Monday Morning, June 29, 2020

Live Session
Room Live - Session LI1-MoM

Plenary & ALD Innovator Award Session: Monday Live

Moderators: Christophe Detavernier, Ghent University, Belgium, Erwin Kessels, Eindhoven University of Technology, the Netherlands

10:00am **LI1-MoM-7 Plenary & ALD Innovator Award Session Welcome Introduction***, **Christophe Detavernier**, J Dendooven,* Ghent University, Belgium*; P Poodt,* TNO/Holst Center, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, Netherlands*; J de Marneffe,* IMEC, Belgium

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10:15am **LI1-MoM-8 Meet the ALD 2020 Innovator Awardee***, **Mikko Ritala**,* University of Helsinki, Finland **INVITED**

Meet the ALD 2020 Innovator Awardee Mikko Ritala of the University of Helsinki, Finland

10:30am **LI1-MoM-9 Selective and Atomic Scale Processes to Enable Future Nano-Electronics***, **Robert Clark**,* TEL Technology Center, America, LLC **INVITED**

The economic driving force of Moore's law has enabled scaling of semiconductor devices to the point that modern feature sizes can be measured in atomic dimensions.[1,2] As shrinking the device footprint becomes increasingly difficult a new scaling paradigm making use of vertical scaling has emerged, initially by adopting non-planar devices, and now by stacking devices on top of one another to create 3D architectures as well.[3] Fabricating 3-dimensional electronic structures with atomic scale dimensions in high yields presents a number of daunting process challenges. Among these are the need to tightly control film thickness, uniformity, morphology, and composition within high aspect ratios. The need for selective deposition of functional films as well as layers used simply for patterning or alignment presents another challenge if we are to transition towards and more bottom-up style of nanomanufacturing. Selective and atomic scale processes are being developed in order to enable a number of self-aligned process schemes as well as scaling boosters required for future device nodes. Dielectric on dielectric (DoD) selective deposition is being developed to enable fully self-aligned vias to address edge placement error challenges encountered when manufacturing advanced interconnects. Selective metal on metal (MoM) depositions are useful for depositing metal capping layers as well as hardmasks. Scaling boosters such as super-vias and buried power rails could benefit from well-controlled processes with topographical selectivity. And dielectric on metal depositions (DoM) could provide relief from the growing overburdens needed to enable chemical mechanical planarization during replacement metal gate integration in the front end. Progress in these areas as well as future needs and an outlook on future device scaling pathways will be presented.

1. (a) Moore, G. E., *Electronics* **1965,***38* (8); (b) Bohr, M.,*Technical Digest of the IEEE International Electron Devices Meeting*, Washington, D.C., **2011**; pp 1-6.

2. Clark, R.D., *Materials* **2014,***7* (4), 2913-2944.

3. Clark, R., Tapily, K., Yu, K.-H., Hakamata, T., Consiglio, S., O'Meara, D., Wajda, C., Smith, J., Leusink, G. *APL Materials***2018**, 6, 050283.

11:00am **LI1-MoM-11 The First Application of ALD Technology in Display Industry***, **Hyun-Chul Choi**,* LG Display, Republic of Korea **INVITED**

TFT-LCD, which has dominated the display industry for the past 20 years, is gradually being replaced by OLED in recent years. OLED is superior to TFT-LCD in terms of image quality and design, but requires more advanced technologies and processes. OLED is vulnerable to moisture and oxygen due to the nature of organic materials, so encapsulation of OLED device plays a very important role to ensure the reliability of OLED. In small-size OLED products, thin film encapsulation (TFE) technology is used to form inorganic and organic layers on OLED device to protect OLED from moisture and oxygen. Atomic layer deposition, one of the semiconductor technologies, is successfully used to form high-quality TFE, which greatly improved the reliability of OLED. In addition, in order to enhance the performance of oxide-based large-size OLED products, MOCVD technology is steadily being researched and developed.

This plenary speech introduces the contribution of semiconductor technologies to the performance and quality of OLED. In addition, we will discuss the possibility of what semiconductor technologies can be applied for the future development of OLED technology.

11:30am **LI1-MoM-13 ALD on Powders for Catalysis***, **Frank Rosowski**,* BASF SE, Germany **INVITED**

Atomic Layer Deposition (ALD) is mainly applied in microelectronics as a thin film deposition technique. In academic research, ALD is also applied for synthesis of catalysts. The main challenge for ALD in this research field is the morphology of the substrate materials, usually small particles with high specific surface areas, e.g. up to 1000 m2/g for zeolites. In industry, catalytic reactors can hold packed beds of several tons of catalyst mass, exposing huge surface areas. But even in academia, where typical reactor loadings are on the gram scale, the surface areas to coat are in the range of hundreds of square meters, several orders of magnitude higher than for any wafer in the semiconductor industry.

