

## ALD for Manufacturing

### Room Hall 3 - Session AM-MoP

#### ALD for Manufacturing Poster Session

**AM-MoP-1 Thin-Film-Transistor Based ALD Sensors**, *K. Yamano, H. Takeda, R. Miyazawa, M. Miura, B. Ahmad, Fumihiko Hirose*, Graduate School of Science and Engineering, Yamagata University, Japan

In-situ monitoring of the ALD process, especially the surface reaction, is important to achieve the optimal condition in the ALD process. In our laboratory, the nanothick TiO<sub>2</sub> channel thin film transistor was developed for UV and gas sensing, where the adsorbed species affected the channel conductance. In the present study, the nanothick TFT was examined for monitoring the surface chemical reaction in the RT atomic layer deposition.

Fig. 1 shows the TiO<sub>2</sub> TFT used for the monitoring. The channel layer was an anatase TiO<sub>2</sub> film which was deposited on a SiO<sub>2</sub>-stacked Si (100) substrate by atomic layer deposition followed by the post-annealing at 500 °C. The Si substrate was heavily doped with antimony to serve as the gate electrode. The SiO<sub>2</sub> layer as the gate capacitor was as thick as 300 nm. The Ti electrodes as drain and source were fabricated on the channel. The gate length and width were 60 and 1000 μm, respectively. The TiO<sub>2</sub> TFT was placed in the room-temperature atomic layer deposition (RT-ALD) chamber as shown in Fig.2. The gate voltage was 0 V while the drain voltage was 20 V during the measurement. In the RT-ALD, we used tetrakis(dimethyl)amido titanium (TDMAT) and plasma-excited humidified argon. The TDMAT pressure was 0.8 Pa and the flow rate of the plasma-excited humidified argon was 5 sccm. The temperature of the reaction chamber was set at RT (22 °C).

During the RTALD process, the drain current waveform was monitored as shown in Fig. 3. The drain current (*I<sub>d</sub>*) was changed cyclically according to the ALD process. In the oxidization step by the plasma-excited humidified Ar, the drain current surged up sharply and then decreased to equilibrium. In the pumping step, the drain current continued to decrease. In the adsorption step of TDMAT, the drain current increased slightly at first and then decreased. Although we have not fully understood the mechanism, we still consider that the surface oxidation and OH densities might affect the drain current. In the oxidization step, the surge-up might result from the initial oxidization of TDMAT, and the surface was covered with OH moieties. In the next pumping step, a certain amount of OH moieties might desorb from the surface as H<sub>2</sub>O, leading to the decrease of *I<sub>d</sub>*. In the TDMAT process, the TDMAT adsorbed on the surface to consume the OH moieties, which caused the decrease of the current. The strong modulation in the oxidizing step suggests that the change in the OH density is correlated with the drain current. We believe that the present TFT sensor can be used for the monitoring of the oxidizing species

**AM-MoP-2 Accurate and Fast Wafer Level Conformality Analysis Method for ALD Films in Manufacturing**, *Thomas Werner*, Chipmetrics OY, Germany; *M. Zaheer, J. Kinnunen, A. Philip*, Chipmetrics OY, Finland; *K. Kühnel, N. Haufe*, Fraunhofer IPMS, Germany

The 3D megatrend and miniaturization of devices in microelectronics has made both high-aspect ratio (HAR) features and conformal coating inevitable in today's semiconductor industry. The extensive list of semiconductor devices relying on HAR structures for their optimal application underscores the critical need for conformality assessment tools. The PillarHall® lateral high aspect ratio (LHAR) test structures stand out as unique measurement test vehicles for the conformality characterization of thin film coating processes<sup>1</sup>. They facilitate accurate and repeatable film penetration depth (PD) profile measurements aiding in the prediction and quantification of step coverage across various high aspect ratio structures. Here in the current research, we demonstrate the significant value of these LHAR test chips in assessing the wafer scale conformality. This knowledge is very crucial for tools aiming conformality on 200- or 300-mm wafers. In our approach, we placed 10 LHAR chips on a 200 mm wafer and aimed for 20 nm thick Al<sub>2</sub>O<sub>3</sub> (TMA+H<sub>2</sub>O thermal ALD) deposition in a crossflow reactor. Our results indicate in some extent the influence of precursor inlet and outlet location in the ALD reaction chamber on both film penetration depth and film thickness of the studied Al<sub>2</sub>O<sub>3</sub>. Apparently conformality variations on different wafer positions that can at least partially be related to the flow dynamics of the crossflow reactor. Furthermore, conformality can depend also on the presence of competing reaction mechanisms and kinetics in the high aspect ratio cavity and cavity opening area which can be derived from the location specific film penetration depth profiles (Fig. 1). Current

research also focused on the industry compatible chip assembly on 300 mm pocket wafers. Contamination data from the 300 mm pocket wafer with chips are shown to demonstrate the compatibility of this approach for the FEOL applications. The study showed that PillarHall pocket wafers provide accurate information of the conformality as well as film growth mechanisms through the film penetration depth profiles in the different positions on the wafer and can be valuable tool in ALD process control and monitoring as well as tool qualification.

#### References

1. J. Yim and O. M. E. Ylivaara et al., Phys. Chem. Chem. Phys., 22 (2020), 23107

**AM-MoP-3 In-Situ Gas Monitoring of ALD Processes Using Remote Optical Emission Spectroscopy**, *Erik Cox, J. Brindley*, Gencoa, UK; *D. Monaghan*, Gencoa

Effective and robust monitoring of individual gas concentrations during the ALD processes offer a unique insight into the process behaviour as well as being an important step in the eventual wide-spread industrialisation of the ALD technique.

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. For these reasons monitoring of precursor gas concentrations during the ALD process is not often undertaken, especially at the production stage.

An alternative gas sensing technique that operates directly at pressures above 10<sup>-4</sup> mbar has been built around remote plasma emission monitoring. This technique involves the generation of a small, remote plasma using an inverted magnetron placed within the ALD vacuum system. Consequently, species that are present within the vacuum become excited in the sensor's plasma, emitting a spectrum of light, which can then be used to identify and monitor the emitting species. Importantly, this plasma, generated inside the sensor, has a sole function as a gas detector and does not affect the ALD process itself.

This work will demonstrate that the sensing method is robust when exposed to the ALD processing environment. Previous work had demonstrated the usefulness of this technique, but limitations were encountered when using a DC voltage to generate the sensor's plasma as contamination and reduced sensitivity developed when used with certain precursors. This work will describe a novel method of generating the detector plasma using a high peak power, low duty cycle pulsed voltage. It will be demonstrated that the pulsed power technique is more effective than DC in preventing contamination of the sensor's electrodes as well as improving the detection sensitivity of common ALD precursors and their reaction by-products.

Examples of this sensing technique's practical uses for Al<sub>2</sub>O<sub>3</sub> processes are discussed; this includes detection of contaminants, optimising purge cycle length and monitoring the reaction dynamics in terms of precursor gas consumption and reaction by-products.

**AM-MoP-4 Batch Coating of Gas Lines by Atomic Layer Deposition**, *Lassi Leppilähti, D. Nevstrueva*, Beneq, Finland

Gas lines in highly sensitive application e.g. in the process equipment in the semiconductor industry are typically made of stainless steel. They can be susceptible to corrosion from process gases such as ammonia or hydrogen fluoride. ALD coatings are excellent as protective coatings due to their high density and defect-free nature.

In this presentation an ALD solution for batch coating of gas lines is discussed. A special setup for coating gas lines was designed for the Beneq P800 system. In this setup the typical box-shaped reaction chamber was replaced with two manifolds splitting the gas feed into 30 parallel lines. These parallel lines could then accommodate series of gas lines substrates with total end to end length of 1 m.

30 pieces of straight 1 m long gas lines were coated with Al<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> to demonstrate the capability of the system. Film thickness and uniformity were monitored on silicon coupons placed inside the manifolds. Al<sub>2</sub>O<sub>3</sub> was deposited from trimethylaluminium (TMA) and water. 52 nm film was grown with 1.04 Å/c growth per cycle and 4.7 % relative standard deviation. Y<sub>2</sub>O<sub>3</sub> was deposited from tris(methylcyclopentadienyl)yttrium and water. 270 nm film was grown with 1.48 Å/c growth per cycle and 5.8 % relative standard deviation.

