

ALD Fundamentals

Room Hall 3A - Session AF-MoA

Precursors and Chemistry: Precursor Design, New Precursors, Process Development I

Moderators: Charles Dezelah, ASM, Prof. Dr. Charles H. Winter, Wayne State University

4:00pm **AF-MoA-11 ALD of Copper and Bismuth Using Pinacolborane as a Reducing Agent**, Anton Vihervaara, T. Hatanpää, K. Mizohata, M. Ritala, University of Helsinki, Finland

High quality metal thin films are an essential material class in the development of new technologies. Copper is the foremost interconnect material in microelectronics and though there is incentive to replace it with other metals, copper will remain an important metal for interconnects for the immediate future. Bismuth on the contrary is less commonly used thin film material but possesses many intriguing characteristics. It has many potential applications suggested in the literature including semiconductor devices, superconductors, and anodes for batteries. These applications require high-quality thin films deposited uniformly over large areas and on 3D structures.

Atomic layer deposition (ALD) is the best method for the manufacturing of complex 3D structures. Several ALD processes for Cu metal already exist, but new ones are constantly sought out to overcome limitations of the existing ones. Bismuth on the other hand does not have such a range of existing ALD processes. As far as we are aware, only one process can be found in literature. [1]

In order to deposit very thin but also completely continuous films, it is important to keep the deposition temperature low. Typically, lower deposition temperatures lead to smaller grains and thus to smoother films. We study novel ALD precursors with a focus on reducing agents, since they are less explored than the metal precursors. To our knowledge pinacolborane has not been used in ALD experiments before, though it has been suggested as a potential reducing agent [2]. Now we investigated it in actual ALD experiments with metal alkoxides. The idea behind using the pinacolborane is that the favorable formation of the strong B-O bond would strip alkoxide ligands from metal precursors.

In our study, pinacolborane was combined with two metal alkoxides, $\text{Cu}(\text{dmap})_2$ and $\text{Bi}(\text{OCMe}_2\text{Pr})_3$, to deposit the respective metals. Depositions were done at low temperatures of 80-130 °C for Cu and 90 °C for Bi. ALD characteristics were confirmed for the Cu deposition. At 100 °C growth rate of 0.12 Å/cycle was observed. Continuous film deposited at 100 °C had a resistivity of 4.2 $\mu\Omega\text{cm}$. Bismuth films were highly oriented and consisted of platelets parallel to the substrate surface. Both films contained only small amounts of impurities.

[1] Precursors and Processes for the Atomic Layer Deposition of Bismuth Metal Thin Films, Daniel Beh, Wayne State University; Z. Devereaux, T. Knisley, Applied Materials; C. Winter, Wayne State University, presented at the 23rd International Conference on Atomic Layer Deposition, Bellevue, July, 2023.

[2] Winter, C. H., Knisley, T. J. US Pat. Appl. Publ. US 2015/0167158 A1.

4:15pm **AF-MoA-12 Ligand Optimization of Volatile Cobalt-Alkoxide ALD Precursor**, Atsushi Sakurai, A. Yamashita, T. Yoshino, Y. Ooe, K. Takeda, M. Enzu, M. Hatase, A. Nishida, ADEKA CORPORATION, Japan

Co thin films have been applied for interconnect applications on many electronic devices to support Cu-based interconnects or to replace Cu itself with device miniaturization. It is extrapolated that the conventional CVD precursor, CCTBA: $\text{Co}_2(\text{CO})_6(^t\text{BuC}=\text{CH})$, could continue to assist in interconnect fabrication. Due to the poor reported thermal stability and area selectivity of CCTBA, however, there has been a great deal of effort to identify an improved Co precursor [1]. For example, Co-diazabutadiene is an attractive precursor to realize area selective Co film growth with thermal ALD processing [2]. $\text{CoCl}_2(\text{tmeda})$ [3], Co-amidinato [4], Co-cyclopentadienide [5] and Co-diketonato [6] were also investigated for specific process requirements. Despite significant development work on Cu-alkoxide precursors, Co-alkoxide precursors remain less documented in the literature [7].

This presentation will share the basic chemistry of Co-alkoxides and how to obtain high vapor pressure, which is a critical property for ALD film growth. In comparison with Cu-alkoxides, high vapor pressure Co-alkoxides are not so easy to obtain. After many kinds of aminoalcohol ligands were

investigated, monomeric SCBA-1: $\text{Co}[\text{OCH}(^t\text{Bu})\text{CH}_2\text{N}(\text{Et})(\text{Me})]_2$ was found to have the optimal vapor pressure (Figs.1 & 2).

ALD Co films grown with SCBA-1 will be also presented. Plasma-enhanced ALD (PEALD) was better to obtain pure Co metal films with low resistivity, though thermal ALD might be preferred for some applications. For future improvement, a strong co-reactant will be necessary for thermal ALD process using SCBA-1.

Reference: [1] ALD2018, S.Ivanov, [2] ALD2017, M.Kerrigan, [3] ALD2018, K.Väyrynen, [4] ALD2019, A.Nishida, [5] ALD2020, G.V.Straaten, [6] ALD2021, N.M.K.Linn, [7] ALD2012, T.J.Knisley

4:30pm **AF-MoA-13 Expanding the tert-Butylimido Framework Beyond Molybdenum: New Refractory Metals and Ligands**, Kieran Lawford, Carleton University, Canada; M. Land, Dalhousie University, Canada; E. Goodwin, Carleton University, Canada; K. Robertson, St. Mary's University, Canada; S. Barry, Carleton University, Canada

Refractory metals (Nb, Ta, Mo, W, Rh; sometimes V, Cr) and their alloys can be found in a variety of applications ranging from dry lubricants, rocket nozzles, surgical equipment, and as protective layers applied to cutting tools to improve cutting and reduces tool wear.¹ We have previously shown great success with incorporating tert-butylimido ligand frameworks into volatile molybdenum deposition precursors,² so we decided to explore the analogous Cr, W, V, Cr, Nb, and Ta compounds.³ We prepared $(^t\text{BuN})_2\text{MCl}_2\text{-dad}$ (M = Cr, Mo, W, dad = 1,4-di-tert-butyl-1,3-diazabutadiene) by addition of dad to coordinatively unsaturated $(^t\text{BuN})_2\text{MCl}_2$ compounds.³ The ancillary dad ligand was chosen because it has previously been shown to yield a volatile and thermally stable scaffold in the Mo analogue.² Following an analogous protocol, the mono imido compounds, $(^t\text{BuN})\text{MCl}_3\text{-dad}$ (M = V, Nb, Ta), were also prepared.³

These compounds were fully characterized using common spectroscopic techniques including multinuclear NMR, FT-IR, and single-crystal X-ray diffraction.³ The volatility of these compounds was measured using thermogravimetric analysis (TGA) and the V, Mo,² and W compounds exhibited good volatilities, with onsets of evaporation between 55 °C and 135 °C.³ We also studied their thermal stabilities by differential scanning calorimetry (DSC) and observed they all undergo decomposition between 154 °C and 189 °C, suggesting similar decomposition pathways³.

EI-HRMS suggests that these compounds decompose with their M=N bond intact, so we decided to explore these compounds as vapour phase precursors of the corresponding metal nitrides. Preliminary deposition experiments showing that these precursors can be used for the single source CVD of MN₂ films.³ This presentation will further discuss preliminary ALD process development for the V, Mo, and tungsten compounds for the ALD of metal-nitride films on a homemade ALD tool.

1. Pierson, H. O. The Chemical Vapor Deposition (CVD) of Refractory Metal Carbides. *High Temp. Mater. Process.* **1993**, 11, 239-246.
2. Land, M. A.; Bačić, G.; Robertson, K. N.; Barry, S. T. Thermal Stability and Decomposition Pathways in Volatile Molybdenum(VI) Bis-imides. *Inorg. Chem.* **2022**, 61(12), 4980-4994.
3. Lawford, K.; Land, M. A.; Goodwin, E.; Robertson, K. N.; Barry, S. T. Synthesis, Characterization, and Single-Crystal X-ray Structures of Refractory Metal Compounds as Precursors for the Single-Source Chemical Vapor Deposition of Metal Nitrides. *Inorg. Chem.* **2023**, 62(51), 21061-21073.

4:45pm **AF-MoA-14 Alkoxide Complexes as Precursors for Coinage Metal and Main Group Element Thermal ALD**, David Emslie, Department of Chemistry, Canada; M. Al Hareri, N. Hoffman, McMaster University, Canada

Thermal ALD methods have been developed to deposit thin films of a wide range of materials. Methods to deposit metal oxides and metal nitrides are now well established, often involving reactions with O₂, O₃, H₂O or NH₃.¹ However, deposition of elemental metals²⁻⁴ (or semimetals) can be particularly challenging, because it typically requires reduction of an element in a positive oxidation state in a precursor complex to the zero oxidation state in the metal (or semimetal) film. This reduction reactivity becomes increasingly challenging for more electropositive elements, and in ALD the choice of reductant (the co-reactant) is limited by the requirement for both the co-reactant and the reaction byproducts to be volatile and thermally stable. Furthermore, suitable choices of reducing co-reactant will depend strongly on the element to be deposited, the oxidation state of the

element in the precursor complex, and the ligands in the precursor complex.

This presentation will describe the development of novel thermal ALD methods to deposit coinage metal and main group elements using alkoxide precursors in combination with pinacolborane (HBpin). The envisioned chemistry involves exchange of hydride and alkoxide groups between the precursor and HBpin, where the driving force for film deposition is the formation of very strong B–O bonds, combined with eventual H₂ elimination. This work also includes the development of new coinage metal precursors, and a study of their volatility, thermal stability, and reactivity.

References

- (1) Miikkulainen, V.; Leskelä, M.; Ritala, M.; Puurunen, R. L. Crystallinity of inorganic films grown by atomic layer deposition: Overview and general trends, *J. Appl. Phys.* **2013**, *113*, 021301.
- (2) Emslie, D. J. H.; Chadha, P.; Price, J. S. Metal ALD and pulsed CVD: Fundamental reactions and links with solution chemistry, *Coord. Chem. Rev.* **2013**, *257*, 3282-3296.
- (3) Knisley, T. J.; Kalutarage, L. C.; Winter, C. H. Precursors and chemistry for the atomic layer deposition of metallic first row transition metal films, *Coord. Chem. Rev.* **2013**, *257*, 3222-3231.
- (4) Hagen, D. J.; Pemble, M. E.; Karppinen, M. Atomic layer deposition of metals: Precursors and film growth, *Appl. Phys. Rev.* **2019**, *6*, 041309.

5:00pm **AF-MoA-15 Fluorinated Silver Alkoxides as Precursors for Atomic Layer Deposition**, *Nick A. Hoffman*, *D. Emslie*, McMaster University, Canada Elemental silver thin films are particularly desirable for photonic, electronic, catalytic, and biological applications.[i] Previously reported methods for thermal Ag ALD are scarce and suffer from poor film morphology.[ii] Additionally, the low thermal stability of Ag(I) precursors often necessitates delivery via direct liquid injection, adding complexities to reactor design.[iii] Herein we present the synthesis and characterization of a series of new fluorinated silver alkoxide complexes, an assessment of their thermal stability and volatility, and their application as precursors for thermal ALD of silver metal.

The fluorinated silver alkoxide complexes, [Ag{OC(CF₃)₃}(PR₃)₂]_n, are readily synthesized following a simple and scalable one-pot procedure. These compounds can be sublimed *in vacuo*, and thermogravimetric analysis (TGA) was conducted to evaluate their thermal properties. Solution-state reactions with various co-reactants yielded silver metal, suggesting a high degree of suitability towards novel thermal ALD processes. The precursor [Ag{OC(CF₃)₃}(PⁱPr₃)₂]₂ was selected as the most promising candidate for ALD, and was used to develop a new method for Ag thermal ALD.