At BasCat, the UniCat – BASF JointLab at Technische Universität Berlin, several projects use ALD as tool to synthesize and modify catalysts. In the field of supported metal catalysts, research is so far done along well-established lines of work, e.g. modifying supported metal catalysts with metal oxide layers, e.g. ZnO, alumina, and alucone. But the research focus lies on catalysts used for selective oxidation reactions, typically consisting of mixed metal oxides or phosphates. Catalysts are usually prepared in two batch sizes. For establishing suitable ALD process conditions, a sample size of about 1.0 cm3 is used. In a second step, catalyst amounts of 10 – 25 cm3 are prepared. It is important that process conditions established on the small scale are easily transferrable to the large scale.

For this purpose, a new and unique test facility was installed at BasCat equipped with a thermogravimetric balance as analytical small scale ALD reactor and a second reactor for catalyst synthesis on a large scale via ALD.[1] Based on our first ALD results, a fixed bed was chosen as reactor geometry for the analytical reactor and the synthesis reactor.

It was demonstrated that the fixed bed geometry is suitable for ALD yielding homogeneously covered substrates, and that scaling-up from 1.0 cm3 to 10 cm3 is possible.[2]

The combination of analytical reactor and synthesis reactor was then successfully used for modifying supported metal catalysts with layers of alumina and alucone,[3] and zinc oxide.[4] Other works included the deposition of rhenium on silver and phosphorus on vanadia.[5]

[1] Strempel, V. E., Naumann d'Alnoncourt, R., Driess, M. and Rosowski, F., Rev. Sci. Instrum., 074102. 2017

[2] Strempel, V., Knemeyer, K., Naumann d'Alnoncourt, R., Driess, M. and Rosowski, F.,Nanomaterials, 365. 2018

[3] Ingale, P., Guan, C., Kraehnert, R., Naumann d´Alnoncourt, R., Thomas, A., and Rosowski, F., Catalysis Today, submitted

12:00pm **LI1-MoM-15 The Flip Side of the Story: Atomic Layer Etching***, **Keren Kanarik**,* Lam Research Corp. **INVITED**

For the past 30 years, this conference has been largely dedicated to understanding the addition of atomically thin films. The flip side of that story is the removal of thin layers of material – Atomic Layer Etching – which only this past decade moved from "lab to fab" and into the mainstream. What took so long? What assumptions had to be revisited? In retrospect, we now understand why silicon was not the best case study system after all. More amenable materials have made it easier to find important benefits, such as the smoothing effect. A new operating regime led us to rethink the definition of an energy window. Such insights are proving vitally important for improving productivity and thus expanding the number of beneficial applications of this technology. While deposition has certainly led the way, etching offers a perspective from the flip side to understanding processes at the atomic scale. This plenary talk will share insights from the past decade, in hopes of continuing to push these complementary techniques forward in building the next generation of semiconductor devices.

12:30pm **LI1-MoM-17 JVST Best Paper Award, Closing Remarks, & Sponsor Thank You***, C Detavernier, J Dendooven,* Ghent University, Belgium*; P Poodt,* TNO/Holst Center, Netherlands*; **Erwin Kessels**,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, Netherlands*; J de Marneffe,* IMEC, Belgium

JVST Best Paper Award will be presented. You are now welcome to view all ALD/ALE On Demand Presentations

Live Session
Room Live - Session LI2-TuM
Technical & Poster Sessions: Tuesday Live

Moderators: Harm C.M. Knoops, Oxford Instruments Plasma Technology, The Netherlands, Paul Poodt, Holst Centre / TNO

10:00am **LI2-TuM-7 Welcome and Introduction***, C Detavernier, J Dendooven,* Ghent University, Belgium*; **Paul Poodt**,* TNO/Holst Center, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, Netherlands*; J de Marneffe,* IMEC, Belgium

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10:15am **LI2-TuM-8 Thermal Atomic Layer Deposition of Noble Metal Films Using Non-Oxidative Coreactants***, **Charles H. Winter**,* Wayne State University **INVITED**