# Monday Evening, August 5, 2024

**AM-MoP-5 Implementing of ALD in Post-CMOS-Compatible 200 Mm Wafer Processes, Rahel-Manuela Neubieser, M. Michel, A. Litke, N. Boysen, Fraunhofer IMS, Germany; A. Devi, Ruhr Universität Bochum, Germany**

The successful implementation of new ALD materials in standard 200 mm wafer fabrication processes poses challenges, particularly concerning post-processing stability of (semi-)conductive materials. This study addresses the critical issue of ensuring the stability of thin layers during post-processing steps such as patterning, chemical etching, and resist removal. Since ALD as a process is primarily predestined for thin layers consisting of a few monolayers, the influence of further process steps must be evaluated all the more critically due to the high surface to layer thickness ratio. For instance, ion beam etching processes can lead to photoresist cross-linking, requiring plasma ashing of the resist. Additionally, chemical selective etching may result in underetching of the photoresist, leading to alterations in critical dimensions as well as typical cleaning processes may attack the sensitive layers. The specific focus of this work is on the post-processing of MoS<sub>2</sub>, a semi-conductive material, deposited by ALD at low temperatures (T = 100 °C) for gas sensing applications. To assess its stability and suitability for industrial high-volume processes, the sheet resistance of the MoS<sub>2</sub> layer is measured before and after typical post-processing steps. By analyzing the sheet resistance of the MoS<sub>2</sub> layer, valuable insights can be gained regarding its stability against further processing steps in semiconductor manufacturing. These insights are crucial for assessing the feasibility of integrating MoS<sub>2</sub> and similar ALD materials into industrial-scale processes.

**AM-MoP-6 Optimization and Scale-Up of MgO Thin Film Production via Thermal Atomic Layer Deposition for Industrial Applications, Muhammad Ahmad, N. Lamminmäki, E. Manninen, P. Kaur, Picosun Oy, Finland**

Magnesium oxide is a versatile material with insulating properties, high dielectric strength, a wide bandgap, high breakdown field, excellent stability, and durability. This study presents the fabrication of magnesium oxide (MgO) thin films via thermal Atomic Layer Deposition (ALD) utilizing sequential exposure of a magnesium precursor and its co-reactant, H<sub>2</sub>O for a batch of 25 wafers of 200 mm diameter. The self-limiting nature of the batch ALD mechanism was established through fine-tuning various parameters including canister and deposition temperatures, metal precursor exposure time, and oxidant pulse time. The film thickness was characterized using ellipsometry, revealing a growth rate of 0.95 Å/cycle. X-ray Reflectivity (XRR) analysis determined the density of the MgO thin film to be 3.50 g/cm<sup>3</sup> with a surface roughness of 1.3 nm. Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA) confirmed the high purity of the magnesium oxide film, exhibiting a stoichiometry close to 1:1 with negligible nitrogen and carbon content and <1.5% hydrogen content. Therefore, the scalability of highly pure, stoichiometric and uniform magnesium oxide is emphasized, underscoring its suitability for industrial applications.

**AM-MoP-7 Method to Evaluate Vapor and Droplet Content from a Direct Liquid Injection Vaporizer using Fourier Transform Infrared Spectroscopy, David Curran, MSP--A Division of TSI**

In the realm of semiconductor technology, high-k dielectrics are a material at the forefront of technological advances. Chemical vapor deposition and atomic layer deposition processes of high-k dielectric precursors are typically delivered by means of a bubbler or a flow over vessel. These precursors often have low vapor pressure and are thermally sensitive, limiting the throughput of the vapor delivery system. Direct liquid injection (DLI) vaporizing 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. However, incomplete vaporization of precursor droplets can lead to imperfections in the deposition.

The method developed in this presentation employs the use of Fourier Transform Infrared (FTIR) spectroscopy to conduct real-time measurements of vapor concentration and droplet content of the outlet stream of a DLI vaporizer delivery system. The spectral measurement yields a signature of the vapor + droplet phases present in the gas cell of the FTIR. The measurement yields two calculated efficiency values, concentration efficiency and evaporation efficiency, both of which require careful calibration to yield accurate results.

Concentration efficiency is an *in-situ* measurement of the vapor phase present in the gas cell of the FTIR, found by integrating over absorbance bands in the IR for each precursor. In this presentation, it is shown that tetraethyl orthosilicate (TEOS) vapor concentrations can be measured rapidly and with high linearity using partial least squares analysis. The molar vapor concentration reported by the FTIR is then compared to the molar

concentration of liquid supplied to the DLI vaporizer and a concentration efficiency is calculated.

Evaporation efficiency is calculated to account for the non-volatility of many of the high-k dielectric precursors. When droplets are present in a participating media, spectral shifts can occur in the measured signal from the FTIR, due to attenuation through a spherical liquid. This calculation couples Mie theory and information about the spectral and thermophysical properties of the liquid phase of the precursor and the droplets generated by the DLI atomizer. By investigating portions of the IR spectra where wavelengths are on the same order of magnitude as droplet diameters in the participating media, the spectral shifts can be quantified, and an evaporation efficiency is calculated. Combined the efficiencies are used to evaluate the DLI vaporizers for high throughput chemical vapor and atomic layer deposition applications.

**AM-MoP-9 Effect of Gas Injection Design on Conformality in High Aspect Ratio Structures in Batch ALD Reactor, A. Smirnov, Yury Shustrov, I. Petras, Semiconductor Technology Research d.o.o. Beograd, Serbia**

ALD is typically characterized by two main steps with self-limiting reactions of reactants from the gas phase with the surface. Each step requires a certain time to ensure complete coverage of the surface by precursor and cleaning of the reactor volume. Thus, in order to improve ALD performance for 300 mm wafers and, especially, with the deep trench structures, it is necessary to increase efficiency of precursors delivery to the surfaces and shorten steps duration.

A comprehensive modeling may help to improve the precursors delivery to the field position, sidewalls, and bottom of the high aspect ratio trench at patterned wafer based on the analysis of the gas flow distribution in ALD reactor. Sensitivity analysis to the operating conditions allows tuning the recipe in order to achieve uniform deposition over the wafer and reduce the duration of precursor deposition and purging steps. However, such models require an accurate connection between reactor-scale and feature-scale (trench, hole, etc.) simulations.

This work is focused on the improvement of Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub> batch ALD performance on the patterned wafers based on the re-design of gas injection system, steps duration, and operating conditions. Integrated modeling approach was developed to consider the self-consistent coupling of modeling tasks at different scales. The reactor-scale model of TMA and HfCl<sub>4</sub> precursors delivery and purging steps include heat transfer and gas flow with chemical reactions. Feature-scale simulations provide the step coverage as the function of trench dimensions based on tracing of molecules within the trench with chemical reactions at the sidewalls and bottom. It is demonstrated for the blanket wafers, that gas injection system with side inlets provides more uniform distribution of the precursor between the wafers and about 30% shorter precursor step duration compared to vertical injection. The suggested ways to re-design the side inlets system demonstrate that the number of wafers in the batch can be increased up to 50 with reasonable duration of the deposition and purging steps. Increasing the trench aspect ratio from 20 up to 100 on the patterned wafers results in a good conformality over the entire wafer area achieved with the several times longer precursor pulses. Integration of the models at reactor and trench scales helps to identify the critical effects of reactor geometry and recipe in order to improve batch ALD process performance on the patterned wafers with high aspect ratio trenches.

**AM-MoP-10 Optical Monitoring of MoCl<sub>5</sub> and MoOCl<sub>4</sub> Vapor Delivery for Atomic Layer Deposition Applications, Berc Kalanyan, J. Maslar, National Institute of Standards and Technology (NIST)**

Molybdenum films deposited using fluorine-free precursors are being explored as a tungsten replacement in logic and memory process flows. Atomic layer deposition (ALD) is well-suited to this task due to its low thermal budget and high conformality, enabling its integration into back-end processing. Hydrogen reduction of molybdenum pentachloride (MoCl<sub>5</sub>) is one of several processes that deposit metallic Mo films<sup>1</sup>. While MoCl<sub>5</sub> is attractive for deposition applications, it is a solid under typical delivery conditions and readily forms volatile oxychlorides upon exposure to trace moisture. Low-volatility solids are challenging for use in high-volume manufacturing because their delivery characteristics can depend on vessel design, operating conditions, and material packaging. Further, the potential existence of oxychlorides in the vapor phase is problematic as those species are also precursors for film deposition<sup>1,2</sup>. An additional complexity is the tendency of MoCl<sub>5</sub> to etch Mo and Mo-containing films<sup>3</sup>. Therefore, a detailed understanding of MoCl<sub>5</sub> delivery and subsequent deposition behavior requires *in situ* measurement of the partial pressures of MoCl<sub>5</sub>

and reactive impurities such as MoOCl<sub>4</sub>.

