

ALD & ALE

Room Grand Ballroom A-G - Session ALD+ALE-MoA2

Student Awards

Moderators: Simon Elliot, Schrödinger, Inc., Prof. Markku Leskela, University of Helsinki, Finland

1:30pm **ALD+ALE-MoA2-1 Student Award Finalist Talk: Thermal characterization and Area Selective Deposition of NHCs, Eden Goodwin, Carleton University, Canada; J. Lomax, University of Western Ontario, Canada; M. Aloisia, C. Crudden, Queen's University, Canada; P. Ragogna, University of Western Ontario, Canada; S. Barry, Carleton University, Canada**

Nanomanufacturing of integrated circuits requires multiple processes involving sequential deposition, etch, and planarization to create architectures consisting of interconnected metal, semiconductor, and dielectric components built upon a substrate. As the smallest components of these devices begin to reach sub nanometer dimensions, device manufacturers must rely upon area selective atomic layer deposition (AS-ALD) to deposit highly tunable and conformal films on selected regions of the substrate. Conventional AS-ALD employs thiol-based inhibitors with long alkyl groups to deactivate non-growth areas. These thiol-based inhibitors are known to have low surfactant density, and can create electron rich sulphur impurities upon removal, and are of large enough size to become incompatible with shrinking device architectures^{1,2}.

In this work we explore N-heterocyclic carbenes (NHCs) as area-selective small molecule inhibitors (SMIs) to replace the larger long-chain thiol SAMs. The electronic and steric tunability of NHCs allow flexibility when using them to selectively protect metal surfaces, due to their preferential binding to metal surfaces over dielectric surfaces. In this work we generate carbenes in situ through the controlled thermolysis of benzimidazolium bicarbonate salts, deliver them to non-patterned metal substrates as well as to patterned metal/dielectric substrates. We probe the thermal characteristics of comprehensive library of benzimidazolium bicarbonate salts through thermogravimetric analysis and differential scanning calorimetry. We quantify the growth behavior of various NHC precursors on gold surfaces, using an in-situ quartz crystal microbalance within a home-built tube furnace reactor. Finally, we demonstrate the selectivity of these NHCs through time of flight secondary ion mass spectrometry imaging and X-ray Photoelectron Spectroscopy of plasma-cleaned substrates coated with NHC films using a Picosun R200 plasma-enhanced ALD tool.

References:

1. Yarbrough, J., Shearer, A. B., & Bent, S. F. (2021). Next generation nanopatterning using small molecule inhibitors for area-selective atomic layer deposition. *Journal of Vacuum Science & Technology A*, 39(2), 021002. <https://doi.org/10.1116/6.0000840>
2. Yasmeen, S., Ryu, S. W., Lee, S. H., & Lee, H. B. R. (2022). Atomic Layer Deposition Beyond Thin Film Deposition Technology. In *Advanced Materials Technologies*. John Wiley and Sons Inc. <https://doi.org/10.1002/admt.202200876>

1:45pm **ALD+ALE-MoA2-2 Student Award Finalist Talk: Reaction Mechanism on ALD Process of Ru and Pt, Heta-Elisa Nieminen, M. Putkonen, M. Ritala, University of Helsinki, Finland**

Detailed reaction mechanism studies help to understand ALD processes and advance the technology through the increased knowledge. As the film growth is dictated by reactions between the precursors on the substrate surface, many ALD processes can be designed around analogous reaction chemistry. One such group of processes is deposition of noble metals by using organometallic precursors together with O₂ as a counter reactant. The reaction pathway for the processes is mainly known, but not all mechanistic details have been confirmed directly in ALD conditions. For example the nature of the dissociated surface oxygen, adsorption of the organometallic precursor, completeness of the reactions and the nucleation of the metallic film require detailed investigation. This work aims to enlighten the mechanisms overall by studying metallic Ru and Pt processes with a set of *in situ* and *in vacuo* techniques.