Atomic layer deposition (ALD)[1,2] growth of noble metal (Ru, Os, Rh, Ir, Pd, Pt, Ag, Au) films is almost universally carried out by treatment of a volatile organometallic or metalorganic precursor with O_2 or ozone at temperatures of 200 °C or higher.[3] These processes lead to combustion of the organic ligands of the surface-bound metal precursors, affording a metal oxide layer, water, and CO_2. At temperatures above about 200 °C, the noble metal oxides decompose to the metals. By this general approach, thin films of Ru, Os, Rh, Ir, Pd, and Pt can be deposited. Despite the success of these existing ALD processes for noble metal films, O_2 and ozone are strong oxidants and can oxidize sensitive layers in microelectronics devices, such as W metal, TiN, and TaN.[4] Thus, combustion-based ALD processes using O_2 or ozone are unlikely to be suitable for depositions on easily oxidized substrates. Herein, we will described our efforts to develop alternative, non-oxidizing co-reactants for the thermal ALD of noble metal films. We will overview the growth of Ru metal films using (η^4-2,3-dimethylbutadiene)(tricarbonyl)ruthenium ($Ru(DMBD)(CO)_3$) with 1,1-dimethylhydrazine and several other N-based molecules.[5] With 1,1-dimethylhydrazine, an ALD window was observed from 200 to 210 °C, with a growth rate of 0.42 Å/cycle. X-ray photoelectron spectroscopy revealed >90% Ru metal in the films, with N (~7%) as the only significant contaminant. Annealing of these films under various atmospheres led to low resistivity, high purity Ru films. We will also report the thermal ALD growth of Re metal films, using Re precursors and nitrogen-based co-reactants.

1. M. Leskelä and M. Ritala, Angew. Chem. Int. Ed. **42**, 5548–5554 (2003).

2. S. M. George, Chem. Rev. **110**, 111–131 (2010).

3. J. Hämäläinen, M. Ritala, and M. Leskelä, Chem. Mater. **26**, 786–801 (2013).

4. S.-J. Lee, S.-H. Kim, M. Saito, K. Suzuki, S. Nabeya, J. Lee, S. Kim, S. Yeom, and D.-J. Lee, J. Vac. Sci. Technol. A **34**, 031509 (2016).

5. S. Cwik, K. N. Woods, M. J. Saly, T. J. Knisley, and C. H. Winter, *J. Vac. Sci. Technol. A* **38**, 012402 (2020).

10:45am **LI2-TuM-10 Mixing It Up: Tuning Atomic Ordering in 2-D Mo1-xWxS2 Alloys by ALD***, **Jeff Schulpen**, E Kessels, V Vandalon, A Bol,* Eindhoven University of Technology, Netherlands

In this contribution, we show how ALD can be used to finely tune the atomic ordering of transition metal dichalcogenide alloys, while at the same time exerting excellent control over their alloy ratio. Transition metal dichalcogenides (TMDs) such as MoS2 and WS2 are promising for many applications ranging from photonics and nano-electronics to photovoltaics and catalysis. Tailoring the properties of these materials is often desired for specific applications. An effective method of enabling such tunability of these materials is by alloying multiple TMDs. Conventionally, investigations on alloys focus on how their properties change as a function of the alloy ratio, i.e. the abundance ratio of the constituents of the alloy. However, alloys also have another degree of freedom, namely their atomic ordering. This ordering can range from random to clustered, and controlling this parameter could enable additional tuning of the properties of TMD alloys.

We employ plasma-assisted ALD[1-2] to synthesize Mo1-xWxS2 films using a supercycle approach. The excellent control over the alloy achieved by this method is evidenced by XPS atomic abundance measurements and Raman spectroscopy, both of which indicate that the alloy ratio varies smoothly as a function of the relative number of MoS2 and WS2 cycles. Control over the atomic ordering of the alloys was achieved by manipulating the ordering of the ALD cycles while keeping the alloy ratio fixed. As a function of the ALD cycle ordering, systematic shifts are observed in the lattice vibration frequencies and in the exciton energies by Raman spectroscopy and visible light absorption spectroscopy, respectively. To understand these effects, density functional theory (DFT) calculations were performed on Mo1-xWxS2 structures of varying atomic ordering. Through comparison with the DFT results, we interpret our experimental results as indeed arising from the atomic-scale ordering of the alloy films. This supports the idea that ALD can be used to tune the atomic ordering of these materials, adding this parameter to the experimental toolbox for tailoring the material properties of TMDs by ALD.

[1] Sharma, A. Low-temperature plasma-enhanced atomic layer deposition of 2-D MoS2: large area, thickness control and tuneable morphology. , 8615–8627 (2018).

[2] Balasubramanyam, S. Edge-site nano-engineering of WS2 by low temperature plasma-enhanced atomic layer deposition for electrocatalytic hydrogen evolution. (2019).