To address this need, we have developed direct absorption measurements in the visible and UV wavelengths to monitor the partial pressures and delivery rates of MoCl<sub>5</sub> and MoOCl<sub>4</sub> under typical ALD conditions. Using spectral signatures<sup>4</sup> of MoCl<sub>5</sub> and MoOCl<sub>4</sub>, we designed high-speed in-line gas analyzers to simultaneously detect both species during flow. The gas analyzer consisted of a broadband source, filters for wavelength selection, and avalanche photodiodes sampled at 1 kHz. Calculations using the spectral response of the analyzers show detection limits of 0.35 Pa and 0.90 Pa for MoCl<sub>5</sub> and MoOCl<sub>4</sub>, respectively. We measured time-resolved absorption in a gas delivery line using UV-vis spectroscopy and the dual-channel non-dispersive gas analyzer. Both measurements showed consistent delivery profiles for MoCl<sub>5</sub> in a flow-over vessel. We also analyzed changes in time-resolved spectra within individual injections and between multiple ALD cycles as an indicator of compositional changes in the vessel headspace. Using results from these measurements, we will present on the sensitivity and the selectivity of the analyzer to MoCl<sub>5</sub> and MoOCl<sub>4</sub>. We will further discuss changes in the vessel output during startup and prolonged cycling.

<sup>1</sup>Lee, et. al., in *AVS 20th Int. Conf. At. Layer Depos.* (Virtual, 2020).

<sup>2</sup>Baum, et. al., US11107675B2 (31 Aug. 2021).

<sup>3</sup>Juppo, et. al. *J. Vac. Sci. Technol. A* **16**(5), 2845–2850 (1998).

<sup>4</sup>Kalanyan, et. al., *J. Phys. Chem. A* **128**(1), 118–128 (2023).

## **AM-MoP-11 Visualizing Precursor Flow During ALD Processes, James Maslar, B. Kalanyan, National Institute of Standards and Technology (NIST)**

The characteristics of precursor transport from a source vessel to a deposition surface depend on many factors such as gas manifold and chamber design as well as specific process conditions. Numerous techniques have been developed to monitor precursor concentrations in ALD processes, including optical and mass spectrometric techniques. The majority of techniques utilized with ALD processes offer high spectral information or high sampling rates but provide little spatial information. The lack of spatial resolution can be a limitation in many applications, particularly those involving flow in complex assemblies or with fast gas switching where it is difficult to predict gas flow patterns. Hence, flow visualization techniques find utility in a number of applications, such as in the evaluation of gas manifold and chamber design, the development of deposition recipes, and the identification of precursor flow excursions. In addition, spatially-resolved data can be used to validate reactor scale models, e.g., digital twins. In this work, precursor flow during ALD was visualized using optical absorption. Optical absorption is straight-forward to implement, making it a convenient technique for imaging measurements. However, maximizing the utility of the measurement sometimes requires interpreting the path length-integrated absorption data within the framework of three dimensional gas flow, which may require complementary flow simulations. MoCl<sub>5</sub> flow was imaged in a research grade ALD chamber (42 mm field of view) and a flow cell (12 mm field of view). These measurements were performed in the visible spectral region using an off-the-shelf 4096 x 3000 pixel CMOS camera operating at approximately 24 frames per second. Tetrakisdimethylamido titanium and isopropanol flow was imaged in a research grade ALD chamber. These measurements were performed in the infrared spectral region using an off-the-shelf 320 x 240 pixel microbolometer camera operating at approximately 30 frames per second. Different operational modes of the cameras will be illustrated and the sensitivity and detection limits will be discussed.

## **AM-MoP-12 Thermal Behaviour of Solid ALD Precursors: Comparison of Visual Imaging Tool and Thermogravimetric Analysis, Jani Viljakka, Volatec Oy, Finland; T. Hatanpää, University of Helsinki, Finland; M. Lashdaf, Volatec Oy, Finland; M. Ritala, University of Helsinki, Finland; M. Tiitta, Volatec Oy, Finland; O. Nilsen, University of Oslo, Norway**

Precursors are the pinnacle of atomic layer deposition (ALD) growth. Whether being solid or liquid, they need to have sufficient volatility and be stable during storage and delivery. Such applicability are typically characterised by thermoanalytical methods, like thermogravimetry (TGA). It is a well-known and highly applicable technique but also has some its shortcomings.

In this work, we present our recent work on the characterization of solid ALD precursors using a visual imaging method named Optical Diagnosis Instrument (ODIN). It works under simulated ALD conditions of precursor delivery, and we compared it with the TGA method. Visual imaging and

thermogravimetric methods give information about the behaviour of solid compounds under the vaporization conditions complementary to each other.

A range of solid compounds were chosen to represent various classes of compounds used in ALD ( $\beta$ -diketonate, amides, cyclopentadienyls, alkoxides, organic acids). The compounds were sublimed in vacuum for purification before the analysis. The sampling for the analysis was made in air or in glove box depending on the sensitivity of the compound. Melting points were measured with the Stuart SMP20 instrument. Thermogravimetric analyses (TGA) were performed with Mettler Toledo TGA/DSC 3+ instrument in 10 mbar vacuum. ODIN-instrument based on the development made in University of Oslo and Baldur Coatings was applied to follow and quantify visual changes during heating in vacuum.

Both TGA and ODIN measurements gave valuable information of the suitability of the compounds for ALD. TGA provide information of the temperatures of different phenomena and the quantitative weight losses. The results of ODIN give insights of vaporization and visual understanding if other phenomena like oligomerization or decomposition occur for the compound during the heating. These methods save a lot of time in the screening phase of the compounds. They are also helpful in the evaluation of the success of the synthesis.

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## **AM-MoP-13 Thin film Conformality Evaluation on a Wafer Level in Thermal ALD Reactor using LHAR Test Structures, Olli Ylivaara, Tietotie 3, Finland; F. Gao, J. Kinnunen, M. Utriainen, Chipmetrics, Finland**

Atomic layer deposition (ALD) is a thin film growth technique that enables precise control of film thickness and conformality over complex three-dimensional structures. Wafer level conformality analysis quantifies the uniformity of film thickness and growth conformality across a wafer on complex topography. Wafer level conformality is influenced by numerous factors, such as the reactor design, the process parameters, and the substrate topography for example. In this work, we use the PillarHall wafer, which consists of arrays of lateral high aspect ratio (LHAR) test structures, to analyze conformality on a wafer level in a thermal ALD reactor using ALD Al<sub>2</sub>O<sub>3</sub> film as a model material. The PillarHall LHAR test structure allows direct and accurate measurement of film thickness inside the LHAR channels using optical analysis methods, including the most advanced Imaging Spectropic Ellipsometer (ISE). We also measure the gap height and membrane bending of the LHAR structure and use the exact dimensions to correct the wafer level data. We compare the wafer level results to a single chip (as well as 7-chips on pocket wafer) conformality. We show that the PillarHall LHAR test structure provides a reliable and comprehensive way to analyze the thin film conformality even at a wafer level and is a way to quantify and improve thin film conformality.

# Tuesday Morning, August 6, 2024

## ALD for Manufacturing

### Room Hall 3E - Session AM-TuM

#### Equipment Design, Precursor Delivery, and Spatial/R2R/Fast ALD

**Moderators:** Dr. Doug Agnew, LAM Research, Ganesh Sundaram, Veeco-CNT

#### 8:00am AM-TuM-1 Development of a Modular Manufacturing Equipment Architecture for Application Tailored Process Options, *Jacques Kools*, Encapsulix SAS, France **INVITED**

The phenomenon of degradation of products by their sensitivity to undesired chemical reaction with the surrounding environment («aging», «corrosion», «tarnishing» etc.) is often a major factor limiting the useful lifetime of these products. Ultrabarrriers mitigate these chemical reactions as they provide a diffusion barrier for the external reactant, which can vary from atmospheric water vapor and oxygen (e.g. for organic semiconductors in OLED and perovskite PV applications), to salt water in automotive or marine applications bodily fluids (which contain salt), ...etc. Among the different methods used for ultrabarrrier deposition, ALD has been found to provide the best performance, due to the low defect density and 3D conformality of the coatings. Furthermore, the unique ability of the ALD method to manipulate the film material at the atomic level provides an exciting avenue to develop application-optimized barrier structures. Thereby it is interesting to combine the primary functionality (i.e. barrier suppressing an undesired chemical reaction) with secondary functionalities (antimicrobial, self cleaning, decorative,...). As a result, advanced ultrabarrrier processes comprise a variety of Atomic Layer Processing (ALP) steps, such as preclean/etch/nanostructuring,, and multilayer/nanolaminate deposition plasma stress release/densification using a variety of metal precursors and oxidizing co-reactants. The combination of this cornucopia of process and associated equipment options, and the large spectrum of application requirements provides both an opportunity and a challenge in the transition from lab to fab: • For the chemical reactants supplier, novel (esp. more selective and sustainable) chemical production flowcharts will meet future industrial and legal requirements. • For the device maker, it now becomes possible to tailor an optimized ultrabarrrier nanostructure to the specific requirements of their application, thus enabling industrial feasibility and creating possible IP in novel processing. • For the equipment supplier, the challenge is to minimize both non-recurring engineering and unnecessary complexity to ensure competitive equipment cost of ownership and reliability. In this talk, we will discuss how Encapsulix addresses these challenges through the development of a modular equipment system, which allows for easy equipment configuration, both prior to delivery and for future upgrades as needed to support a product roadmap. We will review some general architecture aspects, and discuss a number of application examples (e.g. IT, energy and medical)