References:

- [i] Abbas, N.; Shad, M. R.; Hussain, M.; Muhammad, S.; Mehdi, Z.; Sajjad, U. Fabrication and characterization of silver thin films using physical vapor deposition, and the investigation of annealing effects on their structures. *Mater. Res. Express* **2019**, *6*, 116437.
- [ii] See, for example:(a) Chalker, P. R.; Romani, S.; Marshall, P. A.; Rosseinsky, M. J.; Rushworth, S.; Williams, P. A. Liquid injection atomic layer deposition of silver nanoparticles. *Nanotechnology* **2010**, *21*, 405602; (b) Masango, S. S.; Peng, L.; Marks, L. D.; Van Duyn, R. P.; Stair, P. C. Nucleation and Growth of Silver Nanoparticles by AB and ABC-Type Atomic Layer Deposition. *J. Phys. Chem. C* **2014**, *118*, 17655-17661; (c) Mäkelä, M.; Hatanpää, T.; Mizohata, K.; Meinander, K.; Niinistö, J.; Räisänen, J.; Ritala, M.; Leskelä, M. Studies on thermal atomic layer deposition of silver thin films. *Chem. Mater.* **2017**, *29*, 2040-2045; (d) Golrokhi, Z.; Marshall, P. A.; Romani, S.; Rushworth, S.; Chalker, P. R.; Potter, R. J. The influence of tertiary butyl hydrazine as a co-reactant on the atomic layer deposition of silver. *Appl. Surf. Sci.* **2017**, *399*, 123-131.
- [iii] Golrokhi, Z.; Chalker, S.; Sutcliffe, C. J.; Potter, R. J. Self-limiting atomic layer deposition of conformal nanostructured silver films. *Appl. Surf. Sci.* **2016**, *364*, 789-797.

5:15pm **AF-MoA-16 Atomic Layer Deposition of Niobium Carbonitride Thin Films**, *Paloma Ruiz Kärkkäinen*, *T. Hatanpää*, *K. Mizohata*, *M. Putkonen*, *M. Ritala*, University of Helsinki, Finland

While the development of transition metal carbide (TMC) and, particularly, transition metal carbonitride ALD is still in its early stages, transition metal nitrides (TMNs) have numerous well-established processes. The high melting points, outstanding catalytic properties, chemical inertness, and tunable work functions of TMNs and TMCs offer great advantages over metal films while retaining excellent conductivity. The attractive properties of TMCs and TMNs arise from their unique structures, which combines

ionic, covalent, and metallic bonding. Their current and future applications include energy storage, quantum computing, low-cost catalysis, and in semiconductor device contacts, barrier-free interconnect materials and barriers themselves. Furthermore, they exhibit continuity at low film thicknesses, which remains a challenge for metal ALD.

In this work, we present for the first time ALD of NbC_xN_y films. Only a few metal carbonitride materials, such as WC_xN_y, TiC_xN_y, and TaC_xN_y, have previously been deposited with ALD.¹ The ALD of NbC_x is still relatively unexplored with only one process for an amorphous film.² We deposited NbC_xN_y films with NbF₅ and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine [(Me₃Si)₂DHP] at 200–450 °C. The films are crystalline as-deposited and the growth rate saturates to ~1.2 Å/cycle with respect to both precursors at 425 °C. The films show uniform resistivity (~150 μΩcm) across the 5 x 5 cm² substrates. We demonstrate process compatibility on a wide range of substrates, such as Si, TiN, and Mo.

TMCs and TMNs both consist of metal lattices with either C or N in the interstitial sites. Consequently, distinguishing carbide and nitride phases from carbonitrides with common characterization methods such as XRD and XPS is an extremely difficult task.³ Aside from the challenge of determining which carbide and nitride phases the films consist of, the most demanding aspect is differentiating whether the films consist of separate NbC_x and NbN_y phases or NbC_xN_y. We will address the characterization challenges of carbonitrides by conducting extensive analysis with methods such as XRD, XPS, Raman, and ToF-ERDA. We will discuss tuning the properties, such as resistivity and morphology, as well as explore the superconductivity of the films to assess their potential for future applications.

- (1) *Database of ALD processes*. DOI: 10.6100/alddatabase. www.atomiclimits.com/alddatabase (accessed 2024-01-30).
- (2) Klug, J. A. et al. *Journal of Physical Chemistry C* **2011**, *115* (50), 25063–25071.
- (3) Ruiz Kärkkäinen, P. et al. Atomic Layer Deposition of Molybdenum Carbide Thin Films. Manuscript submitted.

5:30pm **AF-MoA-17 Using ALD Precursors as Inhibitors During Area-selective ALD**, *Marc Merckx*, *P. Yu*, *S. van der Werf*, *A. de Jong*, *E. Kessels*, Eindhoven University of Technology, Netherlands; *T. Sandoval*, Universidad Tecnica Federico Santa Maria, Chile; *A. Mackus*, Eindhoven University of Technology, Netherlands

In the pursuit to develop area-selective ALD processes with a high selectivity, the main question that needs to be answered is how to effectively block the adsorption of ALD precursors on the areas where deposition is not desired. One of the most studied instances of precursor blocking is self-limiting precursor adsorption during ALD, i.e., precursor adsorption is blocked when the surface is saturated by precursor adsorbates. To exploit this knowledge, the field of area-selective deposition is exploring the use of plasma-assisted ALD precursors (i.e. precursors that do not deposit material when exposed to a thermal co-reactant) as inhibitors for selective thermal ALD processes.[1,2] However, it can be expected that not all ALD precursors block precursor adsorption equally well. By studying the blocking mechanisms of ALD precursors against other precursor chemistries, important insight can be gained into how to design or select effective inhibitor molecules for area-selective ALD. In this contribution, we systematically study the blocking of ALD precursor adsorption by another ALD precursor molecule for a range of different precursor chemistries as a model system for precursor blocking.

To study the blocking efficiency of ALD precursors, a three step (i.e. ABC-type) ALD cycle was employed. During steps A and B, precursor 1 and precursor 2 are sequentially dosed, such that precursor 2 should be largely blocked by precursor 1. Finally, in step C, O₂ plasma is used as the co-reactant to remove all precursor ligands from the surface. The fraction of material that is deposited by precursor 2 in the resulting film was measured by x-ray photoelectron spectroscopy (XPS) and used as a metric for how effective precursor 1 can block precursor 2. Precursor blocking was studied for bis(diethylamino)silane (BDEAS), tetrakis(dimethylamino)titanium (TDMAT), tert-butylimido-tris(dimethylamino)tantalum (TBTDMT), tris(dimethylamino)cyclopentadienylhafnium (HyALD), and trimethylaluminum (TMA). In general, it was observed that precursors that were effective at blocking precursor adsorption as precursor 1 were also difficult to be blocked when used as precursor 2, and vice versa. In addition, it was found that a CH_x termination is preferred over alkylamino termination for effective precursor blocking. In this contribution, the role that packing, reactivity, and ligand chemistry play in precursor blocking will be discussed.

Monday Afternoon, August 5, 2024

[1] Soethoudt *et al.*, *J. Phys. Chem. C***124**, 7163 (2020)

[2] Nguyen *et al.*, *Nat. Commun.***13**, 7597 (2022)

ALD Fundamentals

Room Hall 3 - Session AF-MoP

ALD Fundamentals Poster Session

AF-MoP-1 Depositing a Uniform Thin Film of Al₂O₃ Using Atomic Layer Deposition (ALD) onto 2D Electronics to Provide Protective Capping and Surface Passivation, S. Lee, J. Lee, A. Cho, D. Ryu, **Hyunbin Chung**, K. Kim, T. Choi, Sejong University, Republic of Korea

Our research focuses on the utilization of passivation layers in semiconductor products to shield materials from environmental degradation. These layers must demonstrate high chemical resistance and a low surface recombination rate to effectively protect the semiconductor surface. Aluminum oxide emerges as a suitable material for such layers due to its excellent chemical resistance, etch selectivity, density (2.5-3.8 g/cm³), and low dielectric constant (ranging between approximately 4 and 9). We investigate the properties of aluminum oxide through atomic layer deposition (ALD) parameter control and post-treatment methods like rapid thermal annealing (RTA) and UV treatment.

Acknowledgements

1. This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT). (No. NRF-2022M3D1A2054488)
2. This work acknowledges the support of the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF; Grant Mo. NRF-2021R1A2C2010781).

AF-MoP-2 Developments in Processing Large Area 2D Materials and Metals via ALD, **Nils Boysen**, R. Neubieser, Fraunhofer IMS, Germany; F. Zimmermann, K. Brinkmann, University of Wuppertal, Germany; M. Michel, Fraunhofer IMS, Germany; T. Riedl, University of Wuppertal, Germany; A. Devi, Ruhr University Bochum, Germany

ALD processing of 2D materials and metals are in great demand to realize next-generation devices with intricate structures and feature sizes in the nanometer regime. The joint research activities between RUB and IMS in collaboration with BUW have focused on the rational development of new precursors and ALD processes on chip- and wafer-level (8"). High quality materials such as MoS₂, WS₂, Ag, and Cu were realized among others, which are highly relevant for different micro- and optoelectronic applications.

The layered 2D materials MoS₂ and WS₂ possess unique functional properties which can be exploited for a variety of applications. In our recent studies, we have developed new MoS₂ and WS₂ ALD processes on 8" Si wafers with promising characteristics of the deposited materials. The thermally-driven ALD process with an amide-based Mo precursor [Mo(NMe₂)₄] and H₂S yielded MoS₂ layers at very low deposition temperature of 100 °C (Figure 1) on glass and Si/SiO₂ substrates. The resulting films exhibited promising gas-sensing behavior towards NO₂, NH₃ and H₂S.^[1] At higher deposition temperatures (> 300 °C), crystalline WS₂ films on 8" Si wafers were deposited. This study not only demonstrates the scalability of MoS₂ and WS₂ on different substrates, but gives a perspective for the fabrication of advanced sensor structures in the future.

In another important field, we focused on the development of Cu and Ag precursors for spatial ALD (SALD) of the respective metals, which are especially important as electrode material for next-generation solar cells. We focused on Cu and Ag precursors based on carbenes that are specifically tailored to impart high thermal stability, while still possessing high reactivity. These new precursors enabled promising SALD processes in terms of very low deposition temperatures (60 °C) and high growth rates. These notable features prompted us to integrate the SALD Ag films in organic solar cells as an electrode material for the first time (Figure 2) displaying encouraging properties.^[2]

In summary, the new and promising developments in terms of precursors and new ALD processes have prompted us to further explore the field of 2D materials and precious metals to make advancements in functional device applications.

AF-MoP-3 Sacrificial Copper Nitride Layer for PEALD of Copper, **Sakari Kettunen**, University of Helsinki, Finland; M. Schalk, Eindhoven University of Technology, Netherlands; M. Chundak, University of Helsinki, Ukraine; M. Ritala, M. Putkonen, University of Helsinki, Finland

Initial island formation during film deposition is well-known, although mostly unwanted behaviour while depositing thin metal films. This agglomeration is a result of the minimization of chemical potential, where coalescence with other metal atoms is preferred especially on silicon and

metal oxide surfaces. While aiming to uniform sub 10 nm metal interconnect films selection of the substrate as well as tailoring interface layers have detrimental role.¹

Cu₃N is considered an interesting seed layer for copper depositions, and it also offers indirect route to metallic copper thin films by annealing due to its low decomposition temperature of ~200 °C under H₂. It has also gained increased interest as catalyst as well as solar absorbing material. Cu₃N has been previously deposited by thermal ALD by using [Cu(^tBuAMD)]₂², Cu(dmamb)₂³ or Cu(hfac)₂⁴ and ammonia at 100-190 °C, depending on the copper precursor used. Also PEALD has been utilised with Cu(hfac)₂ and NH₃ plasma for preparing nanocrystals at 150 °C.⁵

In this work Cu and Cu₃N thin films were deposited by PEALD using Cu(dmap)₂ as a metal precursor. Depositions were carried out by using Beneq TFS-200 either in direct or remote plasma set-up. Copper thin films were deposited while using Ar as carrier gas and H₂ as plasma gas. GPC of 0.21 Å/cycle and 0.37 Å/cycle were achieved in the remote and direct plasma configurations, respectively. Cu₃N was obtained by remote PEALD with GPC of 0.6 Å/cycle at 65 °C when the carrier gas was switched to N₂.

