ALD for Manufacturing
Room Evergreen Ballroom & Foyer - Session AM-MoP
ALD for Manufacturing Poster Session

AM-MoP-1 Cobalt Precursor Supply Chain - Ethics and Risks*, Andreas Wilk,* *A Frey, O Briel,* Umicore AG & Co. KG, Germany*; D Zeng,* Umicore AG & Co. KG

Cobalt precursors are being used as lining and capping materials since a while. The use is beneficial to limit diffusion of copper into the dielectric layer. Additionally deposited cobalt (and longer term ruthenium) metal will displace copper and tungsten because of lower resistivity and these materials require no liner or barrier when used as an interconnect.

Unfortunately, there are significant uncertainties in the supply chain.

Ethical sourcing of Cobalt: While Cobalt is not yet listed as a conflict material like gold, tantalum, tungsten and others, articles published by Amnesty International in Jan 2016 (https://www.amnesty.org/en/latest/news/2016/01/child-labour-behind-smart-phone-and-electric-car-batteries/) and Nov. 2017 (https://www.amnesty.org/en/latest/news/2017/11/industry-giants-fail-to-tackle-child-labour-allegations-in-cobalt-battery-supply-chains/) alerted end users and Semiconductor companies alike about child labor and artisanal mining being used to produce cobalt minerals. Umicore is worldwide one of the largest users of cobalt and has taken significant measures to ensure that cobalt sourced and downstream products supplied by Umicore don't come from unethical sources. This has been audited and certified by an independent firm. Our poster contains more details on these issues.

The manufacture of cobalt precursors requires access to an intermediate called dicobaltoctacarbonyl. This material is currently only manufactured by two minor companies with limited production resources, one of these company is even located in a geographical area, which may add to the supply complexity. The poster details how Umicore plans to overcome this bottleneck and ensure sufficient supply for future growth of the industry.

Cobalt is also a raw material for Lithium batteries. This application is forecasted to grow significantly in future because of the electrification of the automobile. This raises questions about future price development and availability of cobalt raw materials. Our poster reviews the impact on the electronics industry, the impact on the electronics industry and possible solutions.

In addition, we will introduce the latest Co metal precursors as potential candidates for ALD and MOCVD applications.

AM-MoP-2 Homogeneous and Stress Controlled PEALD Films for Large Optics*, Hassan Gargouri,* *F Naumann, S Golka,* SENTECH Instruments GmbH, Germany*; K Pfeiffer,* Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Germany*; V Beladiya,* Friedrich Schiller University, Germany*; A Szeghalmi,* Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Germany

The deposition of homogenous conformal films with a precise thickness control on structured surfaces is essential for numerous applications for semiconductors, sensors and optics. Atomic Layer Deposition (ALD) is the key technology to fulfill the high requirements of such devices e.g. DRAM, MEMS, gratings. Plasma Enhanced Atomic Layer Deposition (PEALD) is an extension of ALD that opens up new possibilities such as an increased choice in materials and precursors, extended process region, and processing at reduced substrate temperatures. The new SILAYO ALD system of SENTECH Instruments GmbH with Planar Triple Spiral Antenna (PTSA) as large planar inductively coupled (IC) plasma source promises highly uniform and conformal ICPEALD deposition. Furthermore, the SILAYO system is equipped with substrate bias to control film stress during the deposition process.

ICPEALD Al_2O_3, SiO_2 and TiO_2 films were deposited on 8-inch silicon (Si) substrates. Trimethylaluminium (TMA), bis(diethylamino) silane (SAM.24) and tetrakis(dimethylamino) titan (TDMAT) were used as metal organic precursors and oxygen plasma was applied as oxygen source for the ICPEALD processes. Due to the low vapor pressure of the Si- and Ti-precursor, the material containers were heated to 70 °C. During the deposition process the substrate temperature of 250 °C was kept constant. Nitrogen (N_2) was used as carrier gas for the precursors and a constant flow of oxygen was applied through the plasma source.

The Al_2O_3 process exhibits a growth rate of 1.4 Å/cycle and an excellent non-uniformity of ± 0.3 % over the 8-inch Si wafer. The 66 nm Al_2O_3 film shows a refractive index of 1.64 with also an excellent non-uniformity of ± 0.08 %. The SiO_2 and TiO_2 processes show a growth rate of 1.1 Å/cycle and 0.6 Å/cycle, respectively. The two processes reveal an excellent non-uniformity of ± 0.7 % or ± 0.8 % over the 8-inch Si wafer. Furthermore, ICPEALD Al_2O_3 films were deposited with substrate bias. Standard Al_2O_3 film shows 97 MPa tensile stress. Applying a bias voltage during the deposition process, the Al_2O_3 film shows compressive film stress between -109 MPa and -144 MPa, depending on the set bias voltage.

