

ALD Fundamentals: Growth and Characterization

Room HB Plant Ballroom - Session AF1-TuM

ALD Precursor Design II

Moderators: Seán Barry, Carleton University, Canada, Charles H. Winter, Wayne State University

8:00am **AF1-TuM-1 Development in Thermal ALD Chemistry since 2010, Markku Leskelä**, University of Helsinki, Finland; *Georgi Popov*, ASM Microchemistry Ltd., Finland; *Miika Mattinen, Mikko Ritala*, University of Helsinki, Finland

We recently published a review on the recent trends in thermal ALD chemistry (1). The review highlighted new ALD precursors and process chemistries based on the ALD database found in atomiclimits.com (2) until the end of 2023. The paper compared the processes published before 2010 (769 processes) to those published after 2010 (942 processes). The number of materials deposited by thermal ALD shows steady increase being 227 before 2010 and reaching 539 at the end of 2023. The most popular material group is oxides which are processed both as binary and ternary compounds.

The ALD process development can be divided to two categories: curiosity and application driven research. In the curiosity driven research the aim is to expand the portfolio of ALD processes by adding new elements and materials to the portfolio. From recent literature ALD processes for less common elements Be, Re, Os can be mentioned. However, the development of new ALD processes is clearly more application-driven and motivated by the most important application areas of ALD: microelectronics, energy technology, and catalysis. Need of new materials in these applications is seen in increased intensity of the development of ALD processes for metals, 2D transition metal dichalcogenides, and halides

Metal halides, alkoxides, alkyl compounds, β -diketonates, and amides/imides are traditional ALD metal precursors. After 2010, amides/imides have increased their importance in new ALD processes. However, heteroleptic complexes containing two or more above mentioned ligands are the largest precursor type in new processes. Metal processes require the use of reducing agents and therefore research on novel reducing agents is vital.

In the presentation we summarize our most important findings from ALD literature between 2010 and 2023 and highlight the newest results from the last two years. The number of published new processes in 2024-2025 seems to stay at the level of the previous years.

References

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8:15am **AF1-TuM-2 Designing Stable Organosilane Precursors for High Quality Silicon Oxide, Taylor Hayes, Anjali Patel, Matthew MacDonald, Manchao Xiao, Haripin Chandra**, EMD Electronics, The Electronics business of Merck KGaA, Darmstadt, Germany

High-quality silicon oxide in a 3D NAND structure is an important material used as an electrical insulator and to form charge trap layers. Additionally, due to the nature of the 3D NAND structure, which achieves an extremely high aspect ratio with several hundred layers, atomic layer deposition (ALD) is critical for obtaining a conformal, high-quality SiO₂ film.

In general, process temperature correlates with film quality; higher process temperatures yield higher quality films. However, in ALD depositions, higher process temperatures necessitate that the organosilane precursor remains stable and self-limiting.

In this paper, we will discuss methods to improve the thermal stability of common organosilane precursors, such as tris(dimethylamino)silane (3DMAS), and evaluate decomposition mechanisms using density functional theory (DFT) modeling.

The Si-H bond in 3DMAS is the weakest link and is prone to thermal decomposition. Replacing the Si-H bond with a Si-CH₃ bond, as seen in tris(dimethylamino)methylsilane (3DMAMS), enhances thermal stability by reducing the energetic feasibility of decomposition pathways. Furthermore, substituting the amino group with a CH₃ group, as in dimethylaminotrimethylsilane (DMATMS), also improves precursor thermal stability.

This paper will explore how higher deposition temperatures and molecular structure significantly influence the experimental film properties achieved using 3DMAS, 3DMAMS, and DMATMS.