While depositing Cu/Cu₃N onto Si substrates it was observed that thin intermediate Cu₃N layer was converted to metallic Cu. According to XPS after removing surface contaminations by sputtering no N 1s signal were detected indicating Cu₃N conversion.

It was observed that to obtain conductive Cu films over 500 cycles (appr. ~11 nm when deposited by remote PEALD) were needed when using Cu(dmap)₂ + H₂ plasma process alone. By contrast, when starting with 75 Cu₃N cycles, already 175 Cu cycles deposited a continuous film with a thickness of 5.7 nm as measured by EDS.

References:

- (1) Y. Yao, et al. *Chem. Mater.* **2023**, 35 (5), 2155–2164
- (2) Z. Li, et al. *Chemical Vapor Deposition* **2006**, 12 (7), 435–441
- (3) J.-M. Park, et al. *Thin Solid Films* **2014**, 556, 434–439
- (4) T. Törndahl, et al. *J. Electrochem. Soc.* **2006**, 153 (3), C146
- (5) L.-C. Wang, et al. *ACS Appl. Nano Mater.* **2018**, 1 (7), 3673–3681

AF-MoP-4 Characteristics of Silicon Nitride Thin Films Deposited Using a Two-Step Plasma Enhanced ALD Process at Very High Frequencies, **DA EUN BAE**, H. KIM, CN1 Co., Ltd., Republic of Korea; S. LEE, DNF Co., Ltd., Republic of Korea; J. CHOI, J. JEONG, CN1 Co., Ltd., Republic of Korea

Despite its many advantages such as high step-coverage, atomic-level thickness control, and uniform film deposition, atomic layer deposition (ALD) processes have encountered difficulties in applications outside of semiconductor manufacturing due to their low deposition rates. Additionally, a high temperature (>400°C) process is required for high-quality properties when the thermal ALD is used for the deposition of nitride films such as SiN_x, AlN, TiN, and TaN, leading to active development of the plasma-enhanced ALD (PE-ALD) processes and its precursor sources.

We have studied the characteristics of silicon nitride (SiN_x) films deposited using a two-step PE-ALD process shown in Fig. 1 at low temperatures (≤200°C) and very high frequencies. Fig. 2 shows the NSi-01 precursor used as the silicon source. The two-step reaction uses NH₃ and N₂ plasma as reactants. The purposes of two-step PE-ALD are high deposition rates, low damage, and reduction of impurity contents. Electron temperature (T_e), ion flux, and ion density were monitored. Thickness and refractive index were measured using ellipsometry. Impurity content was measured through XPS depth profiling. Substrate damage due to plasma was examined by TEM.

AF-MoP-5 Analysis of ALD Thin Films by Combining MEIS and ERDA Techniques, **Aqsa Ashraf**, K. Mizohata, Helsinki Accelerator Laboratory, University of Helsinki, Finland; M. Ritala, HelsinkiALD, University of Helsinki, Finland

Thin film characterization in fast and reliable way is essential for the development of materials synthesis methods for present day and future applications. Requirement of quantitative depth profiling with sub nanometer depth resolution at surfaces and interfaces has pushed ion beam based analytical techniques to their limits and extensive effort in developing new analytical techniques are required. Additional challenge in the analysis of thin films is light impurity elements, especially hydrogen. Ion beam-based materials characterization methods provide stand-alone solutions based on relatively simple kinematics and cross sections. Medium Energy Ion Scattering Spectroscopy (MEIS) has emerged as a powerful technique for

probing surface and near-surface structures with high precision and sensitivity.

MEIS with high resolution spectrometers has increasingly applied to analyze compositional depth profiles of a nano-scale thin films. However, MEIS has limitations in analysis of very light elements in heavier matrix. To overcome these limitations, elastic recoil detection analysis (ERDA) is used. During last decades the ERDA method has become one of the standard techniques, especially for light element depth profiling of the thin films. However, ERDA depth resolution at the surface is order of few nm in the surface region. In this work we present MEIS and ERDA setups for thin film analysis in University of Helsinki.

Understanding the structural and compositional properties of ALD thin films is crucial for optimizing their performance. The present work concentrates on demonstrating benefits gained by the combined use of ERDA and MEIS techniques in the analysis of thin ALD films. Combining these methods high depth resolution is achievable. This integrated approach not only provides a deeper understanding of ALD thin films but also paves the way for the development of innovative materials and devices with enhanced performance and functionality. The advantages and limits of this method are discussed in detail.

Keywords: MEIS, ERDA, Depth Profiling, Elemental Composition, Thin films

AF-MoP-6 Novel Liquid Lanthanide Precursors with Low Viscosity and High Volatility for Atomic Layer Deposition of Lanthanide Oxide Thin Films, Hanbyul Kim, SK Trichem, Republic of Korea; H. Oh, SK trichem, Republic of Korea; B. Ryu, Y. Park, SK Trichem, Republic of Korea

The necessity for highly conformal thin films of transition metals and metal oxides in various technological applications emphasizes the significance of lanthanide precursors. Lanthanide oxide films have many applications in catalysis and semiconductor devices. In this study, we investigated the properties of various Lanthanide precursors for semiconductor devices. Among them, Gadolinium oxide, well-known for its high dielectric constant, substantial band gap energy, elevated refractive index, and consistent thermodynamic stability at high temperatures, is under consideration for integration into CMOS devices, antireflective coatings on solar cells, and passivation layers for III-V semiconductors.^[1]

Lanthanide oxide films have been grown by many techniques, including PVD, CVD, and ALD. ALD is an important technique since it gives Angstrom-level thickness control and can afford conformal coverage in high aspect ratio features. ALD precursors reported to date for Gadolinium oxide films have problems that most of these compounds have solid properties, and these solid precursors usually exhibit undesirably high melting points. Even in liquid phase, they are not suitable for ALD processes due to their high viscosity and low volatility characteristics.^[2]

Herein, we developed various novel liquid lanthanide precursors (Gd, Sm, Dy, Ho, Yb, Lu) with low viscosity, good volatility and excellent thermal stability. The compounds were confirmed by NMR, and evaluated physical & chemical properties such as volatility, vapor rate, melting point, and vapor pressure, thermal stability and chemical reactivity. In this study, we anticipate that the newly developed Lanthanide precursor will be a promising candidate for ALD processes. It possesses properties suitable for application in next-generation semiconductor devices.

References

[1] *Organometallics*. **2021**, *40*, 1270-1283.

[2] *Inorg. Chem.* **2013**, *52*, 286-296

AF-MoP-7 Novel Amidinate Ligand-based Scandium Precursor for Atomic Layer Deposition of Sc₂O₃ Thin Films, Hansol Oh, SK trichem, Republic of Korea; H. Kim, B. Ryu, SK Trichem, Republic of Korea; W. Jeon, Kyunghee University, Republic of Korea; Y. Park, SK Trichem, Republic of Korea

Scandium oxide (Sc₂O₃) thin films are essential for various applications due to their valuable intrinsic material properties and play a broad role in applications. Heat-resistance, high melting point, high optical transparency, high refractive index and laser-damage coatings. [1]

The high dielectric constant (high-*k*) and the large intrinsic bandgap ($E_g = 6.0$ eV) makes this helpful material as a high-*k* material for implementation as a potential gate dielectric in metal oxide semiconductor field effect transistors. [2]

Therefore, some of Sc precursor complexes have been reported; most of these compounds have solid properties, and these solid precursors usually exhibit undesirably high melting points. They have superior thermal

stability but have the disadvantage of low vapor pressure. Furthermore, they are often bulky and suffer from low reactivity with oxidants. [3]

Herein, we developed a novel Amidinate ligand-based liquid scandium precursor with very low melting point, very low viscosity, good volatile and thermal stability to solve this problem. The thermal atomic layer deposition (ALD) of the newly designed scandium precursor has developed using ozone as an oxygen source. ALD growth behavior was observed for the growth of the Sc₂O₃ films within an ALD window of 300 to 320 °C on SiO₂ substrate and a growth per cycle (GPC) up to 0.065 nm/cycle at 300°C. The resulting Sc₂O₃ films possess a cubic phase crystalline structure while avoiding any carbon and nitrogen contamination. We fabricated Sc₂O₃ doped ZrO₂ capacitors with TiN electrode using ALD and evaluated their electrical properties such as dielectric constant and leakage current.

Acknowledgments The authors would like to thank Kyung Hee University for their support and permission to publish this collaborative work.

References

[1] *Thin Solid Films* **368** (2000) 116-124.

[2] *J. Phys. Chem. B*, Vol. 103, No. 43, 1999

[3] *Electrochem. Solid-State Lett.* **9** (6) F45-F48 (2006)

AF-MoP-8 Process Development of Cobalt Metal ALD on Novel ALD Machine, Mathias Franz, L. Kaßner, Fraunhofer ENAS, Germany; C. Thurm, University of Technology Chemnitz, Germany; L. Jäckel, Fraunhofer ENAS, Center for Microtechnologies (ZfM), Chemnitz University of Technology, Germany; M. Daniel, scia Systems GmbH, Germany; F. Stahr, Forschungs- und Applikationslabor Plasmatechnik GmbH, Germany; S. Schulz, Fraunhofer ENAS, Center for Microtechnologies (ZfM), University of Technology Chemnitz, Germany

ALD of metallic films is a broad and ongoing topic of research. The conformal deposition of metallic cobalt is relevant for modern interconnects¹, seed layers for electroplating², and antibacterial coatings³. One of the essential process parameters is the deposition temperature. Especially low process temperatures enable depositions on substrates with a critical thermal budget. Here, we present the process development on the novel scia Atol 200 ALD reactor.

The process development was done on a scia Atol 200 reactor, which was designed and fabricated by scia Systems GmbH in cooperation with Fraunhofer ENAS, the Chemnitz University of Technology, and Forschungs- und Applikationslabor Plasmatechnik GmbH. Figure 1 shows a photo of the ALD reactor. We integrated 2 CEMs, 2 Vapbox Systems, and 2 Bubblers as evaporation units. This provides the opportunity to use a wide range of precursors, including substances with low vapour pressure as well as high vapour pressure. The reactor design was accompanied by CFD fluid flow simulations. Figure 2 shows the precursor concentration on top of the wafer surface. The concentration deviation is less than ±10 %. The process development was done using [Co₂(CO)₈(HC≡CC₆H₁₁)] as precursor. The synthesis was reported earlier by Georgi et al.⁴. The processes took place on standardised 200 mm Si wafers with a preliminary 100 nm SiO₂ layer. We could show that all three types of evaporators were suitable to bring this cobalt complex into the gas phase. The following results are based on evaporations using a bubbler with Ar carrier gas. A full ALD cycle consists of precursor pulse, Ar purge, H₂ plasma pulse, and a second Ar purge. The deposited cobalt films were analysed by *in-vacuo* ellipsometry to determine in-line film growth rates. Figure 2 shows the growth rates in the temperature range from 35 °C to 125 °C showing the ALD window for this process within the range of 50 °C to 110 °C.⁵ The process was optimised regarding pulse and purge duration times to ensure stable saturation conditions. *Ex situ* measurements with XPS confirm that cobalt is in metallic state.