AM-MoP-3 Sensing Response of ZnO Nanotube Gas Sensor Synthesized on Porous Substrate by Atomic Layer Deposition*, Pengtao Lin,* *K Zhang, H Baumgart,* Old Dominion University

Among various Metal Oxide Semiconductor (MOS) gas sensor, gas sensors based on ZnO nanostructures have been widely used due to its large exciton binding energy, wide band gape of 3.37 eV, good electrical conductivity, low cost, and high mechanical stability. In this work, ZnO nanotube nanostructure was introduced into the gas sensor application to ethanol vapor concentration due to its high electrochemical stability, nontoxicity, and, especially, high surface-to-volume ratio. Several coaxial ZnO nanotubes were synthesized on porous substrate to further enhance the sensing response to ethanol vapor with increased reaction surfaces.

In this study, ZnO nanotubes were synthesized by Atomic Layer Deposition (ALD) on Anodic Aluminum Oxide (AAO) with sacrificial Al_2O_3 layers. The Al_2O_3 sacrificial layer was synthesized on AAO by ALD with TMA (Al2(CH3)6) and DI water as precursors. Then ZnO thin films were deposited on the surface of the sacrificial layer with precisely controlled thickness by ALD. The whole procedure is considered as one super cycle. More super cycles were applied to synthesize additional coaxial ZnO nanotubes. To eliminate the sacrificial layer, Precision Ion Polishing System (PIPS) was used to remove the top cover as shown in Figure 1. Therefore, the Al_2O_3 sacrificial layers were exposed for Sodium Hydroxide (NaOH) etching. After the sacrificial layers were removed by NaOH, ZnO nanotube gas sensors were synthesized as shown in Figure 1 (b).

To investigate the sensing performance of ZnO nanotube gas sensors to ethanol vapor, a gas sensor testing system was developed with a sealed reaction chamber and control system with stable temperature control and accurate concentration control. The sensing performance of one ZnO nanotube, two coaxial ZnO nanotubes, and three coaxial ZnO nanotubes to ethanol vapor were measured and analyzed under various ethanol vapor concentrations at different temperatures.

AM-MoP-4 Temperature-based Control of Liquid Precursor Delivery for ALD Processes*, Egbert Woelk,* CeeVeeTech*; K Kimmerle, B Kimmerle,* NSI*; J Maslar,* National Institute of Standards and Technology

Liquid precursors for ALD processes are commonly delivered in an inert carrier gas from a bubbler (an ampoule with a dip tube) or a vapor draw ampoule (an ampoule with no dip tube: the gas in and gas out ports open directly into the ampoule headspace). Compared to some other delivery methods, the use of such ampoules for precursor delivery is relatively straight-forward. However, a potential drawback of using such ampoules is that evaporative cooling of the precursor can lead to a reduction in the amount of precursor delivered over time, i.e., cooling reduces the water vapor pressure and hence the amount of material entrained in the carrier gas. For example, the vapor pressure of water changes 5% per Kelvin at 20°C, while that of trimethylaluminum changes 6% per Kelvin at 20°C. For ALD processes that involve a chemical vapor deposition component, a decrease in the amount of water delivered can be detrimental to deposited film properties. To overcome this drawback, a device has been developed that controls the amount of precursor delivered based upon the precursor temperature. The concept is as follows. A temperature sensor is inserted into a thermowell on the ampoule to below the liquid level. Then, a target temperature is selected that would result in the desired amount of precursor being delivered based on the vapor pressure at this temperature. When flow is initiated through the ampoule, evaporative cooling of the precursor results in a decrease in precursor temperature which is measured with the temperature sensor. To compensate for this decrease, the amount of precursor delivered is increased in one of two ways: (1) the carrier gas flow rate is increased in a flow control mode or (2) the system pressure is decreased in a pressure control mode. In both modes, the amount of precursor is increased to compensate for the decrease in vapor

pressure. To demonstrate the performance of this control device, the precursor partial pressure was measured with and without active control using custom-built optical gas sensors. The time-dependent partial pressure was converted to precursor flow rate assuming that the ratio of the precursor to carrier gas partial pressures equals the ratio of the respective flow rates. A five-element temperature sensor array was used to measure temperature. Flow control was demonstrated by controlling the set point of the carrier gas mass flow controller. Pressure control was demonstrated by controlling the set point of a downstream pressure controller. Water and hexane were utilized to investigate the impact of precursor vapor pressure on controller performance. In addition, both bubblers and vapor draw ampoules were investigated.