8:30am **AF1-TuM-3 Development of Novel Liquid Zr Precursors with Excellent Thermal Stability for High-Temperature ALD Processes in Next-Generation DRAM Capacitors, Taeyoung Lee, Sunyoung Baik, Sungjun Ji, Shinbeom Kim, Woongjin Choi, Kunhee Kim, Yiun Park, Sangbum Han**, EGTM Co., Ltd. R&D Center, Republic of Korea

With the continuous scaling of DRAM devices, dielectric materials that possess both excellent conformality in high aspect ratio structures and high dielectric constants (high-k) have become increasingly critical. Typically, high-temperature deposition processes are essential for the formation of the tetragonal phase of ZrO₂ thin films, which maximizes the dielectric constant. However, conventional cyclopentadienyl (Cp)-based Zr precursors suffer from limited thermal stability at high temperatures, leading to significant issues such as carbon impurity incorporation and particle generation. To address these challenges, we developed a novel liquid Zr precursor (EGTM Zr) with significantly improved thermal stability compared to conventional precursors. Thermal analysis (TGA and DSC) and visual thermal stability tests confirmed that EGTM Zr exhibited negligible discoloration or decomposition residues even after prolonged exposure to temperatures exceeding 200°C. Furthermore, its thermal decomposition temperature was 312°C, approximately 10°C higher than that of the conventional Cp-Zr precursor. Notably, ALD process evaluations demonstrated that the EGTM Zr precursor has a wider ALD process window of 280–380 °C, which is approximately 80°C wider than that of the reference precursor due to its enhanced thermal stability. This wider window allows for higher process temperatures, which promotes the formation of the high-k tetragonal crystalline phase instead of the lower-k amorphous phase, thereby enhancing device performance. Moreover, thanks to its excellent thermal stability, the EGTM Zr precursor can effectively eliminate issues related to carbon impurity incorporation and particle generation. Additionally, the precursor demonstrated superior step coverage compared to the reference, while the widened process window enables the deposition of high-quality, uniform thin films. Consequently, the EGTM Zr developed in this study is expected to be a promising candidate for next-generation high-performance DRAM capacitor applications.

8:45am **AF1-TuM-4 A New Zinc Amidinate Precursor for Thermal and Plasma-Enhanced ALD of ZnO, Pierre-Alexandre Escarcega, Jean-Pierre Glauber, Lars Giebler, Harish Parala, Anjana Devi**, IFW Dresden, Germany

As an n-type semiconductor with remarkable electronic and optical properties, zinc oxide (ZnO) is applicable for various applications. Its wide direct bandgap of 3.3 eV and large exciton binding energy of about 60 meV make it especially promising for use in optoelectronics.^[1] Further attributes, including high electron mobility, optical transparency, piezoelectricity, and biocompatibility, render it a versatile material for diverse technological applications, including channel layer in thin-film transistors (TFTs)^[2,3] or sensing.^[4] However, the integration and efficiency of ZnO in advanced technologies depend on overcoming fabrication challenges to reliably produce high-quality, high-purity thin films and nanostructures. In this regard, atomic layer deposition (ALD) and its variant, plasma-enhanced ALD (PEALD),^[5] were shown to enable the deposition of high-quality, stoichiometric, and conformal films, with atomic-level control over film thickness, even at low temperatures. Despite the sophistication of such deposition techniques, developing advanced processes requires new precursors with optimized properties to broaden process windows and enhance film characteristics.

Our group recently reported a versatile Zn precursor, [Zn(DMP)₂],^[6] a non-pyrophoric alternative to the widely used DEZ, enabling the growth of high-purity ZnO thin films via ALD and PEALD over a broad temperature range. The ZnO thin films were mainly amorphous or of low crystallinity. In our recent attempts to identify new Zn precursors that can enable crystalline ZnO layers at low temperatures, we were successful in synthesizing bis(N,N'-diisopropylacetamidinato)zinc, [Zn(dpamd)₂]. The target compound was successfully synthesized by stabilizing the central zinc atom through the delocalized π system of the amidinate ligand backbone.^[7] While this ligand enhances the thermal stability, its all-nitrogen coordination guarantees sufficient reactivity.

[Zn(dpamd)₂] is a volatile compound with physico-chemical properties suitable for both thermal and plasma ALD. Additionally, its synthesis can be scaled up, and it is non-pyrophoric, a significant advantage for safety and handling. The thermal properties of [Zn(dpamd)₂] were examined using

thermogravimetric analysis (TGA) (Figure 1), which showed promising evaporation behavior. Based on these results, $[Zn(dpamd)_2]$ was used in a thermal ALD process with water as the co-reactant, as well as in a PEALD process with O_2 plasma as the co-reactant. Both methods yielded stoichiometric, high-purity ZnO thin films on Si(100) substrates with self-limiting growth, confirming $[Zn(dpamd)_2]$ as a promising and versatile new ALD precursor.