We demonstrated the successful development of the scia Atol 200 ALD system with a low temperature ALD process for metallic cobalt.

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References

¹ Lanzillo *et al.*, doi: 10.1109/TVLSI.2021.3126541

² Liu *et al.*, doi: 10.1149/1945-7111/ac862d

³ Jeong *et al.*, doi: 10.1016/j.tsf.2008.10.063

⁴ Georgi *et al.*, doi: 10.1039/c4tc00288a

⁵ Franz *et al.*, doi: 10.3762/bjnano.14.78

AF-MoP-9 High Quality TiN Plasma Enhanced Atomic Layer Deposition on SiO₂ Substrate with AlN Interfacial Layer via in situ Atomic Layer Annealing. *Valentina Korchnoy*, Technion Israel Institute of Technology, Israel; *I. Popov*, The Hebrew University of Jerusalem, Israel; *M. Koifman Khristosov*, Technion Israel Institute of Technology, Israel; *M. Lisiansky*, Tower Semiconductor, Israel

TiN layer becomes an important electrode material for devices with complex 3D geometry due to its scalability, compatibility with CMOS technology and low resistivity. The resistivity of thin TiN films depends on many factors, among them crystalline morphology of the film plays a dominant role. There are several factors determining the crystalline properties of TiN films deposited by PEALD. As was shown in [1] the crystallinity of the underlying substrate is an important factor influencing the grain size of a thin TiN PEALD film, and thus, its resistivity. There is few knowledge about the role of the interfacial layer (IL) on structural properties of thin polycrystalline TiN films grown by ALD on amorphous substrate. Crystalline properties of the IL, primarily, lattice matching to on-grown TiN layer and the ability of IL to be introduced in the advanced technology processes are the dominant factors that should be considered. PEALD AlN film as the IL satisfies both these requests. Another factor that promotes crystallinity of AlN PEALD film is the atomic layer annealing (ALA). It supplies an additional energy to the deposition process, stimulates surface reactions, increases the metal adatoms mobility, and thus promotes densification of the deposited film [2].

The purpose of this work was to investigate the effect of AlN IL and ALA technique on the crystalline properties of very thin (~ 14 nm) TiN layers deposited on Si/SiO₂ substrate.

The AlN and TiN layers were deposited on 100 Å thermal oxide layer grown on (001) Si substrate. The deposition was done by PEALD, using either N₂ or NH₃ plasma, by applying layer-by-layer, in situ ALA treatment using Ar plasma in each ALD cycle (FIG.1). The reference TiN samples were grown on the crystalline substrate (sapphire), that enables an excellent matching of AlN IL to the substrate. The reference samples provide data about TiN film grown at perfect conditions.

The study was conducted using numerous analysis techniques (TEM, EELS, STEM, XRD, XRR, AFM) and electrical characterization. The electrical resistivity of TiN films was measured using four-point probe Kelvin structure. The attached Figures 2,3,4,5,6,7 and Table 1 demonstrate the structural and electrical characteristics of 14 nm TiN layer. The lowest known resistivity of 70 μΩcm on the amorphous, and 10 μΩcm on the crystalline substrates were measured. The postdeposition annealing didn't cause significant resistivity change. According to XRR, the densities of the deposited thin AlN and TiN films are close to the bulk densities of these materials. Discussion about the conductivity mechanism in thin TiN layers was considered.

AF-MoP-10 Turning Online ALD and ALE Databases Into AI-Ready Tools for Development of New Sustainable Materials and Fabrication Processes. *Adrie Mackus*, B. Macco, Eindhoven University of Technology, Netherlands; *B. Karasulu*, University of Warwick, UK; *J. D'Souza*, S. Auer, L3S Research Center at Leibniz University of Hannover, Germany; *E. Kessels*, Eindhoven University of Technology, Netherlands

Artificial Intelligence (AI) presents unmatched opportunities to enhance ALD and ALE process development, not just by optimizing efficiency and reducing costs, but notably by driving innovation through data analysis, predictive modeling, and automation. However, the advancement of AI-based process development and material synthesis requires databases with extensive training data as input. Building on popular crowd-sourced databases containing ALD (DOI: 0.6100/alddb) [https://www.atomiclimits.com/alddb] and ALE (DOI:10.6100/aledb) [https://www.atomiclimits.com/aledb] process details as launched by TU/e on www.AtomicLimits.com in 2019, we have set up a program to start making these databases AI-ready. With this, we aim also to explore new opportunities for AI-inspired process development, materials design and autonomous experimentation. Bringing together three parties with complementary expertise, the program will focus on: defining integrated workflows and protocols for AI-aware ALD/E experiments and atomic-level simulation, coupled with the implementation of FAIR principles and neural language model-based knowledge extraction. We believe that the open-domain ALD/E databases resulting from this pilot will enable the AI-driven design of material stacks for highly-scaled devices, thereby reducing material usage and leading to overall more sustainable semiconductor fabrication processes. By sharing the protocols with the

atomic-scale processing community, we hope to create a culture of AI-aware experimentation and simulation.

AF-MoP-11 ALD Process Characterization, Development, and Monitoring Using an Electron Impact Time-of-Flight Mass Spectrometer. *Abdelhak Bensaoula*, C. De Koning, C. Frege, TOFWERK, Switzerland; T. Nelis, BFH, Switzerland; C. Hain, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; C. Guerra, Swiss Cluster, Switzerland

Time of Flight Mass spectrometry (TOFMS) applications extend beyond materials science and technology and include industries spanning automotive, metallurgy, biotechnology, pharmaceutical, aerospace, etc. These mass spectrometers can be equipped with an electron impact (EI) source to measure neutral species, but the inlet stage can be designed to allow for (process) ionized species to be directly detected as well. Current TOFMS capabilities fulfil requirements of most industrial use-cases but the trend in advanced processes is to utilize energetic species to further enhance the manufacturing method. It is thus desirable to measure both the abundance of the neutral species but also that of the native ions. We present here a new member of the TOFMS instruments which allows just that.

The pgaTOF, an EI-TOFMS by TOFWERK, allows full m/q spectra acquisition at >1 kHz, up to 8000 mass resolution and 5 ppm mass accuracy, 10⁶ dynamic range and a nominal mass range of >1000 Th. Thanks to an integrated filtering feature, our instrument allows for reduction/suppression of up to four user-selected masses which permits measurement of both main and trace compounds and avoids detector saturation and degradation issues. This feature is essential in ALD where precursor and purge masses signals are high while that of the reaction products are much smaller. The new instrument extends the EI-TOFMS capabilities to measuring native ions, such as those present in plasma-enhanced ALD. In our experiments, the TOFMS instruments were attached to various ALD reactors running different chemistries (Al, Cu, Li, etc.).

We will first present details of the EI-TOFMS instruments and its time resolution and sensitivity capabilities. We will then give examples of ALD results showing how real-time ALD process monitoring not only permits unique insights into the ALD chemistries, allows for significant time savings in recipes development but also determines excursions beyond the ALD mode or equipment malfunctions.

AF-MoP-12 Tailoring Cobalt Precursors Through Molecular Engineering. *Jean-Pierre Glauber*, J. Obenluneschloß, D. Zanders, Ruhr University Bochum, Germany; S. Barry, Carleton University, Canada; A. Devi, Ruhr University Bochum, Germany

Cobalt based materials are indispensable for numerous applications due to their appealing physical and chemical properties. Their scope of application ranges from integrated circuits (IC) over electrocatalysis to spintronics. Metallic cobalt is promising as interconnects in IC devices.[1] While cobalt oxides are highly efficient for the oxygen evolution reaction (OER),[2] the Weyl-semimetal cobalt disulfide (CoS₂) is interesting for spin-to-charge conversions in the emerging field of advanced spintronic devices.[3] Such targeted applications require a synthesis route that allows film growth with precise thickness control on complex geometries. Atomic layer deposition (ALD) is the method of choice when it comes to meeting these demands and one crucial parameter is the precursor choice as its physiochemical properties directly influences the ALD process characteristics. Surprisingly, in the literature, the class of all-nitrogen coordinated cobalt precursors is rather underexplored.

With our goal to expand the library of Co precursors for ALD, we developed a series of new Co precursors by systematically introducing all nitrogen coordinating ligands to the metal center to fine-tune the volatility, reactivity, and stability. A selection of amides, imides, amide-adducts, pyrroles, and amido-amines have been studied, with particular emphasis on the influence of structural and chemical ligand variations on the physiochemical properties of the organometallic complexes.[4,5,6]. After establishing reliable synthesis routes for the range of Co complexes, characterization by complementary analysis methods (EA, EI-MS, SC-XRD) confirmed the anticipated structures and purity. Finally, thermal analysis and vapor pressure estimation gave first insights on their suitability as ALD precursors.

Among the Co complexes synthesized, the one depicted in **Figure 1 a)** were found to exhibit suitable thermal properties in terms of volatility and stability rendering them favorable for application in ALD processes. Interestingly, some complexes exhibited unusual coordination motifs: [Co{(N^tBu)₂SiMe₂}]₂ arranges in a rare low spin Co(IV) configuration (**Figure 1b)**) and exhibited remarkable thermal stability in TGA (**Figure 1c)**). First

saturation experiments with this compound showed the formation of a stable self-limiting monolayer on an alumina-coated quartz crystal microbalance (QCM).^[6] In summary, we were successful in enlarging the precursor library of Co precursors and the study showcases, how small but distinct changes in the ligand moieties lead to significant changes in the physicochemical properties of the complexes and gives valuable insight for future precursor development.

AF-MoP-14 Optimization of the Growth of Atomic Layer Deposited Ta₂O₅ Thin Films for Large Area Electronics, Xiao Chen, K. Niang, B. Bakhit, Y. Jeon, J. Driscoll, A. Flewitt, University of Cambridge, UK

Tantalum oxide, Ta₂O₅, has been extensively studied as a promising high-k dielectric in semiconductor devices (1), as a capacitor dielectric in memory devices (2), and as an antireflection coating in solar cells (3). Ta₂O₅ has been deposited using various technologies, including e-beam evaporation (4), sputtering (5), and atomic layer deposition (ALD) (6, 7). Among these, ALD is particularly attractive technique due to its ability to precisely control stoichiometry as a result of the self-limiting growth process. In addition, ALD tends to produce thin films with high conformality and good uniformity over a large substrate area. This work focusses on optimization of ALD Ta₂O₅ for large area electronic applications where an amorphous morphology is favored as this allows excellent device-to-device uniformity, and substrate deposition temperature is limited by unconventional substrates such as glass and plastic.

Ta₂O₅ is grown by ALD from pentakis(dimethylamino)Ta (PDMAT) and water using a Savannah system from Cambridge Nanotech/Veeco. We have investigated various ALD process parameters such as the pulse time, purge time, substrate temperatures, and various post-deposition annealing temperatures. We have also investigated the physical, electronic and optical properties of the deposited thin films using various characterization techniques.

We show that the ALD Ta₂O₅ can be produced within a large process window and with good uniformity. At 200 °C, the saturated growth rate is ~ 0.6 Å/cycle, and thickness uniformity of ~ 95% is obtained across a 4-inch diameter wafer. The as-deposited Ta₂O₅ thin films are amorphous and require a post-deposition annealing at ~ 700 °C to become polycrystalline with a textured surface. We will correlate the morphology of the as-deposited thin films with their optical and electrical properties such as dielectric constants and breakdown voltages.

