Refractive Index (R.I.) value >2.3 at 633nm), the application area has been expanded to others such as ARL (Anti-Reflection Layer) and CIS (CMOS Image Sensor) Meta-lens. As such applications often require a thicker material than patterning films, a higher deposition rate is accordingly desirable for commercially viable productivity.

In this paper, a new process sequence was developed to increase the deposition rate while keeping the most of benefits of PEALD including film quality, uniformity, and gap fill capability. The thin film properties were characterized and compared with those of the conventional ALD process. TDMAT was used as the Ti precursor. O₂ plasma was used as the reactant to grow TiO. 27.12MHz-rf source was used to generate a CCP in a commercial PEALD chamber by ASM (QCM TiO XS).

In the case of conventional ALD, there is a limitation in terms of the deposition rate even with the increasing supply of precursor due to the nature of self-limiting reaction phenomenon in PEALD. To overcome this self-limiting reaction, a low-power pulsed-plasma CVD step was introduced in a typical PEALD process cycle. (Figure1.) The new process sequence promotes the film growth by balancing the conformal deposition and the surface treatment. By this means, the new deposition rate increased to 0.94Å/sec by nearly three times compared to conventional ALD (0.34Å/sec). The results of the film deposited on a 12-inch bare Si wafer by the new process shows both uniformity and R.I. are at similar levels as the ones with conventional slow PEALD. In addition, we confirmed the step coverage is more than 80% in the pattern of open CD 90nm with aspect ratio of 3. XPS analysis also shows that the impurity concentrations of 'C' and 'N' were as low as below 2%, which is comparable to conventional PEALD process.

The high deposition rate TiO PEALD process is expected to be applicable to any new emerging applications which requires TiO's PEALD quality yet with higher deposition rate. The ASM's hardware technology enables this new process sequence for a novel PEALD.

3:15pm AM1-WeA-8 Spatial ALD Deposited Functional Layers for Large-Area Inverted Perovskite Solar Modules, Xuwei Jiang, Huazhong University of Science and Technology, China; *Fan Yang*, Luoyu Road 1037, Wuhan, China; *Bin Shan, Rong Chen*, Huazhong University of Science and Technology, China

Perovskite solar cells (PSCs) are a promising candidate for large-scale commercialization, with efficiency and scalability as key factors. However, fabrication of large-area functional thin films including electron transport layers (ETLs), hole transport layers (HTLs) as well transparent conductive electrode, becomes one of the biggest obstacles for the commercial PSCs applications. This study explores low temperature SALD deposited SnO₂ ETL and aluminum-doped zinc oxide (AZO) as transparent conductive oxide electrodes to improve the performance of PSCs modules. By controlling oxygen vacancies through precursor reactivity, we achieved a high mobility of 19.4 cm²/V·s in SnO₂ ETL (deposited at 100 °C) and ultra low sheet resistance to 3.6 Ω/sq for AZO electrode, surpassing commercial FTO (8 Ω/sq). Additionally, textured AZO electrodes, exhibited excellent optical properties with a haze of over 55% and an average transmittance of approximately 90%. Due to the advantages of SALD, the thin films demonstrated good uniformity with only 2.8% nonuniformity in film thickness and 4.6% in sheet resistance over a 400 cm² area. For the 400 cm² PSMs with AZO electrodes achieve a PCE of 20.5% and retain 87% of their initial efficiency after 600 hours of continuous illumination. This exceptional performance stems from the excellent uniformity and mobility of the SALD-deposited SnO₂ ETL and AZO electrode, highlighting the potential of SALD in future PSM fabrication.

References

1. Scalable Deposition of SnO₂ ETL via SALD for Large-Area Inverted Perovskite Solar Cells. Xuwei Jiang, Bin Shan, Geng Ma, Yan Xu, Xing Yang, Wenbin Zhou, Chenhui Li, Fan Yang, and Rong Chen, *Chem. Eng. J. Accepted*.