Deposition of noble metals requires reduction of the metal cation of the precursor molecule to its elemental state. Hence, it is somewhat

counterintuitive to use oxygen as the second reactant. The idea is that the organometallic ligands of the metal precursor itself act as the reducing agents in combustion reactions with O₂ that produce gaseous CO₂ and H₂O byproducts. Earlier reaction mechanism studies have revealed that in addition to combusting the ligands, the O₂ molecules dissociate onto the noble metal surface. This way the combustion reactions occur during both precursor pulses. The O₂ dissociation has suggested to be dependent on the deposition temperature as well as on the noble metal in question. For ruthenium, for example, substantial amount of O₂ is suggested to temporarily adsorb into the subsurface region of the film.

In this work reaction mechanisms are studied by investigating the film surface with *in vacuo* XPS and TPD together with monitoring the film growth with *in situ* QCM. The depositions are done in a commercial flow type ALD reactor using RuCp₂ and MeCpPtMe₃ for metallic Ru and Pt, respectively, together with O₂ as the counter reactant. The assumptions regarding the main reaction pathway are confirmed in our measurements. In addition, detailed analysis is performed to compare these two processes that represent nominally similar reaction chemistry.

2:00pm **ALD+ALE-MoA2-3 Student Award Finalist Talk: Thermal Atomic Layer Etching of Gold Using Sulfuryl Chloride for Chlorination and Triethylphosphine for Ligand Addition, Jonathan Partridge, J. Murdzek, S. George, University of Colorado at Boulder**

Gold (Au) is one of the most revered metals with many uses including as a conductor in electronics. Nanostructured gold is also important in plasmonics and photonics. Au ALE could be used in the fabrication of gold nanostructures. In this study, Au thermal ALE was demonstrated using sequential chlorination and ligand-addition reactions. Sulfuryl chloride (SO₂Cl₂) was used for chlorination and triethylphosphine (P(Et)₃) was used for ligand addition. Sulfuryl chloride is believed to chlorinate the gold surface and form AuCl. Triethylphosphine ligand addition then adds to AuCl and produces volatile AuCl(P(Et)₃) etch products. This demonstration of Au ALE employed a custom quadrupole mass spectrometer (QMS) reactor to identify the etch products. High sensitivity detection is achieved when the etch products exit an aperture and form a molecular beam with line-of-sight to the ionizer. Gold nanopowders were used to maximize the surface area for the ALE reactions. Additional measurements of etch rates during Au ALE were performed using quartz crystal microbalance (QCM) studies. The QMS experiments were performed at 150 °C at partial pressures of 2 Torr for sulfuryl chloride and triethylphosphine. During SO₂Cl₂ exposures, the time-resolved QMS ion intensities for SO₂⁺ relative to the parent SO₂Cl₂⁺ were consistent with the self-limiting chlorination of the gold surface. During P(Et)₃ exposures, AuCl(P(Et)₃)⁺ ion intensity at m/z 350 was observed as the major etch product. Corresponding experiments at 150 °C on Au-coated QCM crystals observed a mass gain for SO₂Cl₂ exposures during chlorination and a mass loss for P(Et)₃ exposures during ligand addition. The mass changes were consistent with an etch rate for Au ALE of 0.63 Å/cycle at 150 °C.

Sequential SO₂Cl₂ and P(Et)₃ exposures were also observed to etch Cu and Ni nanopowders. The etch product during Cu ALE was observed at m/z 432 and assigned to Cu₂Cl₂(P(Et)₃)₂⁺. The etch product during Ni ALE was observed at m/z 366 and assigned to NiCl₂(P(Et)₃)₂⁺. Additional QCM experiments on Cu-coated QCM crystals confirmed Cu ALE at 100 °C. This mechanism of chlorination and ligand addition should be useful for the ALE of many metals that form stable metal chlorides.