#### 8:30am AM-TuM-3 Optimizing Precursor Utilization for Spatial ALD in High Surface Area Substrates, *J. van Himste*, SparkNano B.V., Netherlands; *Paul Poedt*, SparkNano B.V. and Eindhoven University of Technology, Netherlands

Atomic Layer Deposition is well known for its ability to deposit thin films inside high surface area and porous substrates, with precise control of the step coverage and thickness. For these reasons, the use of ALD for new applications is being developed, where this precise control of step coverage and thickness is essential. Examples include the deposition of precious metal electrocatalysts on high surface area catalyst supports for water electrolysis and fuel cells, and the deposition of very thin passivation layers inside Li-ion battery anodes and cathodes. A challenge is that these applications require a high deposition rate and high throughput way of doing ALD, often in a roll-to-roll mode, for which Spatial ALD can be the solution.

Using the precursor dose to control the step coverage and deposition rate inside porous substrates has been widely reported on in literature. The simplest way to increase the deposition rate is by increasing the partial pressure of the precursor. However, next to practical limits in precursor volatility, using high precursor partial pressures can lead to very low precursor utilization rates. With precursor prices ranging from a few \$/gram to 100's of \$/gram, low precursor efficiencies are not feasible for most applications.

Here, we will show the results on modeling and experimental work on optimizing the precursor utilization efficiency during Spatial ALD on a variety of porous substrates. To objective is to minimize the precursor mass flow (e.g. in grams/hr) while ensuring a high enough precursor dose to realize the desired step coverage. By combining experiments and modeling on gas flows, precursor diffusion and surface reactions we can estimate optimized process conditions as a function of aspect ratio, surface area, required throughput, temperature and pressure. We will show that by carefully optimizing the precursor partial pressure and mass flow, precursor utilization efficiencies >90% are possible.

In cases where these high efficiencies are not attainable, or in case of very expensive precursors (e.g. containing precious metals), we have investigated the possibility to reclaim unreacted precursor for recycling. We will show results on precursor reclaim experiments, showing that reclaim efficiencies of up to 90% are feasible. By combining accurate process optimization and precursor reclaim, it is possible to perform ALD with extremely low precursor waste, which is an important enabler for high throughput and low cost Spatial ALD for a range of existing and new applications.

#### 8:45am AM-TuM-4 Development and Scale-up of ALD onto Synthetic Graphite Powder in a Continuous Vibrating Reactor for Battery Applications, *B. Castro*, Forge Nano Inc; *A. Broerman*, *C. Gump*, *Arrelaine Dameron*, Forge Nano

As the demand for improved performance in battery material increases, development of large-scale, high-throughput ALD processes and equipment is necessary to meet production demands. Forge Nano has previously demonstrated ALD deposition onto natural and synthetic graphite over a range of scales (50 g – 50 kg) in both rotary bed and fluidized bed reactors. This process has now been successfully scaled-up to the highest throughput system (ton scale) with a continuous vibrating reactor (CVR). The CVR (and associated product Circe) is a spatial ALD system where the substrate powder travels down a porous deck, driven by vibration. Process gases flow at atmospheric pressure perpendicularly to the powder flow, up through the porous deck, and fluidize the moving powder bed and mixing the particles with the gases top to bottom in the process. The substrate travels through zones of the precursors and purge gases of an ALD cycle (Figure 1).

Reproducibility per batch and relative to successful graphite deposition criteria from smaller ALD batch systems was explored in a CVR system configured to perform 4 TMA/H<sub>2</sub>O ALD cycles. Commercial synthetic graphite was coated at a rate of 33 kg/h, in 45-50 kg batches, at 180°C. Precursor flow was controlled based on the calculated stoichiometry required to achieve 100% titration of available surface sites, as determined in experiments performed in small scale fluidized bed reactors. Samples of coated product were taken from the reactor effluent every 10 minutes. Effluent samples of replicate runs were analyzed using ICP to determine the Al loading, and to characterize the reproducibility of the coating process. For all runs, the deposition of Al was deposited with an average of 84 ± 13 ppm Al (Figure 2). The initial samples for a given run were typically lower in deposition, likely due to the system approaching steady state in terms of substrate and precursor flow. Additional tests with 150% of the calculated stoichiometric TMA flow rate showed the deposition to be self-limiting. Finally, coated material was recycled through the CVR to demonstrate reproducibility that higher deposition levels and bed height and speed conditions were explored to achieve higher material processing rates. Coated materials were tested in coin cells as anode powders for lithium-ion batteries, with performance being compared to coated graphite prepared via more traditional deposition in fluidized bed reactors under vacuum conditions.

#### 9:00am AM-TuM-5 Ultra High Speed Spatial PEALD Using a Novel Precursor Separation Method, *Eric Dickey*, Lotus Applied Technology

Spatial ALD has been shown to significantly improve deposition speed when compared with conventional temporal ALD, and spatial ALD reactors are now available from multiple equipment manufacturers for high-speed batch processing based on a rotating turntable configuration. For deposition of metal oxide films, most of these systems are based on a single metal precursor zone and a single oxidation zone, separated by differential flow and pumping. In this work, we characterize a plasma-based spatial ALD process in which the spatial “separation” of the ALD half reactions is achieved by using a different mechanism. Specifically, all of the gaseous material utilized for the oxidation step is exhausted into the larger overall volume of the reactor, which also contains the metal precursor vapor. Vapor phase interaction between the metal precursor and oxidant is prevented by the neutralization of the oxidation radicals on their path from the plasma to

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the overall volume of the reactor. This radical neutralization is achieved by enclosing the plasma electrode within a gas shroud having a high aspect ratio gas exhaust path into the chamber, allowing radical recombination in this exit path from the plasma. For some precursors that react with atomic oxygen, but not with ozone at the selected processing temperature, it is shown that merely by using this plasma gas exhaust configuration with molecular oxygen gas, effective separation is achieved. This is possible due to the rapid neutralization of atomic oxygen in the gas volume via recombination, given the relatively short mean free path at the pressure used for this process. For metal precursors that are reactive with ozone at the selected processing temperature, additional measures must be used to further enhance ozone depletion in the exhaust path. It is shown that by substituting carbon dioxide for oxygen used as the plasma gas, the amount of ozone exiting the shroud is reduced by orders of magnitude. For further reduction, an active catalyst is applied to the surface of the shroud in the gas exit path, which is shown to again reduce the amount of ozone exiting the shroud. Applying these principles, multiple plasma sources, including the radical neutralization feature, have been deployed in a rotating turntable spatial ALD prototype reactor, with a compact one-meter square footprint. This system demonstrates true PEALD processing of SiO<sub>2</sub> at coating speeds in excess of 25 angstroms per second.

9:15am **AM-TuM-6 An Innovative 3D Solution for High Throughput Roll-to-Roll ALD**, *Diederick Spee*, Kalpana Systems, Netherlands; *A. Ghazy*, Kalpana systems, Netherlands

ALD is currently the state-of-the-art thin film fabrication technology. Semiconductor industry relies on ALD in its manufacturing process [1]. However, the main drawback of the typical temporal ALD is the slow processing times. This has fuelled the creation of batch processing tools, and more importantly spatial ALD (S-ALD). In S-ALD the spatial separation between the precursor and the co-reactant replaces the time distinction of consecutive precursor pulsing, which results in saving processing times [2].

Roll-to-roll (R2R) Flexible substrates have become essential to next-generation applications including batteries, solar cells and OLEDs. It is also essential for packaging materials and barrier layers [3,4]. Nevertheless, scaling up of roll-to-roll (R2R) S-ALD to a manufacturing level with high throughput has been challenging so far.

The challenges entailed in making R2R S-ALD equipment compatible with high volume production environments are mostly related to throughput and up-time. To maximize both simultaneously, perfect precursor separation is necessary to avoid contamination. Particularly at high web speeds, i.e. high throughput can only be achieved with a small gap between deposition head and the substrate. This is challenging when using large, highly flexible substrates.