11:00am **LI2-TuM-11 Deposition of Conductive PEDOT Thin Films with EDOT and $ReCl_5$ Precursors***, **Saba Ghafourisaleh**, G Popov, M Leskelä, M Putkonen, M Ritala,* University of Helsinki, Finland

In this study we used the Oxidative Molecular Layer Deposition technique (oMLD) to deposit the most common conductive polymer – PEDOT. PEDOT is the polymer of ethylenedioxythiophene (EDOT, monomer) and has gained a lot of interest in solar energy and battery applications because it is stable, conductive, flexible and transparent. Here we were able to prepare PEDOT thin films by using a new inorganic oxidizing agent rhenium pentachloride ($ReCl_5$). We extensively characterized the properties of our films with XRD, EDS, SIMS and SEM.

Not many oMLD processes exist. The oMLD of polymers is based on sequential adsorption of the monomer and its polymerization that is induced by oxidation. The challenge in the oMLD of polymers is finding a suitable combination of precursors which is difficult because most organic monomers are non-volatile or unstable at high temperatures. Another challenge lies in finding an agent for oxidizing the organic monomer efficiently. The oxidizing agent should not contaminate the film with impurities, or if impurities are left in the film, they should be easily removed afterwards with post-deposition treatment.

The oxidizing agent used in this process is ReCl5 which has high thermal stability and high oxidizing ability. 3,4-Ethylenedioxythiophene EDOT is used as the organic monomer. With these precursors PEDOT films were deposited at temperatures in the 125-225 °C range. The polymer films were transparent in the visible region and showed high electrical conductivities.

XRD measurements showed that some rhenium residues were present in the polymer films and after the deposition these impurities segregated on the film surface in the form of rhenium oxychloride particulates. The PEDOT polymer is insoluble in water, whereas rhenium oxychloride is soluble. We post-treated the samples with deionized water. The post-treatment removed the contaminating rhenium impurities.

This work is funded by the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement №765378.

11:30am **LI2-TuM-13 Resistless Lithography Based on Local Surface Modification of Halogenated Amorphous Carbon***, **Mikhail Krishtab**,* KU Leuven/Imec, Belgium*; T Kulmala, E Cagin,* Heidelberg Instruments Nano, Switzerland*; S Armini,* Imec, Belgium*; S De Gendt,* KU Leuven/Imec, Belgium*; R Ameloot,* KU Leuven, Belgium

The fabrication of nanoscale devices involves multiple lithography steps which define the device's geometry and its performance. Electron-beam lithography and thermal scanning probe lithography (t-SPL) allow routine printing of features down to few tens of nanometers. Both techniques are based on the traditional resist process flow which relies on **bulk** modification of the sensitive layer to form an initial pattern. However, the achievement of the highest possible resolution requires application of very thin resist films thus making the successive pattern transfer particularly challenging. Inspired by the recent advances in the field of area-selective atomic-layer deposition (AS-ALD), we explored an alternative resistless approach based on local **surface** modification of an amorphous carbon film guiding the growth of a hard-mask layer.

The approach starts from plasma halogenation of a hydrogenated amorphous carbon film (a-C:H) deposited on top of a desired stack to be

patterned (*Figure 1*). The carbon-halogen bonds (C-F, C-Cl) on the surface of the a-C:H prevent ALD growth of an inorganic hard-mask layer. The exposure of the halogenated a-C:H layer to a certain energy source during the appropriate lithography step (heating or e-beam) results in local breaking of the carbon-halogen bonds, which in turn enables the growth of the ALD hard-mask exclusively in the exposed areas. The formed thin hard-mask layer is then used for patterning of the a-C:H by plasma etching.

The complete patterning sequence was demonstrated using Cl_2- and CF_4-plasma treated a-C:H films and ALD TiO_2 ($TiCl_4/H_2O$) as a hard-mask deposition process. After validating the blocking capability of the 3-5 nm thick halogen-rich a-C:H surface (*Figure 2*), we studied its sensitivity to e-beam exposure (*Figure 3*) and its thermal stability (*Figure 4*). It was found that a relatively high e-beam dose was required to get a degree of surface dehalogenation sufficient for the deposition of a pinhole-free hard-mask layer. In contrast, the low decomposition temperature of the topmost halogen-containing surface groups favored t-SPL lithography. The latter appears particularly efficient when combined with an additional 405 nm laser source, exposure to which enabled fast formation of micron-size TiO_2 patterns. The final aspect of our study concerned the reduction of nucleation defects associated with imperfections of ASD TiO_2 process. The repetitive halogenation treatment and post-deposition plasma etching were tested as defect-reduction strategies.