2:15pm **ALD+ALE-MoA2-4 Student Award Finalist Talk: Conformality of Atmospheric-Pressure Plasma-Enhanced Spatial Atomic Layer Deposition of SiO₂ and TiO₂, Mike van de Poll, Eindhoven University of Technology, Netherlands; H. Jain, TNO-Holst Centre & Eindhoven University of Technology, The Netherlands; B. Macco, P. Poedt, E. Kessels, Eindhoven University of Technology, Netherlands**

ALD is the thin-film method of choice for applications involving 3D structured surfaces. This includes, e.g., high aspect ratio structures in DRAM and NAND but also nanostructured optics and particle-based cathodes of Li-ion batteries. The conformal deposition of films can be achieved by sufficiently high precursor doses and co-reactant exposures. Challenges can arise, however, when using spatial ALD configurations for high throughput processing. Moreover, when a plasma is used as co-reactant, the situation can become even more challenging due to the potential loss of reactive plasma species by recombination at surfaces. Here, we present the first systematic study of the conformality of

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atmospheric-pressure plasma-enhanced spatial ALD (PE-s-ALD) complementing our earlier work on temporal PE-ALD at low pressures [1].

Employing the lateral high-aspect-ratio (LHAR) method (enabled by PillarHall™ LHAR test chips by Chipmetrics Ltd), we demonstrate that PE-s-ALD is capable of depositing conformal SiO₂ and TiO₂ films in 3D structures. The films were deposited using an atmospheric-pressure s-ALD tool equipped with a DBD plasma source operated on O₂/N₂. Using plasma exposure times as short as 0.7 s per cycle, aspect-ratios up to 80 and 210 could be conformally coated with SiO₂ and TiO₂, respectively. The penetration depth in the structures was found to be recombination-limited. In order to determine the recombination probability of the O-radicals present in the plasma, the experimental data was analyzed by a reaction-diffusion model. From this model, a relation was obtained between the penetration depth of O-radicals and their recombination probability. The extracted recombination probabilities at atmospheric pressure (i.e., 5.0 x10⁻⁴ for SiO₂ and 3.4 x10⁻⁵ for TiO₂) are comparable to those found in previous work at low pressure.[1] Differently shaped thickness profiles were observed for SiO₂ and TiO₂, showcasing the influence of various side-effects on the conformality of PE-s-ALD. Furthermore, estimations for the plasma time required for reaction-limited growth were made for substrates with various aspect ratios. For low aspect ratios (<60 for SiO₂), this time was found to be even lower than for low-pressure PE-ALD due to shorter saturation times at atmospheric pressure. These results demonstrate the potential of PE-s-ALD as a method for scaling up ALD for high-volume manufacturing.

[1] Arts, K.; Utriainen, M.; Puurunen, R. L.; Kessels, W. M. M.; Knoops, H. C. M. *J. Phys. Chem. C* **2019**, *123*, 27030–27035.

2:30pm ALD+ALE-MoA2-5 Student Award Finalist Talk: "Inverted ASD" with High Selectivity: Polymer on SiO₂ vs. Si-H and Polymer on Si-OH vs. SiO₂, Nicholas Carroll, H. Margavio, G. Parsons, North Carolina State University

Area-selective deposition (ASD) is of considerable interest to augment lithographic patterning, but new strategies are needed to leverage its usefulness. An important target of ASD is control over surface selectivity, including selectivity inversion of a deposition reaction to manipulate two arbitrary patterned surfaces to display either growth or non-growth behavior. However, to our knowledge, work to date is limited to ASD processes with pre-defined growth and non-growth surfaces. Achieving "inverted ASD," where the patterned growth and non-growth surfaces could be selected arbitrarily, for example by precursor choice, surface preconditioning, or other treatments, would provide new capability for ASD process integration, particularly if high selectivity could be attained in either configuration. In this work, we report an inverted ASD process where poly(3,4-ethylenedioxythiophene) (PEDOT) conjugated polymer is deposited with high selectivity on Si-OH vs. SiO₂, or on SiO₂ vs. Si-H, where inversion is achieved by selective modification of the substrate surface energy via treatments with dilute hydrofluoric acid (DHF), (Dimethylamino)trimethylsilane (DMATMS), and water. PEDOT was selected as a case study due to its rapid deposition rate and known selectivity on SiO₂ vs. Si-H [1]. On Si/SiO₂ line structures with chemical oxide from piranha cleaning on the Si region, PEDOT grows uniformly on all surfaces (Figure 1a). However, after removing the oxide layer in 5% DHF for 5 seconds, the PEDOT shows a strong nucleation delay on Si-H (Figure 1b). If the HF-treated Si/SiO₂ is exposed to vapor-phase DMATMS under vacuum conditions, we find that DMATMS selectively passivates the SiO₂, inducing a delay in PEDOT nucleation, and the PEDOT grows only at the boundary region between the Si-H and passivated SiO₂, likely due to passivation defects in this region (Figure 1c). When the passivated Si/SiO₂ pattern is briefly submerged in water, the Si-H becomes hydroxyl terminated without changing the surface state of the SiO₂-TMS, leading to inverted selectivity (Figure 1d-f). Versatile control over selectivity configurations during ASD has implications for deposition of lateral control layers to reduce over-growth defects, blocking layers for non-selective deposition steps, and sacrificial layers for recently reported simultaneous deposition and etching processes [2]. Extension of these surface energy treatment strategies to other materials will provide additional opportunities for selectivity inversion, leading to flexible applications for ASD in manufacturing settings.