AM-MoP-5 Design and Manufacturing of ICP-Type Remote Plasma ALD, *J An,* ***Dohyun Go****, J Shin, B Yang, H Kim,* Seoul National University of Science and Technology, Republic of Korea

Plasma-enhanced ALD (PEALD) is a type of ALD, which utilizes ions and radicals in plasma as oxidants which have higher reactivity than conventional oxidants. Plasma can not only effectively eliminate ligand of precursors but also possibly reduce deposition temperature. While the system of commercial PEALD usually adopt capacitively coupled plasma (CCP) or inductively coupled plasma (ICP), it is usually complicated regardless of plasma generating method; such complexity of system may increase the system cost and hamper the process flexibility.

In this presentation, we show the design and manufacturing of fully functioning compact size PEALD station using ICP plasma chamber. Systematic mechanical design process was applied including quality function deployment (QFD), fluid/thermal analysis, and 3D modeling. In the system manufacturing process, gate valve and stop valve have been modified to increase the versatility of the process conditions as well as the possible deposition of many more materials. In addition, the electrical biasing table was added to the system to control the characteristics of the plasma such as the density and flux of ions, and therefore the crystallinity of the film. Furthermore, the biasing table can be further applied for selectively functionalizing the 2-dimensional materials, e.g., graphene, on metal-patterned substrate, and accordingly selectively depositing ALD films on them. As a result, PEALD station that we have designed and manufactured can provide economic options for researchers who want to explore PEALD processes for novel applications.

AM-MoP-6 ACS™ (Atomically Clean Surface™) Cleaning and Analytical Validation of Recycled ALD Chamber Parts for the Semiconductor Industry, ***Russell Parise****, I Iordanov, B Quinn,* UCT - QuantumClean*; P Sun,* UCT - ChemTrace

ALD deposition has enabled the semiconductor industry to deposit thin, highly conformal films. Foundational to delivering the consistent film quality is managing the quality of the parts within the chamber, especially the recycled parts sent offsite for cleaning. It is an under-recognized challenge to reliably produce “certifiably” clean chamber parts. The highly conformal, high step coverage nature of ALD process results in surface deposits on the parts that are tightly adhered. Additional considerations include: parts fragility, part size, high number of ALD film chemistries, and maintaining tight dimensional tolerances.

To address these challenges, recycled part cleaning processes and metrology validation methods have been developed. The processes are non-destructive and provide for an Atomically Clean Surface™ (ACS™) that meets the micro contamination requirements of the most stringent processes. The validation scope spans impurities identification (e.g. trace metals, particles, and trace impurities) and dimensional measurements (e.g. surface roughness, defects, flatness) via use of equipment such as ICP-MS and CMM. Handling systems to provide for employee ergonomics and to protect the parts will also be discussed with regard to the multi-wafer equipment.

In addition, there is smaller demand to refurbish of valves, fittings, and other parts external to the process chamber that may become coated or damaged. Processes have been adapted to address these components as well as ensuring critical dimensions and surface roughness of mating surfaces is maintained.

This paper will review the technologies developed to clean, rinse, dry, and validate that the recycled parts meet performance requirements for various ALD processes.

Keywords: ACS™, ICP-MS, surface cleanliness, micro contamination, non-destructive, CMM

AM-MoP-8 Process Control and Mass Delivery Optimization from Low Vapor Pressure Precursors, ***Jeffrey Spiegelman****, C Ramos, D Alvarez, Z Shamsi,* RASIRC

Continual device shrinkage and incorporation of new alloy materials has led to difficult thermal constraints for ALD in microelectronic applications. Process temperatures are now required to be to less than 350° C where sub-300° C is desired. PEALD has successfully been used in some applications, but has difficulty for 3D structures and aspect ratios greater than 50.

Therefore more reactive oxidant precursors for thermal ALD have been sought where water and ammonia no longer have sufficient reactivity at reduced temperatures. Examples include anhydrous Hydrogen Peroxide and Hydrazine, which exist as low vapor pressure liquids at room temperature. Delivery of a controlled and stable vapor from a liquid source is more challenging than delivering compressed gases with a mass flow controller. Due to the complex nature of chemical liquid-vapor equilibrium, it is difficult to accurately predict the vapor mass output of a liquid precursor for the wide range of ALD operating conditions when solely relying on theoretical models. The liquid phase is in constant equilibrium with its vapor phase counterpart. Slight changes in one, strongly affect the other.