AF-MoP-15 Bismuth Alkoxides for Deposition of Bismuth Chalcogenides, Jaroslav Charvot, University of Pardubice, Czechia; R. Parkhomenko, M. Knez, CIC nanoGUNE, Spain; A. Bahrami, K. Nielsch, IFW Dresden, Germany; F. Bureš, University of Pardubice, Czechia

Bismuth chalcogenides are semiconductors with attractive properties for thermoelectric applications. ALD of Bi₂S₃,^[1]Bi₂Se₃,^[2]Bi₂Te₃,^[3,4] and Bi₂Te₃^[5] was reported using various precursors. BiCl₃ is the most accessible precursors, but its rather low vapor pressure makes it difficult to evaporate. On the other hand, (Me₂N)₃Bi is very volatile but lacks thermal stability with decomposition starting around 120 °C and suffers from aging. Bismuth alkoxides were investigated previously and (tris(2,3-dimethylbutanolate)bismuth) (DMB₃Bi) was selected, as the best candidate for Bi₂O₃ deposition.^[6]

This study delves further into DMB₃Bi and its analogues, aiming to identify easily accessible and suitable precursors for depositing bismuth chalcogenides by reaction with bis(trialkylsilyl)-, bis(trialkylstanyl)selenides and tellurides. Series of alcoholates is prepared by alcoholysis of (iPr₂N)₃Bi giving corresponding Bi-alkoxides in good yields. This method allows preparation in non-polar solvents like hexane, which makes the separation of products comfortable during up-scaled synthesis. The investigation is expanded further by examination of fluorinated alcoholates, where the best results are obtained with [(CF₃)₂CHO]₃Bi acquired by simple synthesis starting from tris(4-methylphenyl)bismuthine.^[7] Although having a relatively high molecular mass, [(CF₃)₂CHO]₃Bi features high volatility with boiling point at 115 °C (0.5 torr).

Volatility and thermal stability of prepared materials are studied and discussed. Most of prepared precursors remain stable up to 180 °C and sufficient vapour pressure is achieved by heating below 90 °C (ca. 0.5 torr) giving temperature range wide enough for application in ALD. In the last stage, the most promising candidates are tested in ALD with aim to deposit Bi₂Se₃ and Bi₂Te₃.

[1] N. Mahuli, D. Saha, S. K. Sarkar, *J. Phys. Chem. C* **2017**, *121*, 8136–8144.

[2] S. He, A. Bahrami, X. Zhang, M. O. Cichocka, J. Yang, J. Charvot, F. Bureš, A. Heckel, S. Schulz, K. Nielsch, *J. Eur. Ceram. Soc.* **2023**, *43*, 4808–4813.

[3] P. Plachinda, M. Hopkins, S. Rouvimov, R. Solanki, *J. Electron. Mater.* **2020**, *49*, 2191–2196.

[4] T. Sarnet, T. Hatanpää, M. Vehkamäki, T. Flyktman, J. Ahopelto, K. Mizohata, M. Ritala, M. Leskelä, *J. Mater. Chem. C* **2015**, *3*, 4820–4828.

[5] M. Rusek, T. Komossa, G. Bendt, S. Schulz, *J. Cryst. Growth* **2017**, *470*, 128–134.

[6] T. Hatanpää, M. Vehkamäki, M. Ritala, M. Leskelä, *Dalt. Trans.* **2010**, *39*, 3219–3226.

[7] P. C. Andrews, P. C. Junk, I. Nuzhnaya, L. Spiccia, *Dalt. Trans.* **2008**, 2557–2568.

AF-MoP-16 From Microscopic to Macroscopic: How Morphology Impacts ALD and CVD Nucleation Kinetics, Andreas Werbrouck, A. Shearer, S. Bent, Stanford University

Nucleation delay is an intrinsic part of area selective deposition (ASD), (metal) atomic layer deposition (ALD) and chemical vapor deposition (CVD). While much earlier work has been done on this topic, earlier models often substantially simplify the morphology of the film and/or nuclei. Here we fill the gap of how diffusion and reactivity impact morphology and coalescence, and vice versa.

In the first part of this work we describe a kinetic Monte Carlo (KMC) code that allows us to study the time-dependent microscopic evolution of a monolayer in time. We discern three steps in developing a full model: in the first step (reaction), a flux of reactive molecules changes the coverage with substrate- and film-dependent sticking coefficients. In the second step (diffusion), the coverage of the surface stays constant, but the material is allowed to diffuse until it reaches an absorbing state. Finally, steps 1 and 2 are combined to describe a surface that undergoes both deposition and diffusion of the film. The simulations explain how surface morphology influences the reactivity, which in its turn influences the morphology. Intermediate, metastable states include migration of particles across the surface, the merging of nuclei, and typical diffusion-limited aggregation (DLA) morphologies. This depends on the flux of incoming material, sticking coefficients, binding energies and the deposition temperature.

In the second part of this work, the microscopic insights from the KMC are translated into a macroscopic system of equations that can be solved computationally. In this model, the *edge length per surface area* of the deposited material is used as a key parameter to describe the time evolution of the coverage and the thickness. Casting the system as a mathematical problem allows for faster solving, statistical noise due to the limited system size is eliminated, and a distinction between continuous (CVD) and self-limiting (ALD) growth can be made.

Our simulations and the accompanying model explain a range of experimental observations and encompass often implicit and empirical knowledge: e.g., in ASD, why overdosing often results in poor selectivity and why longer purge times can increase the selectivity; for metal ALD, why longer precursor dosing and/or pretreatment of the substrate increase nucleation and why longer purge times change the morphology; and for deposition onto 2D materials, why widely different morphologies are observed.

AF-MoP-17 Novel Imido Cyclopentadienyl-based Niobium Precursors for Atomic Layer Deposition of Nb₂O₅ Thin Films, Dong Hun Shin, H. Oh, J. Chun, SK trichem, Republic of Korea; S. Lee, W. Jeon, Kyung Hee University, Republic of Korea; Y. Park, SK trichem, Republic of Korea

Niobium oxide (Nb₂O₅) has a high-k dielectric behavior that has been used in various applications such as capacitors, insulators, and sensors.^[1] Nb₂O₅ thin film is also a constituent for multimetal oxide systems such as dopant with a high-k material, laminate structures.

Therefore, various Nb precursor complexes have been reported; most of these compounds have solid properties. It is known that solid precursors have disadvantages in the ALD process. Although only a few selected liquid precursors are used, most Nb precursors suffer from low thermal stability issue.^[2]

Herein, we developed a novel liquid imido cyclopentadienyl-based Niobium precursor with high thermal stability (DSC = 339 °C) to solve this problem. The thermal atomic layer deposition (ALD) of the newly developed Niobium precursor has evaluated using ozone as an oxygen source. Self-limiting Growth was observed for the growth of the Nb₂O₅ films at 300 °C on SiO₂ substrate and a growth per cycle (GPC) up to 0.044 nm/cycle. The deposited films exhibited an ALD window of 280 – 320 °C, confirming their process compatibility with ZrO₂ films. And thin film properties such as

crystallinity, impurity content, and film density were confirmed through XRD, XPS, and XRR analysis. We also fabricated Nb₂O₅ doped ZrO₂ capacitors using ALD and evaluate their electrical properties such as dielectric constant and leakage current.

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References

- [1] *Journal of Vacuum Science & Technology A*, **2018**, *36*, 4, 1-9
- [2] *Chem. Mater.*, **2012**, *24*, 975–980

AF-MoP-18 Atomic Layer Deposition of In₂O₃ Thin Films Using New In Precursor, Donghyun Kim, H. Oh, SK Trichem, Republic of Korea; Y. Choi, W. Jeon, Kyung Hee University, Republic of Korea; Y. Park, SK Trichem, Republic of Korea

Indium oxide (In₂O₃) thin films are vital for numerous applications with their advantages such as wide band gap, high optical transparency, electronic properties and excellent chemical stability. In₂O₃ thin films frequently are used in combination with other metals. These days, although many applications require In₂O₃ films to be high-quality in terms of thermal stability and electronic properties for proper metal ratio, but it is hard to control previous indium precursors because of its basic properties (solid phase, low vapor pressure and poor thermal stability, pyrophoric issue etc.). So, it is necessary to develop the new indium precursor to solve the existing problems.^{[1][2]}

We developed a novel liquid indium precursor with excellent volatility (TGA_{1/2} : 137°C), good thermal stability (DSC : 332°C) and non-pyrophoric properties. These properties should be a suitable role in large area and high volume ALD process in addition to high temperature deposition.

The thermal atomic layer deposition (ALD) of the new indium precursor has been evaluated using O₃ as an oxygen source. Self-limiting growth was observed for the growth of the In₂O₃ films at 280°C to 350°C on Si substrate and a growth per cycle (GPC) up to 0.1 nm/cycle at 300°C. The deposited In₂O₃ films possess a cubic phase crystalline structure without any carbon impurity. We fabricated MIM capacitor with In₂O₃ interfacial layer inserted between ZrO₂ and TiN bottom electrode at 300°C. And we evaluated their electrical properties such as dielectric constant and leakage current in priority. Through C-V and I-V data, we confirmed that inserted In₂O₃ film is helpful for capacitor to improve dielectric constant and leakage current values compared to pristine ZrO₂.

Acknowledgments The authors would like to thank Kyung Hee University for their support and permission to publish this collaborative work.

References

- [1] *J. Phys. Chem. C* **2016**, *120*, 9874–9883
- [2] *Chem. Eur. J.* **2018**, *24*, 1–6

AF-MoP-19 Reductive Surface Chemistry with Plasma Electrons, Pentti Niiranen, D. Lundin, H. Pedersen, Linköping University, IFM, Sweden

Depositing elemental films of electropositive metals at low temperature requires powerful reducing agents. We have recently reported on an alternative CVD scheme using plasma electrons as the reducing agents for the deposition of metallic films.¹ The process has been demonstrated using the metallocene's of Co, Fe and Ni, and in addition shown to be inherently area selective to low-resistivity areas.² We call the process electron CVD (e-CVD). However, the deposition chemistry is not understood and we will here describe our efforts to understand it in detail.

Despite employing a pulsed e-CVD process, separating the ferrocene and the argon plasma in time, iron films deposited from ferrocene are contaminated by high amounts of carbon. We will describe how we from quantum chemical modeling and a combination optical emission spectroscopy and mass spectroscopy have formed a plasma chemical model for ferrocene in the e-CVD plasma. From this, we attribute the carbon contamination to redeposition of cyclopentadienyl ligands upon contact with the plasma after desorption during the plasma step.

We studied the electron temperature, electron density and plasma potential in the hollow cathode discharge in our e-CVD process by a modified Sobolewski probe.³ From these measurements we show that the presence of ferrocene in the vacuum chamber has a significant effect on the plasma characteristics, increasing the electron temperature from below 1 eV to 1-5 eV. The electron density at the substrate was found to be in the 10¹⁶ m⁻³ range.

Combining our models for the plasma chemistry and plasma characteristics, with mass spectrometry and our previously developed QCM for e-CVD⁴, we

will propose a surface chemical model for the film deposition in pulsed e-CVD and show indications of a self-limiting surface chemistry.

References:

- ¹ H. Nadhom, D. Lundin, P. Rouf, and H. Pedersen, *J. Vac. Sci. Technol. A* **38**, 033402 (2020).
- ² H. Nadhom, R. Boyd, P. Rouf, D. Lundin, and H. Pedersen, *J. Phys. Chem. Lett.* **12**, 4130 (2021).
- ³ P. Niiranen, A. Kapran, H. Nadhom, M. Cada, Z. Hubicka, H. Pedersen and D. Lundin, *J. Vac. Sci. Technol. A.* (2024)doi: 10.1116/6.0003408
- ⁴ P. Niiranen, H. Nadhom, M. Zanaška, R. Boyd, M. Sortica, D. Primetzhofner, D. Lundin, and H. Pedersen, *Rev. Sci. Instrum.* **94**, 023902 (2023).