ALD for Manufacturing

Room Samda Hall AB - Session AM2-WeA

ALD Equipment II

Moderators: Tae Wook Nam, Sejong University, **Bonggeun Shong**, Hongik University

4:00pm AM2-WeA-11 Spatial Atomic Layer Deposition of Nanolaminate Barrier Coatings Enables Sustainable Packaging, Denys Vidish, University of Waterloo, Canada; *Soumyadeep Saha, Louis Delumeau, Tristan Grovu*, Nfinite Nanotechnology Inc., Canada; *Kevin Musselman*, University of Waterloo, Canada

Plastic waste poses a worldwide challenge because of its detrimental effects on the environment, society, and economy. Flexible packaging materials are being used with different types of single-use plastics. To address their harmful impact on the environment, the packaging industry has been trying to move towards compostable polymer materials such as polylactic acid (PLA). However, these compostable polymers don't provide a sufficient gas-diffusion barrier to protect the product from water vapor and oxygen. For that reason, applying vapor-barrier coatings onto packaging materials is necessary to protect the product. However, most traditional barrier coatings don't perform well on PLA and/or compromise the composability of the packaging. In this work, we introduce nanolaminate barrier coatings for flexible, sustainable packaging materials that are based on alternating nanoscale layers of aluminum oxide (Al₂O₃) and zinc oxide (ZnO). These nanolaminates were deposited using an atmospheric-pressure spatial atomic layer deposition (AP-SALD) system, which is a scalable technique that is compatible with roll-to-roll manufacturing. We show that the water-vapor transmission rate (WVTR) and oxygen-transmission rate (OTR) of PLA and PET films are significantly improved after coating them with nanolaminates and that the performance of the nanolaminates is superior to single-layer barrier coatings. We note that the thickness of nanolaminate layers directly correlates with the improvement in barrier performance until an optimal value is reached. Moreover, we demonstrate that the nanolaminates are much more resistant to cracking under stress than single-layer coatings. They maintain their barrier properties (low WVTR and OTR) after bending and Gelbo flex tests, which is crucial for flexible packaging materials. As a result, we demonstrate nanolaminate coatings deposited via AP-SALD that are very promising for improving the barrier properties of biodegradable materials for the flexible packaging industry.

Wednesday Afternoon, June 25, 2025

4:15pm **AM2-WeA-12 Advancing Atomic Layer Processing for Next Generation Devices: Atlant 3d'S Direct Atomic Layer Processing (Dalp™)**, *Mira Baraket*, ATLANT 3D Nanosystems, Denmark

As the demand for miniaturized and complex devices accelerates across industries, innovative and precise atomic layer advanced manufacturing techniques have become critical. ATLANT 3D's proprietary Direct Atomic Layer Processing (DALP™) technology is redefining thin-film processing by enabling spatially localized, atomically precise material growth with unmatched flexibility. Building upon Atomic Layer Deposition, DALP™ confines gas flows to a micrometer-scale area using advanced microreactors, enabling deposition of diverse materials on complex geometries and substrates with exceptional thickness control and conformality on complex structures.

DALP™ technology tackles key challenges in accelerating innovation within thin-film manufacturing. It enables rapid prototyping by allowing localized, multi-thickness depositions of diverse materials on a single wafer, significantly cutting prototyping timelines from months to hours compared to conventional methods. These capabilities have been demonstrated across diverse applications, including optics and photonics, MEMS, RF electronics, emerging memory technologies, advanced packaging, and energy storage.

This talk will explore ATLANT 3D's advancements in DALP™ technology, focusing on expanded material compatibility, enhanced resolution, and new opportunities it creates for thin-film processing. We will demonstrate how DALP™ technology drives innovation by enabling the fabrication of complete, functional devices. Through case studies, we will highlight how our advanced processing technique have been used to produce components and electronic devices. These examples illustrate how ATLANT 3D's platform not only improves material deposition processes but also revolutionizes prototyping and manufacturing, empowering industries to achieve faster and more efficient innovation.