Kalpana Systems has developed equipment that combines an innovative web transport system with a moving deposition head (Figure S1), in such a way that the position of the substrate, relative to the deposition head, is controlled continuously and accurately.

In addition to providing compatibility with large scale production environments, our 3D machine configuration provides the possibility for deposition of complex layer stacks in one process and enables the efficient coating of porous and high aspect ratio substrates.

We will show our latest results on coatings for flexible PV, OLED and battery electrodes.

[1] J. Sheng, J.-H. Lee, W.-H. Choi, M.-J. Kim, J.-S. Park, *J. Vac. Sci. Technol. A* 36, 060801 (2018)

[2] P. Poodt, D. C. Cameron, E. Dickey, S. M. George, V. Kuznetsov, G. N. Parsons, F. Roozeboom, G. Sundaram, A. Vermeer, *J. Vac. Sci. Technol. A* 30, 010802 (2012)

[3] A.S. Yersak, K. Sharma, J. M. Wallas, A. A. Dameron, X. Li, Y. Yang, K. E. Hurst, C. Ban, R. C. Tenent, S. M. George, *J. Vac. Sci. Technol. A* 36, 01A123 (2018)

[4] P. S. Maydannik, T. O. Kääriäinen, K. Lahtinen, D. C. Cameron, M. Söderlund, P. Soininen, P. Johansson, J. Kuusipalo, L. Moro, X. Zeng, *J. Vac. Sci. Technol. A* 32, 051603 (2014)

9:30am **AM-TuM-7 A Novel Technique for Pulsed Liquid Source Vapor Delivery in ALD and Short-Pulse CVD**, *Kathleen Erickson*, *T. Sandbakken*, MSP - A Division of TSI

The short processing times necessary for ALD and short-pulse CVD pose a unique challenge to precursor vapor delivery. Bubblers or ampoules 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. Direct Liquid Injection (DLI) is a solution to ampoule/bubbler concentration stability and thermal decomposition issues. However, historically, DLI systems have suffered from long liquid flow stabilization times which typically require liquid or vapor divert; wasting expensive liquid precursors, reducing pump lifetimes and reducing throughput. This paper presents an alternative to these two conventional techniques for ALD and short-pulse CVD vapor delivery via a high-speed Liquid Flow Controller (LFC), and a new liquid source vaporizer; exploring the possibility of using DLI for ALD/CVD applications without the use of liquid/vapor divert.

The LFC contains a custom engineered high-precision liquid flow sensor with a scan interval of 11.5ms, enabling liquid flow measurement of sub-1s pulses. The vaporizer has the capacity to effectively vaporize up to 12g/min TEOS (or equivalent), while at the same time having minimal dead and internal volume. The LFC remotely controls a piezo valve on the vaporizer, to provide faster liquid/vapor response. During this study, the LFC/vaporizer combination was used in two ways; 'digital' in which the piezo valve was fully opened at the start of the pulse and then fully closed at the end of the pulse, and 'analog' where the LFC controlled the position of the piezo-valve via a liquid flow-rate feedback loop during the pulse. LFC measured flow rate was monitored by a high-speed data acquisition system, and downstream vapor pressure pulses were measured for pulse height, pulse width, consistency and timing offset. In 'digital' experiments, both a piezo driver and the 2950 LFC were used to fully open/close the piezo valve. The 'analog' experiment included exploring several PID techniques including a variety of voltage offsets, both static and dynamic.

This presentation will briefly detail the hardware and experimental setup used. 25ms, 50ms, 150ms and 500ms liquid/vapor pulse data will be presented. Repeatability, key control criteria, and advantages and disadvantages will be discussed.

9:45am **AM-TuM-8 In-situ Spectroscopic Ellipsometry During Spatial ALD of Al<sub>2</sub>O<sub>3</sub>, ZnO, and SnO<sub>2</sub>**, *Melika Mataghian*, *M. van de Poll*, *S. Ratnasingham*, Eindhoven University of Technology, Netherlands; *H. de Vries*, SALD B.V., Netherlands; *P. Poodt*, Eindhoven University of Technology, Netherlands; *J. Hiffiker*, J.A. Woollam Co., Inc.; *E. Kessels*, *B. Macco*, Eindhoven University of Technology, Netherlands

Atmospheric-pressure *spatial* ALD (S-ALD) is a variant of conventional ALD which can achieve remarkably high deposition rates by moving the substrate at high speeds through different precursor zones that are spatially separated by an inert gas flow. The high through-put of S-ALD offers a great potential for scaling up the ALD processes, in particular, for green technologies such as photovoltaics, batteries and water electrolyzers. More than a decade of research on spatial ALD has led to successful application of S-ALD processes in industry. However to further commercialize S-ALD more material characterizations and process optimizations are needed to extend the material library of this method and introduce it to more applications.

In this work, we showcase the use of ultrafast *in-situ* spectroscopic ellipsometry (iSE) during S-ALD as a valuable tool for characterization and process development. *In-situ* metrology in general has been indispensable in conventional ALD for studying important aspects such as nucleation behavior and reaction mechanisms. Yet, for S-ALD such *in-situ* metrology is much less common, with a few reports on *in-situ* reflectometry, resistance measurements and exhaust gas analysis. This likely relates to the challenges associated with moving substrate, short timescales of cycles, and complicated geometry of the S-ALD reactor. However, *in-situ* metrology for S-ALD could help elucidate potential differences between conventional and spatial ALD due to e.g. widely different time- and pressure scales, and also help investigate unique aspects of S-ALD, such as co-injection of precursors for growth of compound materials. Additionally, using *In-situ* SE enables fast determination of saturations curves which significantly accelerates the process development.

Here we demonstrate that we can effectively perform iSE even for acquisition time of one second on our S-ALD tool using an ultrafast J.A.

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Woollam ellipsometer mounted adjacent to the deposition head. In terms of process development, we highlight that full saturation curves can be obtained in a single deposition run on a time scale of only a few minutes. Moreover, nucleation curve can be easily determined. This was done for common ALD processes for  $\text{Al}_2\text{O}_3$ , ZnO and  $\text{SnO}_2$ . Having this iSE method for S-ALD of conventional binary oxides established, current work focuses also on studying and comparing for example the deposition of ternary oxides using either supercycles or co-injection of precursors.

## Atomic Layer Etching

### Room Hall 3F - Session ALE1+AM-TuA

#### ALE & Sustainability

**Moderators:** Dr. Keun Hee Bai, Samsung Electronics Co., Ms. Leila Ghorbani, KU Leuven and Imec

#### 1:30pm ALE1+AM-TuA-1 Centering Sustainability in Future Plasma-Enhanced ALE Processes, *Nathan Marchack*, IBM Research **INVITED**

Recent progress in the field of artificial intelligence has also highlighted the critical role of semiconductor manufacturing in delivering the necessary compute requirements. Simultaneously, the prospect of future proliferation of such technologies presents serious ramifications for the environment. Examinations of the increases in resource consumption as both software [1] and hardware [2] advance have raised awareness of the need to consider the sustainability of future development. In this talk we will examine this idea as it pertains to plasma-enhanced atomic layer etching (PE-ALE), building off our recent work on reducing gas usage in deep Si etching. [3] We review new results studying mechanisms of halogen substitution on Si surfaces and the need for synergy between all facets of the development process, from substrate materials to gas precursor development. Adopting this focus as soon as possible will strengthen the fundamental role of atomic layer processes in enabling future technologies.

[1] E. Strubel et al., Energy and Policy Considerations for Deep Learning in NLP, Proc. of the 57th Annual Meeting of the Association for Computational Linguistics, 2019, pp. 3645–3650, Florence, Italy.

[2] M.G. Bardon et al., DTCO including sustainability: Power-performance-area-cost-environmental score (PPACE) analysis for logic technologies, IEEE International Electron Devices Meeting (IEDM), 2020, pp. 41.4.1–41.4.4, San Francisco, CA, USA.

[3] O. Isowamwen et al., Characterization of TSV Etch from a Sustainability Standpoint, Proc. SPIE 12499, Advanced Etch Technology and Process Integration for Nanopatterning XII, 2023, 124990H, San Jose, CA, USA.

#### 2:00pm ALE1+AM-TuA-3 Life Cycle Assessment of GaN ALD, *Houyem Hafdi, A. Carlson, H. Pedersen*, Linköping University, IFM, Sweden

ALD is a fast-growing industry; it is estimated to reach 6.2 Billion USD by 2028, which implies that the demand for metals and energy sources is increasing. Hence, the sustainability of ALD, other nanotechnologies, and nanomaterials has become a major concern and needs to be evaluated<sup>1,2</sup>.