11:45am **LI2-TuM-14 Mimicking Chitin and Chitosan Type of Functionality with Novel Thin Films Grown by Molecular Layer Deposition**, ***Karina Ashurbekova***, *M Knez,* CIC nanoGUNE BRTA, Spain

In a bioinspired approach, we are mimicking naturally occurring materials to fabricate hybrid antibacterial and biocompatible thin films for various applications.

In this work we will present a new process for generating chitin and chitosan type of functionality by Molecular Layer Deposition (MLD). A proposed deposition scheme of the underlying chitin-type of MLD process is presented in Fig. 1. Chitin and chitosan are prominent natural biocompatible and biodegradable polysaccharides that exhibit antimicrobial, antifungal and antiviral properties, which could find application in, for example, food packaging.

For the first time sugar molecules, such as, N-acetyl-D- mannosamine and N-acetyl-D-glucosamine, were used as precursors for MLD. Thionyl chloride was used as a chlorinating agent to bind the sugar molecules to the surface. ATR-FTIR spectra of the N-acetyl-D-Mannosamine/$SOCl_2$ MLD film show several bands that are characteristic of chitin.

Besides antimicrobial properties, packaging materials require good barrier properties for water vapor and oxygen. In order to create efficient gas diffusion barriers, various metals (Al, Ti and Zn) were grafted to the chain, creating hybrid Chitin-metal surfaces. In-situ Quartz Crystal Microbalance (QCM) studies show a linear mass increase during sequential dosing of N-acetyl-D-mannosamine and trimethylaluminum (TMA) (Fig. 2A) with a total mass gain per cycle (MGPC) of 20 ng/cm^2 (Fig. 2B).

The obtained hybrid MLD films grown at different temperatures were characterized by ATR-FTIR, X-ray reflectivity (XRR), X-ray photoelectron spectroscopy (XPS), in-situ QCM and Solid-state NMR (ssNMR).

This project has received funding from the European Union´s Horizon 2020 research and innovation programme under the Marie Sklodowska -Curie grant agreement No 765378.

12:00pm **LI2-TuM-15 Closing Remarks & Sponsor Thank You**, *C Detavernier, J Dendooven,* Ghent University, Belgium*; P Poodt,* TNO/Holst Center, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands*;* ***Harm C.M. Knoops,*** Oxford Instruments Plasma Technology, Netherlands*; J de Marneffe,* IMEC, Belgium

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Technical & Poster Sessions: Wednesday Live

Moderators: Christophe Detavernier, Ghent University, Belgium, Jean-François de Marneffe, IMEC

10:00am **LI3-WeM-7 Welcome & Introduction***, Christophe Detavernier, J Dendooven,* Ghent University, Belgium*; P Poodt,* TNO/Holst Center, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, Netherlands*; J de Marneffe,* IMEC, Belgium

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10:15am **LI3-WeM-8 Surface Reactions Between Metals and Diketone induced by Gas Cluster Ion Bombardments***, Noriaki Toyoda, K Uematsu,* University of Hyogo, Japan **INVITED**

Gas cluster ion beams (GCIB) are aggregates of several thousands of gaseous atoms or molecules. Since the thousands of low-energy (several eV) atoms bombard a surface at the same time and the same position, the bombarded area experiences transient high-temperature and high-pressure conditions, which enhance sputtering of atoms or molecules. By using these characteristics, GCIB is now widely used for surface analysis tools in XPS or SIMS system. In recent years, we are investigating the feasibility of GCIB as energetic ions to enhance the surface reactions between adsorbed molecules and target atoms. We have reported ALE process using GCIB for transition metals (Cu and Ni) with diketone (acetylacetone and hexafluoroacetone). We separated each etching step as following; (1) adsorption of diketone molecules on metal oxide, (2) evacuation of residual vapor, (3) irradiation of O_2-GCIB to remove metal oxide. By using 5 keV O_2-GCIB (~ 2eV/molecules), thin layer of nickel oxide with adsorbed acetylacetone is removed. There is no physical sputtering at this energy region, which realizes self-limiting ALE process. From in-situ XPS study, Ni oxide with adsorbed diketone molecules can be removed by Ar-GCIB irradiation. It means that other oxidation method can be used to form metal oxide, and Ar-GCIB can be used for the removal steps. In this talk, we will report surface reactions between metals and diketone induced by gas cluster ion bombardments, and etching characteristics of various metals using GCIB irradiation and diketone.