4:30pm **AM2-WeA-13 Analysis of Controllable Coil Patterns to Improve Temperature Uniformity of Inducted-Heated Susceptor**, *Jihyun Kim, Hakmin Kim, Kwangson Jin, Tae S. Cho*, Wonik IPS, Republic of Korea

To uniform the temperature of wafers and to get higher temperature faster and more efficiently is desired in the semiconductor manufacturing processes such as metalorganic chemical vapor deposition (MOCVD) growth system¹. Induction heating is an alternative technology that provides fast and high temperature heating. In the process of induction heating, the susceptor remains free of physical contact with the work coil or inductor. Nevertheless, the temperature distribution of the wafer on the susceptor is uneven and challenging to manage with a single coil induction heating method, owing to the skin effect of the induced current in the susceptor². The temperature uniformity of induced-heat susceptor was hence investigated with various working coil patterns for induction heating system by ANSYS Maxwell 3D modelling and simulating. The working coil could be divided into a number of multi-turns or multi-layer coils or multi-zone. Then the material of susceptor was graphite with 5mm of thickness and 300mm of diameter. A travelling wave magnetic field was used to induce eddy current in the graphite susceptor. In order to generate the temperature uniformity of graphite susceptor, the phase angle between the currents differ by $\pi/2$ or $\pi/4$, the input current changes from 10A to 30A, and the input frequency varies from 20kHz to 60kHz. The simulation results showed that the temperature distribution of the susceptor was still not uniform with the single layer and multi-layer with the single zone due to the skin effect and heat conductor in the conventional susceptor. However, the temperature uniformity of the susceptor can be greatly improved by dividing several zones of the coil with different input currents and phases with same frequency. That is the temperature uniformity is improved with the multi-zone with multi-layer coil when the currents and phases of each zone are different. Higher temperature and faster heating rate can be obtained by increasing heating frequency and input current, but the lower and higher frequency can bring worse temperature uniformity. The higher magnetic field over the wafer that can affect to the semiconductor process can also be induced with increasing higher frequency and input current. Therefore, selecting the appropriate frequency and input current for the semiconductor manufacturing processes is essential. To enhance the uniformity of temperature in the graphite susceptor to the desired level, it is necessary to identify the appropriate number of coils turns and input current for each zone, as well as the phase difference between the applied currents.