Life Cycle Assessment (LCA) is a process for evaluating possible benefits and different environmental impacts through a product's life cycle based on the defined approaches of ISO 14044<sup>3</sup> and ISO 14040<sup>4</sup>. We will show how to apply the LCA methodology to examine and quantify the sustainability of ALD. We chose GaN as the model material for this study owing our experience of this process and of conventional CVD of GaN, allowing comparisons between conventional CVD and ALD. No research regarding LCA of GaN ALD has been carried out to date.

First, the standard LCA analysis is based on choosing a functional unit, which in our study is the deposition of a 20 nm GaN film from Triethylgallium (TEG) and Ammonia (NH<sub>3</sub>) plasma on a 200nm-diameter silicon substrate. The second step is defining the system boundaries. We chose a cradle-to-gate system that investigates the life cycle phases throughout the entire ALD process. The third step is the inventory analysis where all inputs and outputs are collected, these data include material consumption, electric and thermal energy use, as well as air emissions and by-products. The LCA was carried out based on the Ecoinvent 3 database.

The final step is the impact life cycle assessment, where the results are then transformed into the impact categories of ecotoxicity (ET), global warming potential (GWP), human health (HH), ozone depletion (OD), resource fossil fuels (RFF), human toxicity cancer (HTC), and smog air (SA). We will discuss the sustainability of ALD of GaN from the LCA and pinpoint where the focus should be when making GaN ALD more sustainable.

1. Battisti, R.; Corrado, A. Evaluation of technical improvements of photovoltaic systems through life cycle assessment methodology. *Energy* 2005, **30**, 952–967.
2. Pedersen, H., Barry, S. T., & Sundqvist, J. (2021). Green CVD—Toward a sustainable philosophy for thin film deposition by chemical vapor deposition. *Journal of Vacuum Science & Technology A*, 39(5)
3. ISO 14044; Environmental Management Life Cycle Assessment Requirements and Guidelines. International Standards Organization:

Geneva, Switzerland, 2006.

4. ISO 14040; Environmental Management Life Cycle Assessment Principles and Framework. International Standards Organization: Geneva, Switzerland, 2006.

#### 2:15pm ALE1+AM-TuA-4 Specialization of Atomic Layer Etching to Address Sustainability Challenges, *Philippe BEZARD*, IMEC, Belgium; *A. Fathzadeh*, KU LEUVEN, Belgium

Atomic Layer Etching (ALE) offers many attractive capabilities such as angstrom-level control over etch depth, excellent anisotropy (with plasma ALE) or isotropy (with thermal ALE), across wafer uniformity, and potentially lower damages than conventional plasma etching. However, in practice, it is rare to find an application where all those capabilities are needed at once and all the time. And thus, pure ALE is rarely found as a main etching process. In terms of sustainability, its extremely low throughput imposes the use of many more etch chambers than conventional processes to reach similar throughput, thereby multiplying consumption of process water, compressed air, power for the entire platform hosting the chambers (pumps, chillers, robots, etc.). Addressing the low throughput of ALE, without considering the type of gas used, is a major improvement for the environment. By only selecting the most relevant etching capabilities for a certain application, better trade-off between patterning performance and throughput can be achieved. Several approaches are tackling this issue such as quasi-ALE, Transient Assisted Plasma Etching, or by using ALE only as a corrective step to a faster sub-optimal etching process.

However, Atomic Layer Etching has several advantages which can be exploited to minimize the consumption of gases hostile to the environment (either by their Global Warming Potential or their toxicity/ corrosivity). First, by allowing enough time for the ions to desorb most etch products, the proportion of etchants adsorbed at the top surface that are used for the formation of a volatile product is high. Second, by removing purges and sacrificing full self-limitation, the outgassing of the reactor walls becomes a major supply of reactants. Cyclic processes such as ALE can be tuned for a better usage of the supplied gas than single-step processes. Finally, provided that enough etchant has been supplied to the entire wafer's surface, the excellent etch uniformity across wafer of ALE allows to run conditions maximizing gas usage which would otherwise be rejected in more conventional processes due to unacceptable compromises in uniformity. These unique properties can be exploited and have profound consequences on the design of the process chamber itself. This family of process should be considered as their own special category (not as a slightly different version of dry-etching), and have its own fully dedicated hardware in order to reduce their environmental impact.

#### 2:30pm ALE1+AM-TuA-5 Thermal Al<sub>2</sub>O<sub>3</sub> Atomic Layer Etching Using HF and Hacac Reactants: Etch Enhancement from Refluorination by Product HF During Hacac Reaction, *Andrew S. Cavanagh, T. Colleran, A. Abdulagatov, S. George*, University of Colorado at Boulder

Thermal ALE is typically defined by two sequential, reactant exposures separated by a purge. One reactant modifies the surface and the second reactant volatilizes the modified surface layer. In this study, a new ALE reaction process was identified where the surface modification reactant is also a reaction product of the volatilization reaction. Under these circumstances, etching can continue nearly indefinitely by repeating the exposure of the volatilization reactant. This study explores Al<sub>2</sub>O<sub>3</sub> ALE using HF as the surface modification reactant and Hacac as the volatilization reactant. The reactions were monitored *in situ* using quartz crystal microbalance (QCM) and quadrupole mass spectrometry (QMS). HF fluorinates the Al<sub>2</sub>O<sub>3</sub> surface to AlF<sub>3</sub> in the first reaction and then Hacac volatilizes the AlF<sub>3</sub> surface layer forming Al(acac)<sub>3</sub> and HF in the second reaction. The HF reaction product from the Hacac reaction can then serve as a surface modification reactant to refluorinate the Al<sub>2</sub>O<sub>3</sub>. By performing multiple mini-doses of Hacac after an initial HF exposure, a large etch rate enhancement is observed for Al<sub>2</sub>O<sub>3</sub> ALE compared with a single Hacac mini-dose. Figure 1 displays the QCM response to 10 Hacac mini-doses at 250 °C. Each Hacac mini-dose results in a net mass loss. The first Hacac dose removes the most mass. The 10<sup>th</sup> Hacac dose removes the least mass. The diminishing returns with subsequent Hacac mini-doses are the result of loss of some HF reaction product to the gas phase. If all the HF were recycled, then the HF reaction product could lead to perpetual etching. Similarly, Figure 2 shows the QMS response for successive Hacac mini-doses on HF-exposed Al<sub>2</sub>O<sub>3</sub> at 250 °C. All QMS signals show a diminished response with successive Hacac exposures. The HF<sup>+</sup> signal is evidence of HF produced during the volatilization step that escapes to the gas phase. The H<sub>2</sub>O<sup>+</sup> signal

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is consistent with surface refluorination by HF reaction product. The  $\text{Al}(\text{acac})_2^+$  and  $\text{Al}(\text{acac})_3^+$  signals result from volatilization of the  $\text{AlF}_3$  surface layer. The diminishing response is attributed to the loss of HF to the gas phase. With ten Hacac mini-doses per cycle,  $\text{Al}_2\text{O}_3$  etch rates were determined using QCM between 160 – 300 °C. The largest etch rate of 3.07 Å/cycle [91.0 ng/(cm<sup>2</sup>·cycle)] was observed at 290 °C. The smallest etch rate of 0.04 Å/cycle [1.1 ng/(cm<sup>2</sup>·cycle)] was measured at 160 °C.

**2:45pm ALE1+AM-TuA-6 Elucidating Gas Phase and Surface Reactions of Atomic Layer Etching, Taylor G. Smith**, University of California, Los Angeles; *E. Crumlin*, Lawrence Berkeley National Laboratory; *J. Chang*, University of California, Los Angeles

Atomic layer etching (ALE) is playing an increasingly important role in the manufacturing of nanoelectronics and other devices. Theoretical calculations are often used to screen for viable ALE processes by predicting thermodynamically favorable etch products. However, experimental verification of the predicted etch products is needed. In this work, magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR) and ambient pressure X-ray photoelectron spectroscopy (AP-XPS) are explored as methods to study ALE mechanisms in the gas phase and at the surface.

Recent advances in MAS-NMR rotor design have enabled the study of heterogeneous systems, and this work builds on these advances to study the vapor-solid interactions that lead to etching in thermal ALE processes<sup>1</sup>. A novel MAS-NMR rotor packing method is discussed that is adapted specifically to the study of vapor solid interactions that are the backbone of thermal ALE. This method allows for segregation of a liquid etchant from the solid at room temperature, but exposes the solid to vapor phase etchant when the rotor is heated. MAS-NMR is then used to study the thermal ALE mechanisms of a CuO system etched in <sup>13</sup>C-enriched formic acid vapor, with the results indicating a dimeric product with antiferromagnetically coupled Cu centers, in agreement with predicted results. AP-XPS, in turn, can be used to look specifically at surfaces during thermal reactions. Again, CuO in formic acid is used as a model system to demonstrate the applicability of this technique.