9:00am **AF1-TuM-5 Amidates and Dimethylaminopropyl Groups as Innovative Ligands: New Opportunities for Ru Precursors**, *Jorit Obenluneschloß*, Leibniz Institute, IFW Dresden, Germany; *Niklas Huster*, Ruhr University Bochum, Germany; *Harish Parala*, Leibniz Institute, IFW Dresden, Germany; *Michael Gock*, *Michael Unkrig-Bau*, *Detlef Gaiser*, Heraeus Precious Metals GmbH & Co. KG, Germany; *Anjana Devi*, Leibniz Institute, IFW Dresden, Germany

As the semiconductor industry moves to the 2 nm node and below, Cu as well-established interconnect material in integrated circuits (IC's), is reaching its limits due to diffusion and electromigration. Ru is the most promising replacement candidate in next-generation microchips as the interconnect metal.^[1] Its resistivity is less dependent on thickness than that of Cu and Ru can be introduced without liner or diffusion barrier layers.^[2] A reduction of up to 60% in resistance is expected when Ru vias are used with Cu wires.^[3]

To deposit thin films uniformly on complex-structured substrates, such as those in next-generation gate-all-around field-effect transistors (GAAFETs), atomic layer deposition (ALD) is the preferred method. However, finding suitable Ru precursors that meet ALD requirements, such as high vapor pressure, thermal stability, and high reactivity, is a challenging task for researchers in both academia and industry.

Herein, we showcase and compare two Ru precursors with novel ligand concepts: $[\eta^5\text{-CpRu}(\text{CO})_2(\text{DMP})]$ or dicarbonyl(η^5 -cyclopentadienyl)(3-dimethylaminopropyl)ruthenium, trade name **HeRu31**,^[4] and $[\text{Ru}(\text{CO})_2(\text{N-sBuPrAD})_2]$ or dicarbonyl bis(*sec*-butylisopropylamidate)ruthenium, trade name **HeRu43**.^[5] The former combines the proven half-sandwich structure dominated by a Cp ring with an aminopropyl ligand, which enhances the compound's stability while maintaining excellent reactivity. The reactive Ru-C bonds of this precursor enable facile deposition of Ru metal. The latter precursor relies on the 1,3-N,O-chelating amidate ligand. Introducing mixed N,O-coordination is a promising approach to prevent carbon contamination in deposited thin films. This coordination should also enable facile deposition via the Ru-N bond.

Employing both concepts, complexes with promising thermal properties for ALD have been obtained, as evidenced by TGA (Fig. 1). Both classes are liquid at room temperature, a highly desirable trait for a precursor intended for large-scale implementation. The compounds were identified and thoroughly characterized by NMR, LIFDI-MS, FTIR, EA, and SC-XRD. An ALD process using **HeRu31** and O_2 was developed to deposit dense, homogeneous Ru metal thin films at 280 °C with low resistivities. These new precursors show great promise to advance the deposition abilities for Ru and enable the foreseen adaptation of Ru at the smallest levels of ICs.

References

- [1] L. G. Wen, et al., *ACS Appl. Mater. Interfaces* **2016**, *8*, 26119–26125.
- [2] C. Adelman, et al. in *IEEE Int. Interconnect Technol. Conf.*, IEEE, San Jose, CA, USA, **2014**, pp. 173–176.
- [3] M. H. Van Der Veen, et al. in *2024 IEEE Int. Interconnect Technol. Conf. IITC*, IEEE, San Jose, CA, USA, **2024**, pp. 1–3.
- [4] M. Gock, et al., *Neue Halbsandwichkomplexe Des Rutheniums*, **2024**, WO2024223093A1.
- [5] J. Obenluneschloß, et al., *Dalton Trans.* **2026**, DOI 10.1039/d5dt02610e.