AF-MoP-20 Surface Chemistry of Atomic Layer Deposited of Gallium Nitride Films at Different Process Temperatures, houyem hafdi, P. Mpofu, H. Pedersen, Linköping University, IFM, Sweden

Gallium nitride (GaN) is a commonly used semiconductor owing to its high chemical and thermal stability, which makes it suitable for various applications in modern electronics. The deposition of such materials is favored by atomic layer deposition (ALD) using e.g., triethylgallium (TEG) as a precursor. This study comes as a follow up to our previous work¹ where we proposed a surface ligand removal in ALD of GaN with TEG and NH₃ plasma by adding an additional reactive pulse between the TEG and NH₃/Ar plasma. We hypothesized that the release of C₂H₆ and C₂H₄ leads to the formation of a hydrogen-terminated surface.

Herein, we tested these hypotheses using mass spectrometry to assess the surface chemistry of GaN deposited using ALD with TEG and NH₃ at different substrate temperatures (200–400 °C) and by adding either an Ar plasma pulse (100 SCCM with 2000 W plasma power), H₂ gas pulse (50 SCCM H₂ mixed with 100 SCCM Ar), or H₂ plasma pulse (50 SCCM H₂ mixed with 100 SCCM Ar and 2000 W plasma power). Detailed identification of potential gases released during GaN deposition will be presented and discussed for the hypothesis of surface ligand removal by a reactive extra pulse in the ALD cycle.

Deminskiy, P., Hsu, C. W., Bakhit, B., Rouf, P., & Pedersen, H. (2021). Surface ligand removal in atomic layer deposition of GaN using triethylgallium. *Journal of Vacuum Science & Technology A*, 39(1).

AF-MoP-21 Tuning the Wet Etch Rate of Silicon Dioxide Deposited by Plasma-Enhanced Atomic Layer Deposition, Keerthi Dorai Swamy Reddy, M. Lisker, IHP - Leibniz Institut fuer innovative Mikroelektronik, Germany

Silicon oxide (SiO₂) is one of the quintessential materials necessary for the fabrication of semiconductor devices. Its application in the fabrication varies from being used as an etch stop layer, gate spacer, protective layer to protect sensitive areas around active devices and to maintain their feature size, capping layer, liner oxide, and insulating layer in the formation of through-silicon-via (TSV). Each application has one or many specific stringent requirements such as uniform thickness, stoichiometric layer deposition, minimal impurity content, lower surface roughness, conformality in high aspect ratio structures, low or high wet etch rates, and lower thermal budget. Commonly used deposition methods for SiO₂ are thermal oxidation, low-pressure chemical vapor deposition (LPCVD), plasma-enhanced chemical vapor deposition (PECVD), and atomic layer deposition (ALD). Although thermal oxidation and LPCVD deposition methods can deposit SiO₂ complying with most of the requirements, they have higher thermal budgets and poor step coverage. PECVD can reduce the thermal budget but also results in poor step coverage. Thermal ALD overcomes these disadvantages but can obtain lower wet etch rates only at deposition temperatures above 300 °C. In contrast, the plasma-enhanced atomic layer deposition (PEALD) can obtain low wet etch rates at lower deposition temperatures. Applications like etch stop layer and liner oxide require low wet etch rates similar to thermally grown SiO₂ while applications like insulating layer for TSV formation do not require low wet etch rates. In our work, we study how process parameters in PEALD can be varied so that a spectrum of different wet etch rates can be obtained from a single deposition method and utilized for various applications.

In this work, PEALD of SiO₂ is deposited in a direct plasma ALD tool using Bis(diethylamino)silane and Oxygen as precursors with Argon as the carrier gas at 250 °C. The dependence of process parameters such as RF power and plasma exposure duration has been studied to understand its effect on wet etch rate in Hydrofluoric acid. Figure 1 (PDF) shows the dependence of the etch rate (nm/min) on RF power and plasma exposure time. For a lower RF power (50 W), SiO₂ with a wet etch rate as high as 22 nm/min is deposited which can be applied for TSV formation whereas when RF power is

increased to 150 W, SiO₂ with a low wet etch rate of 7.5 nm/min is obtained which can be applied for gate spacer, liner oxide, and similar applications. The quality of the deposited layers is investigated further by employing various metrology techniques.

AF-MoP-22 Ruthenium Metal ALD from Versatile Diazadienyl Precursor, Jorit Obenluneschloß, D. Zanders, J. Klimars, Inorganic Materials Chemistry, Ruhr University Bochum, Bochum, Germany; *M. Gock,* Heraeus Precious Metals GmbH & Co. KG, 63450 Hanau, Germany; *A. Devi,* Inorganic Materials Chemistry, Ruhr University Bochum, Bochum, Germany

Interest in ruthenium is rising for various equally important reasons. It is a very promising catalyst material for hydrogen and oxygen evolution.^[1] Its organometallic complexes are of significant importance for polymerization as Grubbs catalysts.^[2] Nonetheless, the largest driving force has been the proclaimed use of ruthenium thin films to replace copper as interconnect material in integrated circuits (IC's) and other semiconductor devices.^[3] In this context, chemical vapor deposition (CVD) and atomic layer deposition (ALD) are the viable choices for material synthesis to meet the demands posed for film quality and thickness control across complex structured substrates. For each application the chemical precursor transformed to the metal needs to fulfill different requirements regarding stability, reactivity, and volatility.

After our recent success with ruthenium metal CVD using the Ru^{(tBu₂DAD)(Cym)} precursor, we were motivated to investigate the structurally related precursor Ru^{(IP²DAD)(Cym)} to deposit ruthenium via ALD.^[4] This precursor showed very promising thermal properties (Fig.1) indicating it to be a potential candidate for developing a Ru ALD process. Initial observations have hinted at a high reactivity with oxygen and prompted us to develop a new ALD process using the combustion/oxidative deposition chemistry often observed for ruthenium. This presentation will comprise the process development with respective film analysis and highlight the importance of precursor chemistry. The Ru films were subjected to analysis by means of RBS/NRA, XPS, XRR, AFM, and SEM. The new findings will be discussed in this presentation and differences on the material characteristics obtained from CVD will be compared.

[1]S.-Y. Bae, J. Mahmood, I.-Y. Jeon, J.-B. Baek, *Nanoscale Horiz.* **2020**, *5*, 43–56.

[2]T. Bano, A. F. Zahoor, N. Rasool, M. Irfan, A. Mansha, *J. Iran. Chem. Soc.* **2022**, *19*, 2131–2170.

[3]S. Dutta, S. Kundu, A. Gupta, G. Jamieson, J. F. Gomez Granados, J. Bommels, C. J. Wilson, Z. Tokei, C. Adelman, *IEEE Electron Device Lett.* **2017**, *38*, 949–951.

[4]D. Zanders, J. Obenluneschloß, J. Wree, J. Jagosz, P. Kaur, N. Boysen, D. Rogalla, A. Kostka, C. Bock, D. Öhl, M. Gock, W. Schuhmann, A. Devi, *Adv. Mater. Interfaces* **2022**, 2201709.

AF-MoP-23 ALD of Nd₂O₃ and ALD/MLD of Nd-Organic Thin Films Using New Precursor Combinations, Florian Preischel, Ruhr University Bochum, Germany; *A. Ghazy,* Aalto University, Finland; *J. Debus,* TU Dortmund, Germany; *D. Rogalla,* Ruhr University Bochum, Germany; *M. Karppinen,* Aalto University, Finland; *A. Devi,* Ruhr University Bochum, Germany

The unique 4f-electron shell configuration of rare earth (RE) materials results in exceptional magneto-optical properties. Specifically, Nd₂O₃ thin films feature efficient luminescence and its f-f transitions, that are highly sensitive to external stimuli, could be utilized for next-generation multiparametric sensors.^[1] In this perspective, hybrid Nd-organic materials are especially appealing, as appropriate organic molecules can serve as photoluminescence sensitizers and mitigate concentration quenching effects.^[2] Nd₂O₃ is further known for its high dielectric constant with a low leakage current and could serve as a gate dielectric in downscaled metal oxide semiconductor field-effect transistors.^[3]

Atomic layer deposition (ALD) and combined atomic/molecular layer deposition (ALD/MLD) for hybrid materials, are most favored methods for downscaling of layers due to their precise thickness control and possibility to tune the properties of the resulting material via the process conditions and precursor chemistry. Yet, the full potential of Nd₂O₃ ALD has been constrained, with [Nd(thd)₃] being the only precursor examined. Its oxygen-coordination results in poor reactivity, necessitating high deposition temperatures and restricting the range of possible organic co-reactants for ALD/MLD.^[4,5] This state-of-the-art scenario is a unique opportunity to explore the chemistry of Nd complexes and identify other suitable candidates.

In our search for new Nd precursors, we explored the amidinate-based precursor [Nd(DPAMD)₃], where the chelating ligands stabilize the complex, *Monday Evening, August 5, 2024*

while the M – N bonds facilitate the desired reactivity, as evidenced in our work on CVD of Nd₂S₃ and related RE materials.^[6,7]

Employing [Nd(DPAMD)₃] with water in a thermal ALD process, we achieved the deposition of polycrystalline cubic Nd₂O₃ thin films on silicon substrates under moderate conditions (Figure 1). Thereby, the GPC was constant around 1.5 Å in the ALD window from 200 °C to 300 °C. Moreover, the reactivity and versatility of [Nd(DPAMD)₃] were demonstrated in proof-of-principle ALD/MLD experiments. Beyond the formation of hybrid layers with the frequently used terephthalic acid (TPA), initial experiments with other organics were promising, as confirmed by FT-IR (Figure 2). Our work thus broadens the spectrum of available organics and lays the foundation for the fabrication of previously inaccessible hybrid materials.

Ongoing studies are focused on phase control via the process parameters, investigating the properties of the Nd₂O₃ films by Raman scattering and magneto-photoluminescence spectroscopy and extending the range of organic co-reactants for ALD/MLD.

AF-MoP-24 Thermal Atomic Layer Deposition of Aluminum Nitride Films Using Tris(dimethylamido)aluminum and NH₃, O. Kim, H. Han, Jian Heo, Y. Choi, C. Kim, H. Kim, Sejong University, Republic of Korea; *H. Kim, J. Park,* Hansol Chemical Co., Ltd., Republic of Korea; *W. Lee,* Sejong University, Republic of Korea

Aluminum nitride (AlN) is a dielectric material with high thermal conductivity and electrical resistivity that is being investigated as an insulating or buffer layer for nitride semiconductor devices. However, they are typically prepared by chemical vapor deposition (CVD), which makes integration with temperature-sensitive substrates difficult. Therefore, atomic layer deposition (ALD), which can ensure low process temperature, is required for these applications. Currently, the ALD literature using suitable Al precursors is limited. AlCl₃ suffers from high process temperature and Cl impurities. ALD using Al(CH₃)₃ requires NH₃ plasma as a co-reactant and showed high impurity levels in the film at temperatures of 325°C or higher due to insufficient thermal stability. Thermal ALD using Al(N(CH₃)₂)₃ (TDMAA) has also been reported at 170–400°C [1, 2], but detailed growth kinetics, film properties, and step coverage have not been described. In the present study, we report the effect of process temperature on the growth and properties of AlN films produced by the thermal ALD process using TDMAA and NH₃. First, we investigated the growth kinetics by examining the saturation doses of TDMAA and NH₃ and the ALD temperature window. Then, we investigated the film properties of the deposited films, such as composition, density, crystallinity, leakage current, and step coverage, at different temperatures ranging from 200–350°C. Finally, we discuss the effects of deposition temperature during thermal ALD of AlN.