Transformation of a liquid to a vapor depends on:

1. Ampoule headspace pressure
2. Carrier gas flow rate
3. Liquid precursor temperature
4. ALD precursor pulsing recipe
5. Saturation efficiency of the carrier gas with the precursor vapor
6. Intermolecular forces and binary interactions for multicomponent liquids
7. System heat transfer
8. Ampoule design

A liquid precursor ALD simulation manifold was built to re-create typical ALD conditions. The system is composed of mass flow and pressure flow controllers, pressure sensors, metering valves, vapor mass flow sensors, and several pneumatic valves. Automated test programs control the valves and sensors to simulate custom ALD process recipes. Data collected from the test fixture can quantify liquid precursor/ampoule vapor mass flow rates at different process pressures, carrier gas flow rates, precursor liquid temperatures, and different pulsing recipes. Mass delivery parameters can thus be optimized for process control and material utilization.

Anhydrous hydrogen peroxide gas can be precisely delivered in the range of 20-300 mg/min at moderate temperatures and pressures. Optimized delivery for several recipes will be presented as a function of pressure and liquid temperature. Conclusions pertinent to several low vapor pressure materials will be discussed.

AM-MoP-9 Scaling Low-temperature Thermal ALD of SiO_2 to Batch, *J Kalliomäki, M Mäntymäki, T Lehto, S Shukla, M Kääriä, T Sarnet,* ***Juhana Kostamo****,* Picosun Oy, Finland

Silicon dioxide has become an integral part of the microelectronics industry, due to the abundance of silicon, and the convenient electrical properties of the thermally formed native oxide. As a thin film, SiO_2 can also be used to tailor the mechanical properties of film stacks, act as an etch stop layer or prevent gas diffusion. In industrial manufacturing, the rate of thin film deposition is crucial. Additionally, a low temperature SiO_2 process is desirable to minimize any effect the deposition process will have on other device materials or the substrate itself.

In ALD, SiO_2 has many available chemistries, each with its own pros and cons. The chlorides and chlorosilanes require a deposition temperature of >300°C and can cause particles and chloride impurities in the films. Since these are unacceptable in industrial applications, many amine chemistries have become available. They can fulfil the growth rate, if not always the temperature requirements, required for industrial production.

In general, lower temperature processes is needed as interlayer diffusion must be avoided and the substrates are becoming more sensitive – e.g. organic or polymer substrates might require <200°C thermal budget. The simplest solution, PEALD [1], can however result in sacrificing the higher throughput possibilities that thermal batch ALD can provide. Plasma processes also exhibit limited applicability on higher aspect ratio samples, due to the short lifetime of radical species.

Achieving industrially feasible growth rates at low temperatures with thermal processes is challenging. For example, with a commonly used process such as bis(diethylamino) silane and ozone, the growth rate at

100°C is only < 0.1Å per cycle [2]. Most results in literature are also only on single wafers.

We present a reliable low temperature SiO_2 process with growth rates in excess of 1Å per cycle from 60 to 350°C, on single wafers (Figure 1) and in batches, using a precursor with 3 Si atoms and an amine group. While the film thickness increases linearly with the number of cycles, other properties will need to be a compromise between film quality and deposition temperature – a feature common to many ALD processes. In our example, the impurity content was lower at higher deposition temperatures.

The experiments were made with PICOSUN™ R-200 Adv, P-300B and P-1000 hot-wall ALD systems. Si wafers with native oxide layers were used as substrates. The ALD process, its scalability to larger batches, and various properties of the resulting thin films were evaluated in this study.