9:15am **AF1-TuM-6 Functional Precursor-Driven High-k Atomic Layer Deposition with Improved Throughput and Dielectric Performance**, *Min Chan Kim*, *Seong A Shin*, *Hae Lin Yang*, *Jin-Seong Park*, Hanyang University, Korea

With rapid AI advancements intensifying semiconductor demands, interest in high-k dielectrics for logic and memory applications is increasing [1]. High-k materials enable strong gate control with reduced equivalent oxide thickness (EOT), overcoming scaling limitations. Their high dielectric constant primarily arises from strong ionic polarization associated with a narrow bandgap. However, this narrow bandgap lowers the energy barrier for carrier injection, making high-k dielectrics susceptible to increased leakage current. Elevated leakage leads to charge trapping, which degrades

threshold voltage stability and overall device reliability [2]. Consequently, suppressing leakage current is essential for practical high-k integration.

In this study, we present a strategy to stabilize high-k dielectric thin films through the incorporation of a functional precursor during film growth. Density functional theory (DFT) calculations reveal that the functional precursor, introduced between the metal precursor and the reactant, induces a β -hydrogen elimination reaction that selectively removes residual bulky ligands, thereby exposing reactive surface sites and promoting a chemically stabilized growth surface. This ligand removal mechanism is experimentally confirmed by secondary ion mass spectrometry (SIMS), which shows a pronounced reduction in residual carbon and hydrogen species. Importantly, ligand elimination does not result in void formation but instead facilitates the formation of a denser and chemically more stable dielectric film. X-ray photoelectron spectroscopy (XPS) analysis further indicates a reduced oxygen vacancy concentration and an increased metal-oxygen (M–O) bonding ratio, accompanied by increased film density and reduced surface roughness. As a result of this combined chemical and structural stabilization, metal-insulator-metal (MIM) capacitor measurements exhibit a substantial suppression of leakage current and an increase in the dielectric constant. These results demonstrate that functional-precursor-assisted stabilization effectively mitigates leakage-induced reliability degradation while preserving the intrinsic advantages of high-k dielectrics.

Reference

- 1) Kim, Se Eun, et al. "Atomic layer deposition of high-k and metal thin films for high-performance DRAM capacitors: A brief review." *Current Applied Physics* **64** (2024): 8-15.
- 2) Wilk, Glen D., Robert M. Wallace, and Jám Anthony. "High- κ gate dielectrics: Current status and materials properties considerations." *Journal of applied physics* **89.10** (2001): 5243-5275.

9:30am **AF1-TuM-7 From Facile Routes for Mid-Valent Molecular Synthons to Vapor Phase Growth of Molybdenum-Based Thin Films**, *Titel Jurca*, University of Central Florida

INVITED

ALD technology is established in semiconductor manufacturing and is emerging across broad areas of biotechnology to catalysis. The broad range of substrates, deposition temperatures, and other environmental factors governing the growth and fabrication of this myriad of materials and devices is underpinned by the availability of suitable molecular precursors. Thus, the understanding-based design of novel molecular precursors is pivotal to the continued development of ALD and related vapor phase thin film growth processes (area selective ALD, ALE, CVD). One can envision that a broad range of temperature windows, and ligand chemistries to enable nucleation and subsequent growth are necessary; as well as the design rules to tune those properties on the molecular scale. Currently, the scope of available molecular precursors across the majority of metals of interest is narrow, as is the understanding-based knowledge which governs their design.

For practical reasons, the majority of precursor synthesis often stems from a narrow pool of stable, commercially available, and often fiscally reasonable metal halide precursors. To broaden the pool of ALD precursors, we begin by broadening the pool of accessible metal halide salts; *the precursors to the precursors*. Using stoichiometric silanes, high-valent, mid d-block metal (e.g. Mo, W, Nb, Ta) halides can be controllably, stoichiometrically reduced to highly reactive mid-valent synthons (e.g. MoCl_3 from MoCl_5). The reactions are facile and produce only H_2 and recoverable and reusable chlorosilanes as byproduct. The resulting mid-valent metal chlorides form ideal starting points towards new precursors for ALD.

From this thrust, we leveraged an MoCl_3 synthon to generate the first homoleptic Mo(III)tris-amidinate and guanidinate species. These complexes expand the known scope of tris(amidinate) and tris(guanidinate)M(III) molecules to now include Mo, and add to the very limited knowledge of homoleptic mononuclear Mo(III) coordination complexes. We explore the impact of modifications to the ligand framework, and their implications on synthetic viability, volatility and applicability towards the growth of Mo-based materials by ALD.

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