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References [1] G. Liu et al., ECS Trans. (2011) [2] A. I. Abdulagatov et al., Russ. J. Gen. Chem. (2018)

AF-MoP-25 High-Temperature Atomic Layer Deposition of Silicon Oxide Thin Films Using Tris(dimethylamino)silane and Ozone, O. Kim, Y. Choi, Changgyu Kim, H. Kim, W. Lee, Sejong University, Republic of Korea

As the number of memory stacks of three-dimensional vertical NAND devices continues to increase, the aspect ratio of the channel hole also increases proportionally. Therefore, the use of atomic layer deposition (ALD) processes to fabricate dielectric layers is inevitable. In addition, high-temperature deposition is essential to achieve excellent film properties comparable to those of conventional oxidation-based methods. However, reports on high-temperature ALD of SiO₂ are limited. For ALD processes using tris-DMAS, feasibility at 200–400°C and surface reaction at 550°C have been reported [1, 2], but detailed information on growth characteristics and thin film properties have not been described, especially for temperatures higher than 600°C. In this work, we report the effect of deposition temperature on the growth kinetics and film properties of SiO₂ deposited by alternating injections of tris-DMAS and O₃/O₂. The deposition temperature was varied from 400°C to 700°C. First, we studied the reaction mechanism using in situ quartz crystal microbalance (QCM) at 400°C and measured the saturation dose of the precursor. Next, we investigated the growth rate and step coverage as a function of deposition temperature to determine the ALD temperature window. Finally, the physical and electrical properties of SiO₂ prepared at different temperatures were analyzed and compared. As a result, we propose that 600°C is the optimal ALD temperature to obtain film property and step coverage simultaneously.

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References [1] B. B. Burton et al., *J. Phys. Chem. C* (2009) [2] S. Ahn et al., *J. Vac. Sci. Technol. A* (2017)

AF-MoP-26 Ozone-based Atomic Layer Deposition of Titanium Dioxide (TiO₂) using TTIP, Dharsana Pulikkottil Dinesh, O. Nilsen, H. Sønsteby, University of Oslo, Norway

Atomic layer deposition (ALD) is a key method for industrial applications of functional oxide thin films in the ICT industry; especially binary oxides for high- κ dielectrics^[1,2]. This study investigates an approach for the deposition of titanium dioxide (TiO₂) thin films through ozone-based atomic layer deposition (ALD) utilizing titanium isopropoxide (TTIP) as the Ti precursor. We employ TTIP as the titanium precursor due to its stability and potential for enhanced film quality^[3], while ozone serves as an alternative to the traditional water-based processes, which allows Ti to be used in deposition of complex oxides. This is especially important for complex oxides where a hygroscopic intermediate is present at any stage during the process.

The deposition involves alternating exposure to the substrate with sequential pulse-purge cycles of TTIP and O₃, leading to the formation of TiO₂ thin film in a self-limiting nature. The study systematically explores the influence of process parameters such as precursor exposure time, ozone dose and temperature on the film growth and properties. Characterization techniques, including XRD, spectroscopic ellipsometry, UV-VIS spectroscopy, FTIR, and XRF, are utilized to study the surface morphology, chemical and structural characterization, substrate-film interface studies and thickness uniformity.

The results reveal a systematic understanding of the ozone-based ALD process using TTIP, with optimized deposition parameters leading to uniform and crystalline TiO₂ thin films. The films show promise in utilizing ozone based ALD with TTIP for deposition of higher order complex oxides containing titanium such as barium titanate, which is an excellent ferroelectric and photonic material.

References

- [1] R. W. Johnson et al., *Materials Today*, **17**(5), 236-246(2014)
- [2] S. M. George, *Chemical Reviews*, **110**(1), 111-131 (2009)
- [3] R. Vikrant et al., *The Journal of Physical Chemistry C*, **112**(26), 9552-9554 (2008)

Keywords: Atomic layer deposition; thin film; Ozone-based ALD; Transition metal oxides; TTIP precursor

AF-MoP-27 Design and Installation of an Advanced Reactor for in-Situ Studies of ALD and ALE by the TU/E Technical Team, Caspar van Bommel, M. Merckx, J. Zeebregts, C. van Helvoirt, F. van Uittert, E. Kessels, A. Mackus, Eindhoven University of Technology, Netherlands

Advancement in atomic-scale processing requires in-depth understanding into the reaction mechanisms of deposition and etching reactions, driving the need for in-situ diagnostics during the processing. In this work, a reactor designed and installed by our group's technical team for the study of surface reactions during ALD and ALE is described, with the focus on in-situ infrared spectroscopy at sub-monolayer sensitivity.

In-situ IR spectroscopy has been demonstrated to be a very powerful tool to study the mechanisms of ALD and ALE.[1,2] However, to achieve sub-monolayer sensitivity, substrate material dependent solutions are required, i.e. the use of pressed powder, attenuated total reflection (ATR) configurations for dielectrics, or grazing incident reflection adsorption IR spectroscopy (RAIRS) for metals. To accommodate a wide range of mechanistic studies we designed the reactor with the capability for in-situ transmission and reflection IR spectroscopy. A mount on the back flange of the reactor was designed such that the sample (and sample holder) can be installed vertically (for transmission) or horizontally (for reflection).

The system is a hot wall reactor that is equipped with a loadlock, has the capability to bias the substrate for ion energy control, has up to eight precursor/inhibitor bubbler capacity, and is pumped down using a turbomolecular pump backed with a roughing pump. Inspired on particle beam study setups in the fields of surface science and plasma physics, the setup has the option to install up to four plasma, light, or particle sources at a 45 degree angle. This option allows for individual studies on the effects of radicals, ions, and photons during ALD. Alternatively, these connections can be employed for additional in-situ diagnostics, e.g., optical emission spectroscopy (OES), quadrupole mass spectroscopy (QMS). This

contribution will outline the design and capabilities of this home-built reactor.

- [1] Goldstein et al., *J. Phys. Chem. C* **112**, 19530 (2008)
- [2] Mameli et al., *ACS Appl. Mater. Interfaces* **10**, 38588 (2018)

AF-MoP-28 Novel Hybrid Ligand Liquid Ta Precursor for High Temperature (> 480 °C) ALD Ta₂O₅/TaN Process, Hyunju Jung, K. Cho, S. Baik, W. Choi, S. Kim, J. Jeong, H. Kim, H. Lee, J. Kim, EGTM R&D, Republic of Korea

Ta₂O₅ has been developed for high- κ oxide of DRAM or resistive layer of RRAM, In addition, TaN has been developed for gate metal or barrier metal of Cu interconnects in semiconductor devices.^{1, 5, 7} Several liquid metal organic Ta molecules have been used for precursors of ALD Ta₂O₅ and TaN process. However, carbon impurity in the film due to low ALD temperature window of the metal organic precursors are strong obstacles to deposit impurity free film.⁸ Thus, low deposition temperature is a challenge for liquid metal organic precursors to deposit high quality film.^{1, 2, 4, 8}

Novel liquid Ta precursor with halide and metal organic ligand was developed for high temperature ALD Ta₂O₅ and TaN process. (Table 1). ALD window of new Ta precursor was estimated by ALD Ta₂O₅ process with O₃ reactant. Growth rate per cycle (~ 0.45 Å/cy) of ALD Ta₂O₅ is constant up to 480 °C (Fig 2), which is highest ALD temperature window of liquid Ta precursors reported up to now.

These organic-halide Ta precursor also has self-limiting growth characteristics. Metal organic Ta precursors tend to decompose, leading to an gradual increase in growth per cycle (GPC) with feeding time. In contrast, Halide Ta precursors has self-etching characteristics, resulting in decreased GPC with feeding time.^{4, 9} The development of organic-halide ligand Ta precursors overcome challenges related to GPC saturation degradation, (Fig 1) allowing for deposition of conformal films in high aspect ratio 3D structure.

This novel liquid Ta Precursor allows its application in high-temperature ALD processes. These characteristics are crucial for deposition of high-quality thin film in semiconductor devices.^{2, 4, 5}

References

1. H. C. M. Knoops, Materials Innovation Institute M2i, Journal of The Electrochemical Society, 155 12 G287-G294 2008
2. Virginie Brize ´, STMicroelectronics, Chem. Vap. Deposition 2011,17, 284–295
3. Charles Musgrave, Stanford University, J. Phys. Chem. C 2011, 115, 11507–11513
4. M. Lemberger, Friedrich-Alexander-University, Surface & Coatings Technology 201 (2007) 9154–9158
5. Nicholas A. Lanzillo, IBM, Appl. Phys. Lett. 116, 164103 (2020)
6. Yicheng Li, Huazhong University, Nature Communications (2023) 14:4493
7. Changhwan Choi, Applied Surface Science 579 (2022) 152118
8. A. Correia Anacleto, Thin Solid Films 519 (2010) 367–372
9. Christoph Adelman, imec, Chem. Vap. Deposition 2012,18, 225–238

AF-MoP-30 Impact of TMA Precursor Flow Rate on ALD-Processed Al₂O₃ Thin Films: Experimental and Simulation Insights, Júlia Karnopp, Aeronautic Institute of Technology, Brazil; N. Azevedo Neto, T. Vieira, Aeronautics Institute of Technology, Brazil; J. Sagás, Santa Catarina State University, Brazil; R. Pessoa, Aeronautics Institute of Technology, Brazil

Thin films are essential for enhancing the surface properties of bulk materials. Atomic Layer Deposition (ALD) plays a crucial role in this context due to its precise control over atomic-scale layer growth and its ability to produce uniform, conformal coatings. There has been extensive experimental and theoretical research on the thermal ALD process of Al₂O₃, focusing on the effects of various process parameters. However, the impact of precursor flow rate on the process has been minimally explored. This parameter is often not reported in standard ALD procedures, likely because of the challenges in directly measuring vapors from complex liquid or solid precursors.

This study investigates the effects of varying the TMA flow rate on the Al₂O₃ deposition process. Using a kinetic model, we simulate the deposition dynamics under different flow conditions. Precursor flow rates were determined based on system conductance. The simulation results were then compared with experimental data. Experimentally, Al₂O₃ films were deposited at varying TMA and H₂O flow rates at 150°C and 200°C. The properties of these films were evaluated using optical reflectance techniques and Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy.

The experimental results showed that lower TMA flow rates led to the formation of thinner films, suggesting a limited availability of TMA for surface reactions. As the TMA flow rate increased, a noticeable increase in film thickness was observed. At 150°C, film thickness reached a saturation point, while at 200°C, film thickness peaked and then decreased under the same conditions. Moreover, a significant influence of deposition temperature was observed, with higher temperatures leading to thinner films due to enhanced desorption rates. FTIR analysis indicated the potential for optimizing TMA flow rates to improve film purity by reducing carbon contaminants.

Simulations provided insights into the behavior of film thickness, confirming the experimental observation that film thickness increases and then saturates with rising TMA flow rates. This saturation is a consequence of the limited number of available sites on the surface for reactions. The TMA flow rate also profoundly influences the surface chemistry dynamics, changing the coverage fractions of species such as dimethylaluminum and monomethylaluminum. Variations in TMA flow rate significantly modified the partial pressures and reaction rates during deposition, impacting film formation dynamics and process efficiency.