4:45pm **AM2-WeA-14 Closing Remarks and Awards in Tamna Hall A**,

Author Index

Bold page numbers indicate presenter

— A —

Artyushkova, Kateryna: AM-MoP-8, 2

— B —

Bae, Da Eun: AM-MoP-5, 2

Bae, Seungwan: AM-MoP-4, 1

Baraket, Mira: AM2-WeA-12, 7

Bellet, Daniel: AM-MoP-2, 1

Besprozvanny, Dmytro Besprozvanny: AM-MoP-7, 2

Biderman, Norb: AM-MoP-8, 2

— C —

Chen, Rong: AM1-WeA-8, 6

Cho, Guyoung: AM-MoP-4, 1

Cho, Tae S: AM-MoP-9, 2

Cho, Tae S.: AM2-WeA-13, 7

Choi, Jae Ho: AM-MoP-5, 2

Choi, Jong Hyun: AM-MoP-15, 4

Curran, David: AM1-WeA-5, 5

— D —

Delumeau, Louis: AM2-WeA-11, 6

Devi, Anjana: AM-MoP-2, 1

Dreher, Paul: AM-MoP-3, 1

— E —

Eskelinen, Kalle: AM-MoP-13, 3

— F —

Ferryman, Amy: AM-MoP-8, 2

— G —

Gao, Feng: AM-MoP-13, 3

Geum, Dahye: AM-MoP-4, 1

Grovu, Tristan: AM2-WeA-11, 6

Gu, Yeahyun: AM1-WeA-7, 6

— H —

Han, Changhee: AM-MoP-1, 1

Han, Hyeondo: AM-MoP-4, 1

Han, Jae Yeon: AM-MoP-5, 2

Han, Jeongmin: AM-MoP-4, 1

Hartmann, Dominik: AM-MoP-3, 1

Horvat, Frank: AM-MoP-6, 2

Hwang, Hyunsik: AM-MoP-1, 1

— J —

Jang, Sung Kyu: AM-MoP-15, 4

Jeon, Taeho: AM-MoP-1, 1

Jeong, Jae Hack: AM-MoP-5, 2

Jiang, Xuwei: AM1-WeA-8, 6

Jin, Kwangson: AM2-WeA-13, 7

Johnston, Liam: AM-MoP-2, 1

Jung, Doyoung: AM-MoP-4, 1

Jung, Eunsun: AM-MoP-9, 2

— K —

Kalanyan, Berc: AM1-WeA-3, 5; AM-MoP-14, 3

Kamphorst, Rens: AM1-WeA-4, 5

Karttunen, Jani: AM-MoP-13, 3

Khromchenko, Vladimir: AM1-WeA-3, 5

Kim, Eungseo: AM-MoP-9, 2

Kim, Hakmin: AM2-WeA-13, 7

Kim, Hyeong Wook: AM-MoP-1, 1

Kim, Hyeongkeun: AM-MoP-15, 4

Kim, Hye-Young: AM-MoP-15, 4

Kim, Hyunchul: AM1-WeA-7, 6

Kim, Hyung Min: AM-MoP-5, 2

Kim, Jihyun: AM2-WeA-13, 7

Kim, Kangwon: AM-MoP-10, 3

Kim, Seul-Gi: AM-MoP-15, 4

Kim, Sungbae: AM1-WeA-7, 6

Kim, Sunho: AM-MoP-10, 3

Kinnunen, Jussi: AM-MoP-13, 3

Knoops, Harm: AM-MoP-7, 2

Koo, Bonuk: AM-MoP-9, 2

Kurek, Agnieszka: AM-MoP-7, 2

— L —

Law, Marcus: AM-MoP-12, 3

Lee, Hyeon: AM-MoP-4, 1

Lee, Seungheon: AM-MoP-4, 1

Lee, Sung-Eun: AM-MoP-1, 1

Lee, Wei Ti: AM-MoP-10, 3

Lim, Heonhyeong: AM-MoP-1, 1

— M —

Maslar, James: AM1-WeA-3, 5; AM-MoP-14, 3

Meesters, Gabrie M.H.: AM1-WeA-4, 5

Min, Gyeongwon: AM-MoP-4, 1

Muñoz-Rojas, David: AM1-WeA-1, 5; AM-MoP-2, 1

Musselman, Kevin: AM2-WeA-11, 6

— N —

Nam, Hojin: AM-MoP-1, 1

Nguyen, Viet Huong: AM1-WeA-6, 6

— O —

Obenlűneschloű, Jorit: AM-MoP-2, 1

— P —

Park, Jae-Min: AM-MoP-1, 1

Park, Jungeon: AM-MoP-4, 1

Park, Sangjoon: AM-MoP-1, 1

Patscheider, Jűrg: AM-MoP-3, 1

Philip, Anish: AM-MoP-13, 3

Pilz, Julian: AM-MoP-3, 1

Powell, Michael Powell: AM-MoP-7, 2

— S —

Saedy, Saeed: AM1-WeA-4, 5

Saha, Arpita: AM-MoP-7, 2

Saha, Soumyadeep: AM2-WeA-11, 6

Shan, Bin: AM1-WeA-8, 6

Shin, Hyungjoo: AM1-WeA-7, 6

Shin, Yoonjeong: AM-MoP-15, 4

Shu, Yi: AM-MoP-7, 2

Song, Dongkun: AM-MoP-4, 1

Stoll, Torsten: AM-MoP-10, 3

— U —

Utriainen, Mikko: AM-MoP-13, 3

— V —

van Ommen, J. Ruud: AM1-WeA-4, 5

Vidish, Denys: AM2-WeA-11, 6

— W —

Wu, Kaiqiao: AM1-WeA-4, 5

— Y —

Yang, Fan: AM1-WeA-8, 6

Yang, Heechang: AM-MoP-10, 3

Yoo, Hyung Keun: AM-MoP-10, 3