Area Selective ALD
Room Tampa Bay Salons 3-4 - Session AS2-WeM
ASD Process II

Moderators: Anjana Devi, Leibniz Institute, IFW Dresden, **Nicholas Strandwitz**, Lehigh University

10:45am **AS2-WeM-12 Perfect Selectivity vs Practical Sustainability in ASD**, ***Nupur Bihari,*** Lam Research Corporation **INVITED**

Area selective deposition (ASD) continues to emerge as a pivotal technique for enabling next–generation semiconductor manufacturing, particularly as device geometries shrink and integration demands intensify. However, the long–standing goal of achieving perfectly selective growth often drives processes toward excessive complexity, high precursor consumption, and limited long–term sustainability. In this work, we explore the practical balance between achieving robust selectivity and maintaining overall process efficiency, emphasizing the potential benefits of reducing chemical usage without compromising integration–relevant performance. By adopting a more pragmatic viewpoint, we demonstrate that high–quality selectivity does not necessarily require aggressive surface treatments, extreme exposure times, or high precursor flows. Instead, a carefully tuned, eco–friendly process regime can deliver excellent material discrimination while significantly lowering chemical burden and overall environmental impact.

To evaluate performance under these more sustainable conditions, we employ top–down scanning electron microscopy (TDSEM) as a straightforward yet powerful metrology approach. TDSEM enables rapid assessment of nucleation behavior, feature–scale uniformity, and pattern fidelity, providing a clear window into the relationship between precursor flow, growth onset, and ultimate selectivity. Our results show that excellent selectivity can still be reliably achieved even when precursor usage is dramatically reduced, illustrating the feasibility of simplifying ASD processes for manufacturing–scale deployment. Electrical resistance–capacitance (RC) measurements and integrated wafer–level data further confirm that processes exhibiting modest deviations from perfect selectivity can nonetheless support high–performance interconnect scaling and patterning fidelity. These findings challenge the traditional assumption that optimal integration requires flawless selectivity and instead suggest that controlled, minimal nucleation on non–growth surfaces may be tolerable - especially when weighed against the benefits of lower cost, reduced chemical waste, and substantially improved throughput.

Taken together, this work highlights the value of shifting from a perfection–driven mindset to a more holistic framework that prioritizes precursor efficiency, environmental responsibility, and integration robustness. By demonstrating that sustainable, lower–chemistry ASD regimes can still meet stringent device requirements, we outline a more realistic and scalable pathway for adopting ASD in high–volume semiconductor manufacturing. This approach not only reduces overall process strain but also strengthens the connection between small–scale laboratory studies and real–world wafer–level performance, ultimately enabling faster development cycles and broader implementation of ASD–driven patterning strategies.

11:15am **AS2-WeM-14 Photoassisted Chemical Vapor Deposition as a Strategy for Area Selective Deposition of Ru:Implications for Developing an ALD Process**, *Christopher Brewer,* University of Texas at Dallas*; Rashmi Singh,* University of Florida*; James Pugh, Anjali Sharma,* University of Florida*; Amy Walker,* University of Texas at Dallas*;* ***Lisa McElwee-White,*** University of Florida

Photoassisted chemical vapor deposition (PACVD) is a potentially attractive technique for metallization of thermally sensitive substrates. Prior PACVD results from (η^3-allyl)Ru(CO)$_3$Br, CpRu(CO)$_2$Me, and (COT)Ru(CO)$_3$ have demonstrated that allyl and Cp ligands remain incorporated in deposits, while the COT ligand was not detected. Subsequently, a library of (η^4-diene)Ru(CO)$_3$ and (η^2-alkene)Ru(CO)$_4$ precursors that undergo photochemical ligand loss at room temperature has been prepared and their solution photochemistry studied. Using -CH_3, -OH, and -COOH terminated self-assembled monolayers (SAMs) as model substrates, we have investigated the use of these precursors in area selective deposition. We demonstrate that the (η^4-diene)Ru(CO)$_3$ precursors show a strong deposition preference onto -COOH functionalized SAMs, while (η^2-alkene)Ru(CO)$_4$ precursors show a deposition preference onto the -COOH and -OH functionalized SAMs. The -CH_3 functionalized SAMs are a non-growth surface for all the precursors screened. The deposition results will be discussed in context of precursor design for ASD and development of related ALD processes.