10:45am **LI3-WeM-10 ALE 2020 Best Student Paper Award Talk: Isotropic Plasma ALE of Al_2O_3 using SF_6 Plasma and TMA***, Nicholas Chittock, M Vos, A Mackus,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands

Isotropic ALE is typically achieved using thermal chemistries, while plasma ALE processes are generally anisotropic in nature due to directional ions generated by the plasma. In this work, a plasma ALE process for isotropic etching of Al_2O_3 is introduced which involves SF_6 plasma exposure and TMA dosing. This process demonstrates that a fluorine containing plasma can serve as a viable co-reactant for ALE, and that plasmas can also be utilized for isotropic ALE.

From Fourier transform infrared spectroscopy (FTIR) analysis it was deduced that the SF_6 plasma step eliminates surface methyl groups while also fluorinating the surface. This fluorinated region is then removed by dosing TMA, similar to the pathway for the thermal HF/TMA ALE process.[1-5] A decrease in the Al-O IR absorbance peak for increasing ALE cycles indicates that the process is effective for etching Al_2O_3.

Self-limiting ALE behavior of this etch process was confirmed by measuring saturation curves for SF_6 plasma exposure and TMA dosing using in-situ spectroscopic ellipsometry, yielding an etch per cycle (EPC) of 3.1 Å/cycle at a substrate temperature of 260 ˚C. Higher EPC values than previously observed in the literature for thermal ALE of Al_2O_3 were obtained over the investigated substrate temperature range of 155 – 285 ˚C.[1-5] Furthermore a significant EPC of 0.83 Å/cycle was already achievable at the low substrate temperature of 185 ˚C. Performing multiple doses of only one half-cycle does not lead to observable etching of either Al_2O_3 or HfO_2 surfaces, while the complete ALE cycle was effective for etching both materials, thereby demonstrating the synergy of the ALE process. The measured EPC of HfO_2 ALE is 1.1 Å/cycle using the SF_6 plasma TMA process, which is higher than previously reported for a similar thermal HF/TMA process.[6] The isotropic nature of the plasma ALE process was demonstrated by transmission electron microscopy (TEM) analysis of 3D trench structures, with the Al_2O_3 thickness on Si trench structures being analyzed before and after etching. This work highlights that the use of plasmas allows for extension of the operating space for isotropic ALE by offering lower temperatures, higher EPC values and alternative plasma co-reactants.

1. Lee, Y., et al., Chem. of Mater. , **28**, pp.2994 (2016)

2. Cano, A., et al., J. of Phys. Chem. C ***123*** , 10346 (2019)

3. DuMont, J., et al., J. of Chem. Phys , **146**, 052819 (2017)

4. Zywotko, D., et al., JVST A , **36**, 061508 (2018)

5. Hennessy, J., et al., JVST A , **35**, 041512 (2017)

6. Lee, Y., et al., Chem of Mater. **28**, pp.7657 (2016)

11:15am **LI3-WeM-12 Monolayer Lithography: Exploiting Inhibition Contrast from the Extreme Ultraviolet Irradiation of Organic Monolayers for Area Selective Depositions***, Rudy Wojtecki,* IBM Research - Almaden **INVITED**

The enablement and miniaturization of technologies, such as electronic devices, are largely dependent on patterning materials. For instance, polymer resists can be used to create a broad range of desired feature geometries that continue to extend the capabilities of nanoscale fabrication at a remarkable rate. The 7nm technology node, which is reliant on extreme ultraviolet exposures exposures, may still rely on chemically amplified resists (CARs) from previous technology nodes. However, at critical dimensions (CDs) and below, CARs reveal increasingly difficult challenges to achieve the resolution and line edge roughness demanded by future technology generations. These include: the low absorbance of organic polymeric materials can lead to low aerial image contrast and may require higher dose exposures that reduce throughput. An alternative bottom-up approach to patterning using an organic monolayer and subsequent area selective deposition technique that can be tuned to a positive or negative-tone image generation. The method of aerial image generation in monolayer lithography takes advantage of two processes that can be used to build contrast in image development as the sensitivity of the organic itself is not alone sufficient for high contrast imaging: (i) removal of a desired organic material after exposure and (ii) a post exposure area selective deposition. These organic materials exhibit a non-linear relationship in a subsequent area selective deposition (ASD) image development step using atomic layer deposition (ALD), a key component for the development of a high-resolution system. This approach provides a method that utilizes the thinnest possible organic material and a pattern development step that produces an effective etch mask for pattern transfer.