[1] J.-S. Kim et al., *Chem. Mater.* **33**, 23(2021)

[2] S. K. Song et al., *ACS Nano*. **15**, 7(2021)

2:45pm ALD+ALE-MoA2-6 Student Award Finalist Talk: Plasma Isotropic ALE of GaN Using SF₆ Plasma and TMA, Nicholas Chittock, W. Kessels, Eindhoven University of Technology, The Netherlands; H. Knoops, Oxford Instruments Plasma Technology, Netherlands; S. Elliott, Schrödinger, Ireland; A. Mackus, Eindhoven University of Technology, The Netherlands

GaN is an enabling material for advanced radio frequency (RF) and power semiconductor devices due to its improved material properties compared to Si.¹ Typically, reactive ion etching (RIE) is used in GaN device fabrication which can result in a thick contamination layer and rough etch front that degrades device performance. In this work, an isotropic plasma ALE process using SF₆ plasma and TMA has been developed for GaN, allowing accurate film thickness control, removal of O and C contamination, and surface smoothing.

From density functional theory (DFT) studies performed with the Schrödinger Materials Science Suite it was determined that the SF₆ plasma/TMA chemistry was likely to result in ALE behavior. Natarajan-Elliott analysis revealed the fluorination reaction is in the preferred self-limiting regime, which suggests it is a suitable modification step. Additionally, the predicted ligand-exchange reaction between GaF₃ and TMA was found to be energetically favorable, with higher temperatures resulting in a more negative free energy change.

Experimental results support the observations from DFT: saturation curves of both half-cycles at 150 °C and 300 °C give etch rates of 0.31 ± 0.01 and 0.40 ± 0.02 nm/cycle, respectively. Soft-saturation behavior of the SF₆ step suggests that the process follows a diffusion-driven fluorination mechanism, similar to ALE of Al₂O₃.² A relatively thick (~10 nm) partially oxidized surface layer was present on the GaN surface before etching due to the oxyphilic nature of GaN. After ALE, the C and O content were significantly reduced, with only a small increase in F content detected by XPS, demonstrating that this process can remove film contamination. Evaluation of the EPC as a function of temperature reveals an ALE temperature window between 150-300 °C. Below 150 °C the EPC decreases rapidly and no etching is observed at 100 °C. Compared to thermal isotropic ALE of GaN reported in literature,³ a higher EPC is achieved, highlighting a benefit of plasma isotropic ALE. AFM studies show smoothing of the GaN film post ALE, with a reduction of the RMS roughness from 2.6 ± 0.1 nm to 1.9 ± 0.1 nm after 25 nm of ALE.

The ability to accurately control GaN film thickness, while simultaneously smoothing and removing contaminants, makes isotropic plasma ALE a good candidate for post RIE surface cleaning. Consequently, isotropic ALE will be a valuable technique for the fabrication of future 3D GaN-based RF and power semiconductor devices.¹

1. Zhang, Y. et al. *Semicond Sci Technol* **36**, (2021).
2. Chittock, N. J. et al. *Appl Phys Lett* **117**, 162107 (2020).
3. Johnson, N. R., et al. *Appl Phys Lett* **114**, 243103 (2019).