[1] Won et al. (2010), IEEE Electron Device Lett. 31 (2010)

[2] Hirvikorpi et al., Appl. Surf. Sci. 257 (2010)

AM-MoP-10 A Novel Technique for Pulsed Liquid Source Vapor Delivery for ALD and Short Pulse CVD, ***Kathleen Erickson***, *E Ellsworth,* MSP - A Division of TSI

In recent years, ALD and short pulse CVD have been integrated into more and more commercial microelectronic processes due to the superior thin film qualities these techniques can deliver. In addition to the slower processing time, many of these ALD/CVD processes use expensive liquid precursors, particularly for metal oxides, adding to the expense of moving from less precise PVD to higher performance ALD/CVD. When using liquid precursors in ALD, CVD and MOCVD, standard practice is to use an ampule or a direct liquid injection vaporization technique with a diverter valve. With an ampule or bubbler, an ALD valve is often used to provide a quick pulses of vapor concentration. However there are some limitations to this technique. The source liquid must be pre-heated, not ideal for thermally sensitive liquids; the delivered vapor concentration can be variable and difficult to control; and mass delivery rates are limited. With direct liquid injection vaporization techniques, a diverter valve is typically used to dump the liquid vapor while the vaporized concentration is stabilized; leading to wasted liquid precursor which can be upwards of $10,000 per liter. This paper presents an alternative to these two conventional techniques to provide a vapor from a liquid source for ALD or short pulse CVD. Using the new Performance Enhanced Turbo-Vaporizer, on/off pulsed data will be presented as an option to improve throughput, reduce processing costs and to widen process options.

The PE Turbo-Vaporizer was designed to minimize dead volume; minimize heat required for vaporization; and provide a wider process window, including maximized vapor concentrations. This direct liquid injection technique features a fast response time and stable concentration output while reducing the need for preventive maintenance. This new vaporizer design enables the possibility of turning on and off the vapor delivery fast enough for ALD processes, but without the need to use a diverter valve – reducing processing time, and reducing the amount of liquid used. Pulsed flow experiments were performed using several different liquid control methods and liquid precursors, including data taken with and without the use of a liquid flow controller. 25ms, 50ms, 150ms and 500ms data will be presented. Repeatability, complexity of the liquid control scheme, key control criteria, and advantages and disadvantages will be discussed.

ALD for Manufacturing
Room Grand Ballroom E-G - Session AM1-WeM

Spatial ALD, Fast ALD, and Large-Area ALD

Moderators: John F. Conley, Jr., Oregon State University, Paul Poodt, Holst Centre / TNO

8:00am **AM1-WeM-1 Impact of Operating Parameters on Precursor Separation in "Air Hockey" Spatial Atomic Layer Deposition Reactor***, John Grasso, B Willis,* University of Connecticut

A defining characteristic of atomic layer deposition (ALD) is the sequential exposure of a surface to self-limiting, saturating reactions. Temporal ALD operates through intermittent purge cycles, while spatial ALD relies on physical separation accomplished by delivering reactants through a deposition head located in close proximity to the substrate's surface. An inert gas stream placed between precursors acts as a diffusional barrier to prevent mixing. A dysfunctional barrier results in gas phase reaction and non-ALD growth. To understand the impact system parameters have on the efficiency of the gas barrier, this work presents a COMSOL Multiphysics study of the fluid dynamics and concentration diffusion for the system.

We present a case study for ALD of alumina by trimethylaluminum (TMA) and water using a novel spatial ALD system analogous to an air hockey table. In contrast to other spatial ALD reactors that are limited by mechanical constraints, dispersed nitrogen inlets float a substrate overtop an injector region to deposit films within a deposition gap of less than 100 µm. The flotation height, or deposition gap, is a function of the fluid pressure underneath the substrate. An accurate height estimation from the parameters is necessary to evaluate the efficiency of the gas barrier. *In-situ* -height measurements are used to validate the COMSOL model, and the results are in good agreement for different operating conditions.

This work investigates how diffusivity, deposition gap, inert flow rate, and geometric design influence the effectiveness of precursor separation by evaluating the concentration of the precursors at the substrate surface. Small deposition gaps prevent precursor intermixing, however the diffusional barrier is not effective when the inert flow rate is low. Specifically, high diffusivity enables the precursors to readily diffuse beyond their ideal zone, cause gas phase reactions, and lead to CVD growth. Additionally, the uniform surface exposure of reactant is altered, leading to non-uniform growth at the edges of the deposition area. Successful precursor separation can be achieved at large flotation heights when the inert flow is large; however, the precursor concentration at the surface becomes low. These conditions may lead to insufficient saturation of the surface and non-ideal ALD growth. Stationary deposition experiments are utilized to demonstrate the ability of the model to predict non-ALD behavior. Additionally, the geometric design of the reactor plays a critical role in preventing precursor intermixing.