11:45am **LI3-WeM-14 Super-Conformal ALD of Metallic Mo Films by Simultaneous Deposition and Etch***, Jean-Sebastien Lehn,* EMD Performance Materials*; C Dezelah,* ASM, Finland*; J Woodruff, R Kanjolia, D Moser, T Polson,* EMD Performance Materials

Super-conformal ALD processes, where more material is deposited at the bottom of a narrow trench or via versus its top, are needed for future generations of micro-electronic devices. Standard conformal ALD processes are unable to fill a via/trench without leaving a hollow seam. Using a conformal ALD process to fill re-entrant features, where the opening is narrower compared to the features' bottom, will lead to a void. These defects result in performance and reliability problems.

Recently disclosed super-conformal ALD processes require additional steps compared to the normal ALD sequence. A bottom-up deposition process had been developed for copper, relying on catalytical iodine atoms.[1] The addition of a nitrogen-plasma based inhibiting step,[2] or of etching steps,[3] had been demonstrated as pathways to bottom-up growth. These approaches, however, lengthen the deposition process, and may lead to increased impurities.

A new simple ALD process to deposit molybdenum films only at the bottom of vias is presented here.[4] It uses only two precursors, $MoCl_5$ and CHD (2-methyl-1,4-bis(trimethylsilyl)-2,5-cyclohexadiene), a strong reducing agent active at low temperatures where H_2 is inactive. This process does not require a catalyst, a growth inhibitor, or an additional etchant. This is possible as $MoCl_5$ quickly deposits a monolayer of $MoCl_x$ while it slowly etches Molybdenum (Scheme in Figure 1). The etched Molybdenum species can also be re-deposited on available sites. The ratio between the etch and the deposition depends on the gas phase concentration of chemical species. Increasing the $MoCl_5$ dose leads to a slowly-increasing deposition rate and a rapidly-increasing etch rate; therefore the Molybdenum deposition rate shows a maximum when the $MoCl_5$ dose is varied (Fig. 2a).

When depositing Molybdenum inside vias, chemical species' concentrations vary with the depth within the via. It is therefore possible to deposit Molybdenum only at the bottom of vias – a super-conformal process (mechanism shown in Fig. 2b). Fig. 2c shows SEM/EDS of vias with Molybdenum deposited only at the bottom of vias. Molybdenum can also be selectively deposited between substrates (the deposition/etch ratio is substrate-dependent during the nucleation phase). Characterization of films grown with this new ALD process will be shared.

* EMD Performance Materials is a business of Merck KGaA, Darmstadt, Germany.

(1) Au Y. et al. J. Electrochem. Soc. **158**, D248 (2011)

(2) Lai et al. US 9748137

(3) Fu et al. US 9595466

(4) Lehn, J.-S.M. et al. WO 2018/234567 A1

(5) Klesko, J.P. et al. Chem. Mater. **27**, 4918 (2015)

12:15pm **LI3-WeM-16 Process Optimization in Atomic Layer Deposition Using Machine Learning**, *A Yanguas-Gil, S Letourneau, A Mane, N Paulson, A Lancaster,* ***Jeffrey W. Elam,*** Argonne National Laboratory

Process development and process optimization are ubiquitous, resource-intensive tasks in thin film research and development. The goal of these activities is to find the set of process parameters (e.g. temperature, pressure, and flow) that maximize film quality at minimal cost. Typically, this is accomplished by coating a substrate (e.g. a silicon wafer) under a given set of conditions, measuring the film properties ex situ, and adjusting the conditions to improve the film quality. This activity can consume significant time and resources, especially if an additional goal is to achieve uniform films across a large substrate. Process development can be accelerated and economized using in situ measurements. For instance, quartz crystal microbalance (QCM) measurements can be employed to monitor film thickness in real time as the deposition conditions are varied. However, this still requires the careful attention of a skilled operator to make informed choices based on experience and intuition. An alternative strategy is to use machine learning (ML) to analyze the QCM data in real time and adjust the growth conditions based on an algorithm. To explore this possibility, we used ML to optimize the atomic layer deposition (ALD) of Al_2O_3 with trimethyl aluminum (TMA) and H_2O in a viscous-flow tubular reactor using in situ QCM measurements. We initially developed the ML code using simulated QCM data generated by a 1-D model of ALD transport and reaction. This allowed us to tailor the algorithm to ensure saturation of the TMA and H_2O ALD reactions and to converge efficiently on the optimal dose and purge times. We examined several ML algorithms including Bayesian optimization, physics-inspired optimization, and random optimization. An additional benefit of these simulations was that we could explore the effects of non-ideal behavior such as a CVD component to the surface reactions and strong interaction between the reaction products and the surface. Next, we interfaced the ML code to our ALD system and allowed the algorithm to optimize the TMA and H_2O timings. We observed rapid convergence, as predicted by our simulations, and found that the ML algorithm was capable of adapting to variations in the initial conditions such as the precursor partial pressures and the carrier gas flow rate. We are now building an array of QCM sensors to measure the thickness simultaneously at 10 locations along our flow tube, and we hope to report on ML opimization of thickness and uniformity using this array.