<sup>1</sup> A. Chamas, L. Qi, H.S. Mehta, J.A. Sears, S.L. Scott, E.D. Walter, D.W. Hoyt, *Magn. Reson. Imag.* **56**, 37 (2019).

**3:00pm ALE1+AM-TuA-7 Thermal Atomic Layer Etching of Ta with NbCl<sub>5</sub> and O<sub>2</sub>, Juha Ojala, M. Chundak, M. Vehkamäki, A. Vihervaara, M. Ritala**, University of Helsinki, Finland

The widely used Cu interconnects in integrated circuits require diffusion barriers to prevent the diffusion of Cu into dielectric layers and contamination of Cu by the constituents of the dielectric layers. Materials used for this barrier layer include TiN, TaN and Ta metal. Processing these materials in a controllable manner becomes critical as the interconnects and barrier layers need to shrink to accommodate the smaller feature sizes in future integrated circuits. Atomic layer etching (ALE) is one such controllable method, which can be used to thin deposited layers, selectively etch unmasked areas of films, and to remove unwanted deposits in additive manufacturing methods, e.g., as a corrective step in area-selective deposition.

We present an isotropic ALE process for etching metallic Ta, based on oxidation of the surface layer with O<sub>2</sub> and etching of the resulting oxide with NbCl<sub>5</sub>. The ALE process was studied using XRR and EDS thickness measurements as well as with XPS studies. The films were characterized before and after etching using XRD, EDS, SEM, and AFM. Effect of the film crystallinity on the etching process was studied in detail, along with oxidation of the films during etching.

Etching was studied at 300–400 °C using Ta films consisting of a mixture of cubic α-Ta and tetragonal β-Ta, as well as films consisting solely of α-Ta. It was found that the β-phase of Ta etches much more readily and is also prone to etching with NbCl<sub>5</sub> even without the oxidizer. Etch per cycle (EPC) of at least 2.0 and 4.0 Å was found for etching α-Ta at 300 and 350 °C, respectively. Gas phase etching of Ta<sub>2</sub>O<sub>5</sub> and other oxides with NbCl<sub>5</sub> was also studied.

Dissolution of oxygen into the Ta films during etching was evident, and even a suboxide phase was observed during prolonged experiments. Otherwise, partially etched films were free of impurities. The mixed phase films showed development of island-like morphology due to the different EPC of the two phases, whereas the α-Ta films etched uniformly and had smooth surfaces. This study shows that thermal ALE of Ta is simple to perform in principle, but the phase composition of the metal can have significant effect on etching characteristics.

**3:15pm ALE1+AM-TuA-8 Atomic Layer Etching of Tantalum: Unlocking the Etching Mechanism by in-Vacuo XPS Studies, Mykhailo Chundak, J. Ojala, M. Putkonen, M. Ritala**, University of Helsinki, Finland

Atomic layer etching (ALE) has emerged as a promising tool/method for nanofabrication technologies, offering the incomparable precision and control in material removal processes. The etching mechanism involves a set of self-limiting surface reactions that achieve the atomic-scale precision, uniform etching and volatilization of the modified surface. The reaction mechanism depends on the varieties of factors like chemical energy, kinetic energy etc. To elucidate the mechanisms of the reactions we used the cluster tool setup in HelsinkiALD laboratory<sup>1</sup>. The tool allows us to study the reactions with surface science techniques in vacuo after interrupting the reactions at each pivotal step giving us new insights about the reaction intermediates and thereby processes occurring at the surface.

Here we present results of the etching process of tantalum metal thin films. Tantalum, renowned for its exceptional corrosion resistance, holds significant importance across various industries, including microelectronics, catalysis, and energy storage. The 40 nm thick Ta films were first deposited via filtered cathodic arc discharge (FCAD) and subsequently subjected to an intricate etching process at 300 °C with NbCl<sub>5</sub> and O<sub>2</sub> within the cluster tool. Stoichiometry of the films was studied by X-ray photoelectron spectroscopy (XPS) at each step of the etch process. Initially the tantalum films were subjected to sputtering using Ar<sup>+</sup> ions to effectively remove the oxide layer, ensuring a pristine surface for subsequent reactions. Following this, controlled oxidation with O<sub>2</sub> gas was implemented to form surface oxides on the tantalum films. Finally, the tantalum films were exposed to NbCl<sub>5</sub>, allowing for the observation of chemical composition changes indicative of the etching process. Notably, the etchant effectively removes the tantalum oxide layers starting from the highest oxidation states until the lower ones resulting in the stoichiometry reminiscent of the surface after sputtering.

Through systematic investigation and analysis, this study provides insights into the complex dynamics of atomic layer etching applied to the Ta thin films. The findings contribute to a better understanding of the ALE processes and valuable insights into precise control of the materials modification for further technological applications.

(1) Nieminen, H.-E.; Chundak, M.; Heikkilä, M. J.; Kärkkäinen, P. R.; Vehkamäki, M.; Putkonen, M.; Ritala, M. In vacuo cluster tool for studying reaction mechanisms in atomic layer deposition and atomic layer etching processes. *Journal of Vacuum Science & Technology A* **2023**, *41* (2). DOI: 10.1116/6.0002312 (accessed 1/30/2024).

## Atomic Layer Etching

### Room Hall 3F - Session ALE2+AM-TuA

#### A.I. for ALD and ALE, and Wet-Chemical ALE

**Moderators:** Eric Liu, Tokyo Electron America, USA, Dr. Kazunori Shinoda, Hitachi, Ltd.

**4:00pm ALE2+AM-TuA-11 Application of Machine Learning to Atomic-Scale Process Development, Satoshi Hamaguchi**, Osaka University, Japan  
**INVITED**

For the development of new atomic-scale processing such as atomic layer etching (ALE) and atomic-layer deposition (ALD), efficient selection of precursor gases and other process conditions is desired among a large number of possible combinations of them. Artificial intelligence (AI) and machine learning (ML) techniques are expected to facilitate this selection. In this presentation, after briefly reviewing recent developments in data-driven plasma science [1] for process development and control in general, we discuss a method to predict the sputtering yields/etch rates of materials by ion impact based on experimental and simulation data of sputtering yields/etch rates. In such predictions, the sputtering yield typically depends on a relatively small number of physical parameters that characterize the surface material and incident ions (such as the masses of the surface material atoms and incident ions). However, the availability of large sputtering yield data is crucial for accurate prediction. Because experimental data for specific material and ion combinations may not be available, physics-based numerical simulations can be used to augment these data. For example, classical molecular dynamics (MD) simulations can be used to provide sputtering yield data but interatomic force-field models for “unfamiliar” materials are often of questionable accuracy. A method to develop ML-based interatomic force-field models is presented with an example of Si etching, and the challenges of such methods for general materials are discussed.



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[1]R. Anirudh, et al., "2022 Review of Data-Driven Plasma Science" IEEE Trans. Plasma Sci. 51(7) 1750-1838 (2023).

## 4:30pm ALE2+AM-TuA-13 Surrogate Models for One-Shot ALD and ALE Process Transfer Across Reactors and High Aspect Ratio Substrates, *Angel Yanguas-Gil, J. Elam*, Argonne National Laboratory

Being able to predict the behavior of ALD or ALE processes when transferred from a lab setting to manufacturing would help accelerate the adoption of ALD and ALE in a wide range of applications, from energy materials to microelectronics. Current approaches require extensive tool time and characterization or, when assisted by simulations, accurate models carefully tuned to each specific process. In addition to reducing the risk and cost of adopting new processes, being able to predict the behavior of a specific precursor across reactors and types of substrates can also be used to discriminate processes that struggle to perform well under more challenging conditions present in manufacturing. A key challenge is our lack of information about many ALD and ALE processes. This includes not only the surface kinetics, but in many cases the precursor pressure in the reactor or upstream precursor consumption. It is therefore key to understand how can we compensate for this lack of information with more readily available experimental data.

In this work, we tackle this problem from a machine learning perspective. In particular, we have focused on using surrogate models as tools to help us understand the following two questions: 1) how can we predict process performance across reactors and substrates?; 2) what are the key experimental observables that we need in order to make such connection? Building on our prior work on artificial neural networks for ALD process optimization,[1] we constructed surrogate models trying to connect experimental data under lab conditions with key process metrics relevant for manufacturing. These include predicting throughput, precursor utilization, process variability across large area substrates, or expected conformality. These models are built using datasets from simulations that have been shown to agree well with experimental data for a few known processes, such as  $Al_2O_3$  growth from trimethylaluminum and water.[2] Our results show that a careful experimental design involving the characterization of film thickness at predefined reactor conditions under undersaturated conditions is often enough to compensate for the lack of knowledge of a specific process. The downside is that the surrogate models are dependent on the specific reactor geometry. However, within a given reactor, surrogate models show predictive behavior across a wide range of surface kinetics and precursor pressures as long as the process kinetics is represented in the training set.