3:00pm ALD+ALE-MoA2-7 Student Award Finalist Talk: Competition between Deposition and Etching Reactions in ALD of Indium Gallium Zinc Oxide (IGZO), Jaan Cho, Hongik University, Republic of Korea; J. Cho, J. Jeong, Hanyang University, Republic of Korea; B. Shong, Hongik University, Republic of Korea

Indium gallium zinc oxide (IGZO) is considered as active material for thin-film transistors (TFTs) and NAND flash memory devices due to its high charge carrier mobility, low off-currents, and long-term stability. Along with the recent trend of miniaturization and structural complication of electronic and optoelectronic devices, atomic layer deposition (ALD) method is becoming essential. Especially, the elemental composition and the resulting material properties of multicomponent thin films can be precisely modulated with the ALD method. IGZO thin films with controllable composition can be manufactured using supercycle ALD by controlling the injection sequence and ratio of each elemental precursors [1]. However, in ALD of multicomponent materials, the atomic composition of the deposited films is often different from the ratio of the precursors injected during the deposition process. Such deviation in the composition of the multicomponent thin films versus the ALD recipe may originate from etching of an element in the substrate by another precursor during the deposition process [2]. In this study, the deposition and etching reactions between In-Ga-Zn elements during ALD is evaluated through density functional theory (DFT) calculations. Trimethylindium (TMI), trimethylgallium (TMG), and diethylzinc (DEZ) were considered as precursors; indium oxide (In₂O₃), gallium oxide (Ga₂O₃), and zinc oxide (ZnO) were used as substrate materials. It was found that DEZn has the highest

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reactivity, so that the etching of In or Ga by Zn would be the most preferable, possibly resulting in decrease of In and Ga and increased Zn content in the deposited films. Our results show good correspondence with experimentally observed dependency of the compositions of IGZO on the sequence of the supercycle ALD.

References [1] J. Alloys Compd. 2022, 903, 163876; [2] ACS Appl. Mater. Interfaces 2021, 13 (33), 40134.

3:15pm **ALD+ALE-MoA2-8 Student Award Finalist Talk: Atomic Layer Deposition of Semimetallic TiS₂ Contact Layer on MoS₂-based Thin Film Transistor for Contact Resistance Reduction, Jeongwoo Seo, H. Yoon, S. Lee, J. Yoo, Yonsei University, Korea; Y. Nam, J. Lim, Samsung Display Co., Ltd., Republic of Korea; S. Chung, H. Kim, Yonsei University, Korea**

Two-dimensional transition metal dichalcogenides (2D TMDCs) have been researched as promising materials for electronic devices owing to their outstanding electrical and mechanical properties. Among 2D TMDCs, molybdenum disulfide (MoS₂) has been considered as an ideal semiconducting material for thin film transistor (TFT) with high mobility, on/off ratio, and drain current level. However, high contact resistance at the interface between the metal and MoS₂ channel remains as a main challenge to be overcome for high performance MoS₂-based TFT.

High contact resistance at the interface originates from the high Schottky barrier height (SBH). Among various factors, metal-induced gap state (MIGS) causes Fermi level pinning, resulting in high SBH. Since MIGS occurs due to the unwanted gap states under the metal contact, semimetallic material as additional contact layer between the metal and semiconductor can be a solution to suppress the MIGS and further reduce the contact resistance.

In this study, ALD TiS₂ was used as semimetallic contact layer for the improvement in the contact between the channel and metal for MoS₂-based TFT. ALD TiS₂ (~10 nm) was directly deposited on the CVD-grown MoS₂, followed by Ti/Au evaporation for the metal deposition. Owing to the low temperature (~100°C) process of ALD TiS₂, smooth semimetallic TiS₂ can be deposited as contact layer without introducing defects in MoS₂ channel. Compared to the contact without TiS₂ contact layer, it showed significant improvement in electrical properties. Drain current has been increased about 100 times, owing to the semimetallic nature of TiS₂. In addition, threshold voltage, mobility, and subthreshold swing have been improved as well. These results suggest that ALD TiS₂ can be used as an appropriate contact layer for the high performance MoS₂-based TFT with low contact resistance.

Acknowledgement

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