11:30am **AS2-WeM-15 Highly Selective Ru Growth on Metallic Substrates against Dielectric Surface via Inherent Area-selective Atomic Layer Deposition Using a Novel Ru Precursor**, ***Hideaki Nakatsubo,*** *Masato Iseki,* TANAKA PRECIOUS METAL TECHNOLOGIES Co., Ltd., Japan*; Shintaro Chiba,* EEJA Ltd., Japan*; Iaan Cho, Hyungjun Kim,* Yonsei University, Republic of Korea*; Bonggeun Shong,* Hanyang University, Republic of Korea*; Debananda Mohapatra, Jeongha Kim, Soo-Hyun Kim,* UNIST, Republic of Korea

Area-selective deposition via atomic layer deposition (AS-ALD) offers a bottom-up approach to fabricate complex and functional nanostructures, being robust for the scaled architectures even with any 3D structures compared to the conventional top-down approach using multi-patterning processes. Inherent-type AS-ALD is the most simplified process, exploiting intrinsic adsorption properties of the precursors depending on the substrates. Compared to inhibitor-assisted area-selective processes, the inherent AS-ALD also highlights practical advantages such as reducing fabrication steps or eliminating concerns of residual inhibitors, which is attractive for the application of interconnect metallization.

Although the inherent AS-ALD has typically suffered from a lower selectivity compared to that of inhibitor-assisted one, a higher inherent selectivity against Si-based dielectrics such as SiO_2, low-k or SiN is essential for the intended purposes (e.g., void-free/seamless bottom-up metallization). Therefore, we demonstrated high selectivity against SiO_2 via Ru thermal AS-ALD using a novel Ru precursor, [Ru(TMM)(*p*-cymene)], and O_2 as a reactant without any inhibitor or other area-selective activation methods. This precursor has two different ligands, trimethylenemethane (TMM) and isopropylmethylbenzene (*p*-cymene), and exhibits high thermal stability (> 400 °C). A previous report on this precursor revealed that a surprisingly long incubation period of >1000 cycles was observed on SiO_2 while only ~8 cycles were required on TiN at 300 °C [1], overcoming the challenges of high selectivity which previous Ru AS-ALDs have suffered from. Computational simulations in the same report also discovered that dissociative adsorption proceeds on metallic substrates such as Ru, but is energetically unfavorable on SiO_2, providing the theoretical support for the high inherent selectivity against SiO_2.

In this study, we expand our understanding of the inherent AS-ALD Ru on technologically important metallic substrates including Ru, TiN, Mo, W against dielectric substrates such as SiO_2, low-k, SiN, Al_2O_3. The results demonstrate that the high selectivity against dielectrics was confirmed both on blanket wafers and patterned substrates. We also discuss how process conditions affect the selectivity and the experimental factors required to emerge the selectivity with mechanistic insights.

[1] H. Nakatsubo *et.al.*, *Adv. Sci.*, **2025**, e19209.

11:45am **AS2-WeM-16 Mechanistic Insights into Area-Selective Etching of Ruthenium** , ***Iaan Cho,*** Yonsei University, Republic of Korea*; Soo-Hyun Kim,* Ulsan National Institute of Science and Technology, Republic of Korea*; Hyungjun Kim,* Yonsei University, Republic of Korea*; Bonggeun Shong,* Hanyang University, Republic of Korea

As interconnect linewidths continue to scale down, ruthenium (Ru) is being considered as an alternative to copper (Cu) owing to its favorable resistivity and reliability at reduced dimensions. For practical integration, area-selective deposition (ASD) is suggested as an alternative fabrication method to confine Ru growth to conductive growth regions while suppressing deposition on dielectric non-growth areas (NGAs) [1]. However, since nucleation of Ru on the NGAs such as SiO_2 can limit the applicability of the process, addition of oxidative etch-back steps within ASD are suggested to enhance the overall deposition selectivity [2]. In this study, the mechanistic origin of the selectivity in oxidative etching of Ru was investigated using machine-learning interatomic potential (MLIP) based energetic analyses and molecular dynamics (MD) simulations. Several different environments of Ru nuclei on metallic and dielectric substrates, such as Ru adatoms, sub-nanometer clusters, and extended heterointerfaces are considered. The results indicate that Ru species on dielectric surfaces are readily oxidized and desorb as volatile RuO_4 upon exposure to oxidant such as O_3, whereas Ru on metallic surfaces are less susceptible to oxidative loss under comparable conditions. This substrate-dependent reactivity upon oxidation and desorption is consistent with experimentally reported selectivity enhancements in the supercycle ASD processes. These results clarify the selective oxidative etching of Ru and provide a mechanistic basis for optimizing Ru ASD for advanced interconnect integration.

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