8:15am **AM1-WeM-2 Plasma Enhanced Spatial ALD of Silver Thin Films at Atmospheric Pressure***, **Tim Hasselmann,*** University of Wuppertal, Germany*; N Boysen,* Ruhr University Bochum, Germany*; D Theirich,* University of Wuppertal, Germany*; A Devi,* Ruhr University Bochum, Germany*; T Riedl,* University of Wuppertal, Germany

A wide range of opto-electronic devices, such as solar cells and light emitting diodes, require electrodes that are highly conductive and at the same time transparent. Ultra thin (thickness < 10 nm) silver (Ag) films can provide these properties.[1,2] Plasma enhanced atomic layer deposition (PE-ALD) would be a suitable coating technique that allows for homogenous film growth on large areas at low temperatures with precise thickness control. Since ALD is originally a vacuum based technique, limitations towards high throughput processing and low-cost manufacturing occur. These drawbacks can be overcome by spatial PE-ALD at atmospheric pressure.[3] In our earlier work, we have shown outstanding (conductive) gas diffusion barriers and more recently, the growth of Ag films from a novel halogen-free precursor, by spatial PE-ALD at atmospheric pressure.[4-6] In this work, we provide detailed growth studies of Ag thin films grown from this novel 1,3-di-tert-butyl-imidazolin-2-ylidene silver(I) 1,1,1- trimethyl-N-(trimethylsilyl) silanaminide [(NHC)Ag(hmds)] precursor by spatial PE-ALD. An atmospheric pressure dielectric barrier discharge with Ar/H_2 as working gas is used. Saturating behavior with growth rates of about $2.4x10^{14}$ atoms/(cm^2 cycle) (corresponding to an equivalent of 0.42 Å/cycle), determined by RBS, at a very low deposition temperature of 100°C is shown, with only small amounts of residual carbon (~1.5 at.%) and Si (~0.8 at.%) in the films. Percolated and conductive Ag films with a low sheet resistance of 0.9 Ω/sq (resistivity: 10^{-5}Ωcm) are demonstrated. Furthermore, the influence of the deposition temperature in a range from 80°C to 120°C on the growth characteristics is discussed. All results are compared to those obtained from the more established precursor [Ag(fod)(Pet_3)] (FOD).[7] The prospects to use these ALD grown Ag layers to create highly conductive electrodes for perovskite solar cells are discussed.

[1] K. Zilberberg et al., J. Mater. Chem. A 4, 14481–14508 (2016)

[2] Y. J. Yun et al., Adv. Funct. Mater. 27, 1701513 (2017)

[3] P. Poodt et al., J. Vac. Sci. & Technol. A 30, 01A142 (2012)

[4] L. Hoffmann et al., ACS Applied Mater. & Interfaces 9, 4171 (2017)

[5] L. Hoffmann et al., J. Vac. Sci. & Technol. A 36, 1, 01A112 (2018)

[6] N. Boysen et al., Angew. Chem. Int. Ed. 57(49) 16224-16227 (2018)

[7] M. Kariniemi et al., Chem. Mater., 23(11), 2901–2907. (2011)

8:30am **AM1-WeM-3 Low Temperature Spatial PEALD of Silicon Nitride Films from Aminosilane Precursors and DC Direct Plasma***, **Eric Dickey,*** Lotus Applied Technology **INVITED**

PEALD of silicon nitride using aminosilane precursors in combination with N_2, N_2:H_2, or NH_3 plasma has been widely studied in recent years. Most of this research has been conducted in conventional pulse-purge reactors, employing RF plasma from either indirect Inductively Coupled Plasma (ICP) or direct Capacitively Coupled Plasma (CCP). While the use of RF plasma is a necessity for pulse-purge ALD reactors, Spatial ALD provides an opportunity to use a simple DC direct plasma. This is due to the fact that most interior surfaces of the reaction chamber, including the plasma electrode, are not coated with the dielectric film, as growth occurs only on the surfaces that are exposed to both the plasma and the precursor. In this work, a spatial ALD system incorporating a rotary disc substrate holder and DC diode plasma was used to deposit silicon nitride at temperatures between 300 and 350°C, from bis(diethylamino)silane (BDEAS), bis(tertbutylamino)silane (BTBAS), diisopropylaminosilane, (DIPAS), and "New SAM" supplied by Air Liquide. N_2 and N_2:H_2(4%) were used as the plasma gas, with an operating pressure between 0.5 and 1.2 Torr. Refractive index values as high as 2.14 at 633nm were attained, and wet etch rates in dilute hydrofluoric acid (1%) as low as 1 nm per minute were measured. RBS compositional analysis for stoichiometry and contamination was performed on a subset of samples, and showed significant variation depending on the precursor and plasma gas used.