[1] A. Yanguas-Gil and J. W. Elam, *J. Vac. Sci. Technol. A* 40, 062408 (2022)

[2] A. Yanguas-Gil, J. A. Libera and J. W. Elam, *J. Vac. Sci. Technol. A* 39, 062404 (2021)

## 4:45pm ALE2+AM-TuA-14 Ligand-Assisted Surface Layer Formation in Wet Atomic Layer Etching of Molybdenum, *Tulashi Dahal, K. Abel*, Tokyo Electron America Inc.; *N. Levtschin*, TEL Manufacturing and Engineering of America, Inc.; *T. Hurd*, Tokyo Electron America Inc.; *A. Rotondaro*, Tokyo Electron America Inc.

There are many applications for molybdenum in the semiconductor industry including metallization in logic BEOL and 3-D NAND. These applications often require partial etch back where the post-etch morphology is critical to device performance. Wet atomic layer etching (ALE) offers materials removal with Angstrom-level precision following two sequential, self-limiting, wet processing steps. In the first step, a Mo surface is exposed to an oxidizing solution that forms a self-limiting oxidation layer. In the second step, this layer is selectively dissolved in a second solution. Formation of a self-limiting Mo oxidation layer is challenging due to the solubility of molybdenum oxides in aqueous solution, which leads to continuous Mo etch and rougher post-etch morphology. Solubilization of Mo oxides can be delayed in a non-aqueous oxidizing solution. Mo surface oxidation in non-aqueous solution is, however, not self-limiting (Fig. 1). The post-etch morphology of Mo in cyclic etch experiment using non-aqueous oxidizing solution is rougher compared to the starting coupon owing to preferential grain boundary etching. Here we present our results on improving the self-limiting nature of Mo oxidation layer by adding a ligand to the oxidizing solution. Aqueous oxidation of Mo leads to a continuous etch, non-aqueous oxidation leads to a delayed etch, but adding a ligand to the oxidation solution leads to the formation of a stable passivation layer (Fig. 1). Cyclic etch experiments were carried out to estimate the Mo etch

rate by exposing the Mo coupon in non-aqueous solution with and without a ligand. The drop in Mo ER from  $\sim 0.10$  nm/cycle to  $\sim 0.07$  nm/cycle after adding millimolar amount of ligand in the oxidizing solution indicates the changes in surface chemistry with ligand (Fig. 2). The dissolution of modified layer can be significantly increased via enhanced dissolution kinetics at an elevated temperature nearly doubling the Mo etch rate ( $\sim 0.12$  nm/cycle). Mo ER ( $\sim 0.12$  nm/cycle) is constant from 5 mM to 100 mM of ligand and drops to  $\sim 0.08$  nm/cycle for higher ligand concentration remaining constant thereafter. The drop in Mo etch rate with higher ligand concentration may be attributed to the piling up of surface products that are less soluble in the dissolution chemistry B. The measured RMS roughness and the SEM images (Fig. 3 and inset) show that addition of a ligand decreases the post-etch surface roughness to the level of the unetched reference coupon. We attribute these differences in etch rate and post-etch morphology to improvements in the conformality and self-limiting nature of the surface oxidation layer with the addition of a ligand.

## 5:00pm ALE2+AM-TuA-15 Wet Atomic Layer Etching of Ruthenium, *Kate Abel*, Tokyo Electron America, Inc.

We have developed a new process chemistry for atomic layer etching (ALE) of ruthenium (Ru) using wet chemistry at room temperature. Unlike plasma- and thermal-ALE, material removal in wet ALE is achieved through selective dissolution of a self-limiting passivation layer rather than volatilization. In wet ALE, a self-limiting surface layer is chemically formed upon exposure to the first etching solution. The surface layer must be insoluble in this solution, but readily soluble in the second etching solution in order to complete the ALE cycle. The dissolution of the surface layer in the second solution may occur either through intrinsic solubility of the modified layer or through a selective reactive dissolution process. Additionally, the second solution must be unreactive with the freshly exposed metal surface. Sequential exposure to both etchants is therefore required for material removal. A diagram of this process is shown in Figure 1.

Forming a self-limiting layer on Ru that is capable of being selectively solubilized in a second solution is challenging. The common oxides,  $RuO_2$  and  $RuO_4$ , are unsuitable –  $RuO_2$  requires harsh, non-selective chemicals to be removed and the low melting point, volatility, and high solubility of  $RuO_4$  prevent the formation of a stable passivation layer. Many non-oxide Ru compounds are known. Synthesis from the metallic state, however, generally requires oxidation to less stable intermediate oxidation states.

In this talk, we show that self-limiting passivation of the Ru surface can be accomplished by controlling both the oxidation potential and co-reactants present in solution. We pair an oxidizer with a variety of co-reactants in solution to show that the chemistry at the Ru surface can be changed from a continuous dissolution process to the formation of a self-limiting surface layer by changing the identity of the co-reactant. In the self-limiting case, completion of the wet ALE cycle can be accomplished through reactive dissolution of the Ru surface layer in a second etching solution. We present quartz crystal microbalance data to show how the oxidation conditions, co-reactant identity, and dissolution conditions influence the behavior of the Ru surface in this cyclic etch process.

## 5:15pm ALE2+AM-TuA-16 Combined Dry-Wet ALE for Tungsten: A Surface Characterization Study, *Cinzia Chan*, KULeuven, Imec, Italy; *J. de Marneffe*, IMEC, Belgium; *C. Gort*, TU Darmstadt, Germany; *J. Serron, M. Agati*, IMEC, Belgium; *J. Hofmann*, TU Darmstadt, Germany; *S. De Gendt*, KULeuven, Imec, Belgium; *D. van Dorp*, IMEC, Belgium

The continuous device scaling towards atomic-scale dimensions is facing challenges due to increasing complexity at both architecture and structure level. At these scales, the requirements for etching processes are limited to angstrom level. Therefore, atomic layer etching (ALE) and cleaning (ALC) are currently extensively studied as they utilize self-limiting reactions to etch surfaces with high control.

Tungsten is a material of high interest as it is currently being explored for MRAM and spintronic applications<sup>[1,2]</sup>. The reported ALE processes are halogen-based plasma<sup>[3,4]</sup> and often require high temperatures ( $>200$  °C) to form volatile byproducts<sup>[5,6]</sup>. However, limitations on the thermal budget and the use of plasma processes may be incompatible or detrimental to the exposed materials in the device stack. Therefore, we propose a combined dry-wet ALE approach that consists of a self-limiting oxidation step (dry) combined with a selective oxide removal step in acidic solution. The advantage of a selective wet etch is that it does not induce any physical or structural damage (e.g. amorphization) as compared to a full dry approach.

The proposed dry-wet ALE method was investigated on W blanket layers and patterned structures. Surface oxidation was performed through an O<sub>2</sub>

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plasma treatment at 60 °C, followed by oxide product removal in dilute HCl solution at RT. Inductively coupled plasma mass spectrometry (ICP-MS) was used to study oxide etching kinetics and selectivity by quantification of the etched surface density of W in time. During the first minutes a rapid removal of W oxide was observed followed by a gradual lowering of the etched surface density towards a constant level that corresponds to the background etch rate of the metal. An oxide/metal etch selectivity of ~100 was found. Selectivity could be further improved by lowering the dissolved O<sub>2</sub> concentration in the etchant. While ICP-MS quantification and TEM inspection revealed that the bulk of the oxide is removed within 20 minutes, post-operando XPS measurements confirmed that a remaining interfacial (sub)oxide monolayer was only removed after 60 minutes of immersion in the acid. Conductive AFM measurements agreed with these observations. The etch per cycle was 0.8nm/cycle while the surface morphology was maintained.

[1] K. Kumar *et al.*, *Phys. Rev. Appl.*, 10, 1, 2021

[2] M. Costa *et al.*, *J. Phys. Condens. Matter*, 30, 305802, 2018

[3] D. S. Kim *et al.*, *Plasma Process. Polym.*, 16, 9, 2019

[4] K. Shinoda *et al.*, *Proc. of SPIE*, 10589, 1, 2024

[5] N. R. Johnson *et al.*, *ACS Appl. Mater. Interfaces*, 9, 34435, 2017

[6] W. Xie *et al.*, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.*, 38, 022605, 2020

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