12:30pm **LI3-WeM-17 ALD/ALE Student Awards, Closing Remarks, & Sponsor Thank You**, *C Detavernier, J Dendooven,* Ghent University, Belgium*; P Poodt,* TNO/Holst Center, Netherlands*; E Kessels,* Eindhoven University of Technology, Netherlands*; H Knoops,* Oxford Instruments Plasma Technology, Netherlands*;* ***Jean-François de Marneffe,*** IMEC, Belgium

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Author Index

Bold page numbers indicate presenter

— A —
Ameloot, R: LI2-TuM-13, 2
Armini, S: LI2-TuM-13, 2
Ashurbekova, K: LI2-TuM-14, **3**
— B —
Bol, A: LI2-TuM-10, 2
— C —
Cagin, E: LI2-TuM-13, 2
Chittock, N: LI3-WeM-10, **4**
Choi, H: LI1-MoM-11, **1**
Clark, R: LI1-MoM-9, **1**
— D —
De Gendt, S: LI2-TuM-13, 2
de Marneffe, J: LI1-MoM-17, 1; LI1-MoM-7, 1; LI2-TuM-15, 3; LI2-TuM-7, 2; LI3-WeM-17, **5**; LI3-WeM-7, 4
Dendooven, J: LI1-MoM-17, 1; LI1-MoM-7, 1; LI2-TuM-15, 3; LI2-TuM-7, 2; LI3-WeM-17, 5; LI3-WeM-7, 4
Detavernier, C: LI1-MoM-17, 1; LI1-MoM-7, **1**; LI2-TuM-15, 3; LI2-TuM-7, 2; LI3-WeM-17, 5; LI3-WeM-7, **4**
Dezelah, C: LI3-WeM-14, 4
— E —
Elam, J: LI3-WeM-16, **5**
— G —
Ghafourisaleh, S: LI2-TuM-11, **2**
— K —
Kanarik, K: LI1-MoM-15, **1**
Kanjolia, R: LI3-WeM-14, 4
Kessels, E: LI1-MoM-17, **1**; LI1-MoM-7, 1; LI2-TuM-10, 2; LI2-TuM-15, 3; LI2-TuM-7, 2; LI3-WeM-10, 4; LI3-WeM-17, 5; LI3-WeM-7, 4
Knez, M: LI2-TuM-14, 3
Knoops, H: LI1-MoM-17, 1; LI1-MoM-7, 1; LI2-TuM-15, **3**; LI2-TuM-7, 2; LI3-WeM-10, 4; LI3-WeM-17, 5; LI3-WeM-7, 4
Krishtab, M: LI2-TuM-13, **2**
Kulmala, T: LI2-TuM-13, 2
— L —
Lancaster, A: LI3-WeM-16, 5
Lehn, J: LI3-WeM-14, **4**
Leskelä, M: LI2-TuM-11, 2
Letourneau, S: LI3-WeM-16, 5
— M —
Mackus, A: LI3-WeM-10, 4
Mane, A: LI3-WeM-16, 5
Moser, D: LI3-WeM-14, 4
— P —
Paulson, N: LI3-WeM-16, 5
Polson, T: LI3-WeM-14, 4
Poodt, P: LI1-MoM-17, 1; LI1-MoM-7, 1; LI2-TuM-15, 3; LI2-TuM-7, **2**; LI3-WeM-17, 5; LI3-WeM-7, 4
Popov, G: LI2-TuM-11, 2
Putkonen, M: LI2-TuM-11, 2
— R —
Ritala, M: LI1-MoM-8, **1**; LI2-TuM-11, 2
Rosowski, F: LI1-MoM-13, **1**
— S —
Schulpen, J: LI2-TuM-10, **2**
— T —
Toyoda, N: LI3-WeM-8, **4**
— U —
Uematsu, K: LI3-WeM-8, 4
— V —
Vandalon, V: LI2-TuM-10, 2
Vos, M: LI3-WeM-10, 4
— W —
Winter, C: LI2-TuM-8, **2**
Wojtecki, R: LI3-WeM-12, **4**
Woodruff, J: LI3-WeM-14, 4
— Y —
Yanguas-Gil, A: LI3-WeM-16, 5