9:00am **AM1-WeM-5 Development and Characterization of an Atmospheric Pressure Plasma Reactor Compatible with Open-Air Spatial ALD***, H Rabat, F Zoubian, O Aubry, N Dumuis, S Dozias,* GREMI Université d'Orléans/CNRS, France*; C Masse de la Huerta, A Sekkat, V Nguyen,* LMGP Grenoble INP/CNRS, France*; M Bonvalot, C Vallée,* LTM-UGA, France*; D Hong,* GREMI Université d'Orléans/CNRS, France*; **David Muñoz-Rojas,*** LMGP Grenoble INP/CNRS, France

Dielectric Barrier Discharges (DBD) are widely used for atmospheric pressure plasma generation. The possibility of their adaptation in custom-made configurations makes them potential candidate to assist deposition processes. In fact, the increased need of high-quality thin films forces to improve the deposition techniques. New processes should be able to work in less constrained conditions such as atmospheric pressure rather than vacuum and to have faster deposition rates while respecting the same high quality of the deposited films. In this paper we present the development of a surface dielectric barrier discharge plasma reactor to assist an atmospheric spatial atomic layer deposition process. The plasma was generated by a surface dielectric barrier discharge powered by a microsecond pulsed high voltage power supply. The dissipated power was measured for different configurations, and thanks to the micro discharges imaging, it was observed that the thickness and the shape of the dielectric barrier influenced the micro discharges distribution on the dielectric surface. The plasma reactor exhaust gas was chemically analyzed by FTIR spectroscopy and micro gas chromatography. The ozone concentration was determined as function of frequency of the power supply. Initial results of utilization of the new compact atmospheric plasma head to deposit functional materials by open-air high-throughput plasma-activated SALD will be provided.

9:15am **AM1-WeM-6 Fast Plasma ALD Employing de Laval Nozzles for High Velocity Precursor Injection**, ***Abhishekkumar Thakur***, *J Sundqvist,* Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany*; S Wege,* Plasway Technologies GmbH, Germany

ALD based self-aligned multiple patterning (SAxP) has been the key process to continued chip scaling. SAxP demands PEALD for low temperature and conformal deposition of spacers on photoresist features for the subsequent etch based pitch splitting. ALD is limited by low thru put that can be improved by raising the growth per cycle (GPC), using new ALD precursor, preforming batch ALD or fast Spatial ALD, shrinking the ALD cycle length, or omitting purge steps to attain the shortest possible ALD cycle. Today's latest and highly productive platforms facilitate very fast wafer transport in and out of the ALD chambers. Current 300 mm ALD chambers for high volume manufacturing are mainly top-down or cross-flow single wafer chambers, vertical batch furnaces, or spatial ALD chambers.

In our research developing fast PE ALD processes, we use top down gas flow via showerhead to ignite a 60 MHz plasma (CCP) in a 300 mm chamber. The chamber has been modified to attain ultra-short (≤10 ms) ALD precursor pulses along with good uniformity using a ring injector (WO2017194059A1) with integrated de Laval nozzles enabling high speed, all-round precursor injection across the wafer. We used the well-known TMA-O_2 PEALD process to deposit Al_2O_3 for the hardware development and the productivity benchmarking.

Initially we used a single capillary injector for PEALD of Al_2O_3 at room temperature (30 °C), wherein we shrunk the TMA pulse length from 2000 ms down to 15 ms maintaining the constant 1.7 Å GPC (Fig. 1), which confirmed the self-limiting nature of the TMA half-reaction. With the de Laval ring injector the saturation started at 10 ms of TMA pulse length (Fig. 2), which is the tested switching limit of the electro-pneumatic ALD valve. The process linearity (Fig. 3) and the saturation curve indicated the ALD nature of the process. For 50 ms of TMA pulse, a wide ALD temperature window (30-120 °C) with constant 1.3 Å GPC was extracted (Fig. 4). Even with very short pulses we achieved a very good uniformity from wafer center to the edge. XPS analysis of the deposited Al_2O_3 indicated that the film deposited at 120 °C were more oxidized than the films at 30 °C with the single injector. However, the elemental composition for films deposited with TMA pulse of 10 ms vs. 50 ms was indistinguishable. A surface carbon contamination (Table 1) was observed due to the wafer exposure to the outer atmosphere post processing. However, angular XPS depth profiling revealed no detectable amounts of carbon in the "bulk of the film". The complete ALD process optimization results including plasma pulse optimization, conformality and 300 mm wafer scale uniformity will be presented at the conference.

9:30am **AM1-WeM-7 Development of a Meter Scale ALD Optical Coating Tool for Astronomical Mirror (and other) Applications**, *D Fryauf,* University of California Santa Cruz*; A Phillips,* University of California Observatories*; A Feldman,* Structured Material Industries, Inc.*; N Kobayashi,* University of California Santa Cruz*;* ***Gary Tompa***, Structured Material Industries, Inc.

Atomic Layer Deposition (ALD) is best known for depositing electronic device films, but it also offers great promise for producing transparent barrier films on optics - such as large concave metal-coated astronomical observatory telescopic mirrors. To date, ALD coatings on mirrors has been limited to relatively small-sized optics and certainly not ones with their mounting hardware attached. We have designed, constructed, and tested a new ALD tool to apply uniform ALD coatings on planar and curved substrates up to 1m in diameter. The new tool has been named the Meter Scale ALD (MS-ALD) tool. The MS-ALD tool employs a unique chamber design that isolates a large substrate surface to be coated by utilizing the substrate itself as an internal wall of the process chamber. This configuration allows the backside of the optic to be isolated from the front side process environment allowing robust transparent uniform protective dielectric coatings to be grown on telescope mirrors with their backside support hardware in place. Conceptual design, modeling, implementation, results, scalability, and future direction of this new tool are discussed for coating large astronomical telescope optics, specifically protective coatings for aluminum and silver surfaced mirrors as well as other future large structures and, ultimately, semiconductor wafers. To demonstrate the potential of this new design, aluminum oxide has been deposited by thermal ALD using trimethylaluminum and water at a reaction temperature of 60°C. Growth rates, dependence on precursor pulse times, and chamber purge times, show that the two half-reactions occur in a saturated regime, matching characteristics of ideal ALD behavior. The aluminum oxide deposition process parameters of the MS- ALD are compared with those of a conventional 100 mm wafer-scale ALD tool. Saturated ALD growth was realized with a simple scaling factor applied to precursor pulse and purge times. Growth was demonstrated using more than fifty 100 mm diameter wafers mounted on a glass substrate to represent a meter scale mirror. The results show promising application of transparent robust dielectric films as uniform barriers across large, and at times complex, optical components at the meter scale are now possible.

9:45am **AM1-WeM-8 From Wet-lab to Cleanroom: An Integrated ALD-CVD Process for the Large-area Deposition of Ultrathin Zeolitic Imidazolate Framework Films**, ***Ivo Stassen***, *A Cruz, R Ameloot,* KU Leuven, Belgium

Robust and scalable thin film deposition methods are key to realize the potential of the combined nanoporosity and hybrid organic-inorganic chemical modularity of metal-organic frameworks (MOFs) in electronic devices [1]. Here, we report the first fully integrated and highly-controllable vapor deposition process for MOFs (MOF-CVD) [2], as recently implemented in a 200 mm modified commercial ALD reactor. The process consists of two-steps: (1) atomic layer deposition for the metal oxide precursor, and (2) subsequent stop-flow reaction with the sublimated organic linker at elevated pressure and non-isothermal temperature conditions. As our selected test case, the optimized MOF-CVD process for ZIF-8 (zinc-2-methylimidazolate) showcases smooth, pinhole-free and large-area uniform ultrathin films that are highly nanoporous. Our process distinguishes itself from previous works as it permits single-chamber deposition, under mild conditions and without the need for a separate post-deposition crystallization steps; to the best of our knowledge, it is the only MOF thin film deposited *via* an integrated ALD-CVD method on large area substrates to date. Through its implementation in a single-chamber, the MOF-CVD reaction mechanism was studied using a combination of time-resolved *in situ* ellipsometry and QCM monitoring, and *ex situ* thin film characterization techniques. We will present the impact of relevant deposition parameters in the form of a MOF-CVD deposition-rate process chart. Our method shows great promise to ease the manufacturing of devices based on MOF thin films, as will demonstrated by a sneak preview of ongoing application projects.

[1] Stassen, I., Ameloot R., *et al.* An updated roadmap for the integration of metal–organic frameworks with electronic devices and chemical sensors. Chem Soc Rev 46, 3185–3241 (2017).

[2] Stassen, I., Ameloot R., *et al.* Chemical vapour deposition of zeolitic imidazolate framework thin films. Nat. Mater. 15, 304–310 (2016).

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