AF-MoP-31 Lab-Scale Fixed Bed Reactor for Atomic Layer Deposition on Particulate Materials: Initial Results, Jorge A. Velasco, M. Ossama, C. Gonsalves, S. Larkiala, S. Andsten, Aalto University, Finland; K. Salonen, Elabs Oy Engineering, Finland; J. Rask, J. Stang, V. Miikkulainen, S. Jääskeläinen, R. Puurunen, Aalto University, Finland

Atomic layer deposition (ALD) has developed into a valuable instrument for the preparation of porous high-surface-area heterogeneous catalysts. Once on the material, the ALD material can for example act as active sites, promoters or overcoating to postpone catalyst deactivation.

Reactor configurations such as fixed bed, fluidized bed, and rotating drum can be applied to make ALD on particulate materials. Also, reactors meant for thin film processing are used for similar purposes by placing the particulate material on a tray and letting gaseous reactants flow over and diffuse into the bed.

Operating conditions of ALD reactors for particulate materials differ significantly from mainstream thin film reactors. Larger reactant doses are needed to saturate the surface of particulate materials with surface areas of 100's of m² per gram (compared to ~0.1 m² of a typical silicon wafer). Reactant amount scales directly with the surface area to be coated. In addition, with pore diameters in the order of few to tens nanometers, typical porous materials can have extremely high aspect ratios (HAR) in the order of ~10⁵. Longer reactant exposures are needed to coat HAR materials to allow the ALD reactant to diffuse into the porous structure.

From the various types of reactor configurations for ALD on particulate materials, we have chosen a fixed bed reactor since it offers an appropriate contact of gas and solid, straightforward application of heating and flow, and flexibility regarding the size and shapes of the particulate material.

The design of our self-constructed ALD reactor setup allows the coating of a few grams of porous high-surface-area materials for fundamental laboratory-scale studies. Operation can be performed under vacuum or atmospheric pressure. Loading and unloading the particulate material inertly is possible. Pre-treatment of the particulate material can take place at temperatures up to 800 °C under controlled gas flow. ALD reactants (liquid or powders) can be loaded inertly in reactant source vessels which can be heated up to about 200 °C and delivered to the reactor using a carrier gas. Delivery of gaseous sources from gas cylinders is included. The setup is equipped with an afterburner and a condenser for treating the unreacted reactant. Gas analysis of the gas stream downstream or upstream the reactor is possible at atmospheric pressure via a mass spectrometer connected online.

In this work, we present initial results of using the self-constructed ALD reactor setup. The results include the response of the temperature control system during heating and cooling steps and the performance of the reactant delivery system.

AF-MoP-32 Low Energy Ion Scattering Analysis of ALD 2D Materials, Philipp Brüner, T. Grehl, IONTOF GmbH, Münster, Germany; D. Shin, A. Ruiz de Clavijo, S. Lehmann, Leibniz Institute for Solid State and Materials Research, Dresden, Germany

2D materials, such as transition metal dichalcogenides or graphene, are a widely studied class of materials with promising applications in such fields as microelectronics, energy storage, bioengineering, or thermoelectricity [1][2]. While ALD with its self-limiting properties and sub-nm precision provides an ideal method for growing 2D materials, the physical and

chemical characterization of the obtained films is challenging for surface analytical methods. Especially for ultra-thin films consisting of only few atomic layers or even a sub-monolayer only, most analytical techniques suffer from their limited surface sensitivity, often including, and thus averaging over, both the deposited film and the growth substrate.

In this study, we present analytical results of low energy ion scattering (LEIS) applied to a variety of ultra-thin 2D material samples, including Sb₂Te₃ and SnSe. In LEIS, the energy spectrum of noble gas ions scattered from the sample surface is recorded. The evaluation of elemental peaks in the resulting spectra allows the quantification of the elemental composition of the first atomic layer [3]. This extreme surface sensitivity of just a single atomic layer, combined with composition analysis, is unique to LEIS and makes it especially useful in the study of ultra-thin films. In addition, sub-surface scattering signal from deeper layers gives information about sample composition and layer thickness up to depths of 10 nm.

We show how combining the top atomic layer sensitivity with layer thickness information allows us to quantify the surface coverage of the deposited films, identify surface impurities with high sensitivity, and make a statement about the growth mode of the films. While ALD should in theory grow films in a perfectly controlled layer-by-layer manner, the deposited films often show various degrees of island growth, where parts of the substrate are quickly covered by a multilayer film, while other parts of the substrate have not yet begun to initiate film growth.

[1] J. Yang et al., *Small* 2023, 2306350. <https://doi.org/10.1002/smll.202306350>

[2] *ACS Appl. Mater. Interfaces* 2022, 14, 48, 54034–54043. <https://doi.org/10.1021/acsmi.2c16150>

[3] "Low-Energy Ion Scattering" in *Characterization of Materials - Second Edition* ISBN 978-1-118-11074-4 - John Wiley & Sons.

AF-MoP-33 Plasma-Enhanced Atomic Layer Deposition Processes for Low-Temperature SiN_x with Aminosilane Precursors, Hyeonjin Choi, J. Kim, Y. Ko, H. Chae, Sungkyunkwan University (SKKU), Republic of Korea

In this work, a comparative study on aminosilane precursors for low-temperature plasma-enhanced atomic layer deposition (PEALD) of silicon nitride (SiN_x) was investigated. Dimethyl(tert-butyl)aminosilane (DMTBAS) and bis(tert-butyl)aminosilane (BTBAS) were used as silicon precursors, and ammonia (NH₃) was used as a nitrogen source in the PEALD processes. Process temperatures were varied from 50 to 350°C, and process conditions were optimized by precursor flow rate, ammonia flow rate, RF power, and plasma time. The effect of process variables was investigated with a spectroscopic ellipsometer(SE), X-ray photoelectron spectroscopy(XPS), and Fourier transform infrared spectroscopy(FT-IR). Growth per cycle of SiN_x with DMTBAS was 1.2Å/cycle from 50 to 150°C, and BTBAS was 0.7Å/cycle from 150 to 350°C. The small molecular volume of the DMTBAS reduces the steric hindrance during initial adsorption, which enables higher growth per cycle. Additionally, the mono-ligand structure in DMTBAS results in relatively low carbon content in the SiN_x films compared to those deposited with BTBAS.

AF-MoP-34 Characterization of Sticking Probability for Various ALD Chemistries Relevant for Artificial Solid Electrolyte Interphases, Léo Lapeyre, K. Mackosz, W. Szmyt, L. Pethö, J. Michler, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; P. Raynaud, LAPLACE, France; I. Utke, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

With the increasing demand for longer life time and safer batteries, atomic layer deposition (ALD) has become the method of choice for the synthesis of artificial solid electrolyte interfaces [1-3] (SEIs) due to its outstanding thickness control and conformality of deposited films, allowing the surface modification of porous cathode active material (CAM) from batteries electrodes in a unique way. In this context, the ALD process has to be optimized in order for precursors to diffuse in the high aspect ratio (AR) and porous 3D structures of CAMs, aiming for the full coverage of the active material. Namely, the diffusivity of precursors must be maximized to ensure a proper insulation of the CAM by the ALD thin films and prevent the CAM degradation induced by the electrochemical reaction with the electrolyte.

Szmyt *et al.* (2022) [4] developed a set of scaling laws describing the different ALD regimes (reaction- or diffusion-limited) and their corresponding surface coverage with respect to coating depth and sticking probability. Eq. (1) shows the expression of the coverage in the diffusion-limited regime, i.e. the dominating regime when depositing on high AR and porous substrates. From coverage profiles, this regime allows to determine the sticking probability of precursors, by measuring the coverage profile of

the chemisorbed film and obtaining λ_c . Consequently, the relation between described by Eq. (2) enables us to determine the sticking coefficient.

In our work, we apply this model to porous Si structures (series of cylindrical holes, see Fig. 1), allowing to determine the reaction front of the coating inside the pores. The penetration depth and, therefore, the sticking coefficient of given precursors can be determined, following Eq (2). By selecting specific ALD process parameters, such as the precursor pressure and the exposure time in the reactor, the penetration depth and coverage rate can be maximised. The influence of substrate temperature on the chemisorption probability is additionally investigated, in the objective of modifying the ALD regime and improve the conformality of deposited films. This optimisation step is then applied to various ALD processes involving different precursors and coating materials, including Li-based films.

AF-MoP-35 Deposition of High Quality Aluminium Fluoride Layers through Optimization of a PEALD Process using $\text{Al}(\text{CH}_3)_3$ and SF_6 , E. O'Connor, Fabian Steger, C. Sturzenegger, D. Schachtler, H. Thomé, RhySearch, Switzerland

Metal fluorides are of interest for various applications given their properties of low refractive index, wide bandgap and high transparency. Physical vapour deposition techniques have most frequently been used to deposit Aluminium Fluoride (AlF_3). In recent years there have also been a few reports on the growth of AlF_3 via ALD. This is of increasing interest for optical applications, particularly where conformal coatings are required on component geometries of increasing complexity. In this work AlF_3 films were deposited using a PEALD process with a trimethylaluminum ($\text{Al}(\text{CH}_3)_3$) precursor and a sulfur hexafluoride (SF_6) plasma. The depositions were performed in an Oxford Instruments FlexAL ALD system. A number of the PEALD parameters were optimized to deposit high quality AlF_3 films. Spectroscopic ellipsometry results indicate that the material has a low refractive index of 1.35 (@633nm). Atomic Force Microscopy demonstrates that the layers have low surface roughness comparable to the underlying substrate. The film density of 2.95 g/cm^3 as measured through X-ray reflection compares favourably to densities previously reported for both thermal and plasma enhanced ALD of AlF_3 . Compositional analysis to examine the incorporation of impurities shows no evidence of residual sulfur in the layers from the SF_6 plasma process. The optical performance of the films was also studied with regard to the PEALD process parameters, and relevant results will be presented including Laser Induced Deflection, Laser Induced Damage Threshold and Total Integrated Scattering.

AF-MoP-36 Characterization of Elemental Composition of ALD Films Using Ion Beam Analysis, Jaakko Julin, M. Laitinen, S. Kinnunen, T. Sajavaara, University of Jyväskylä, Finland

The knowledge of elemental composition of atomic layer deposited (ALD) films should be of interest to anyone depositing or using ALD films in some application. Ideally the stoichiometry, impurity concentrations as well as the thickness, or areal density (atoms/cm^2), of the deposited films should all be known with sufficient accuracy.

Most ALD films and interfaces contain impurities from partially reacted precursors (e.g. H, C, N, Cl, ...) or contamination from deposition tools (e.g. F) or from ambient exposure (O). Precise knowledge of the composition is often the key to understanding the electrical, optical, mechanical or other physical properties of the deposited films.

ALD films are well suited for elemental characterization with ion beam analysis (IBA) techniques using MeV ion beams. Classical IBA techniques, such as Rutherford Backscattering Spectrometry (RBS) and Elastic Recoil Detection Analysis (ERDA) require laterally homogenous films over the measured spot, typically several square millimeters. The main advantage of these methods is that they enable standard-free quantitative analysis of impurity concentrations and areal densities irrespective of the chemical composition or matrix. The depth of impurities can be determined with a depth resolution down to 1 – 2 nm at the surface. The chief disadvantage is that these methods require the use of a 1 – 3 megavolt electrostatic ion accelerator and the analysis is usually performed by a specialist in this field; typically not an ALD researcher.

This presentation aims to demonstrate the usefulness of IBA methods to the ALD/ALE community. Examples of IBA in general and RBS and ERDA in particular in ALD research will be shown. We have performed, for example, areal density measurements around 10^{14} atoms/cm^2 (1 $\text{at.}/\text{nm}^2$) of Hf [1] and Eu [2] with relative uncertainties within few %, measured impurities in low-temperature ALD of SbO_x [3], determined Fe/Zn ratios of intermetallic ALD films [4] and studied hydrogen incorporation by using heavy water as a precursor [5].

Jyväskylä actively works towards lowering the barriers of IBA, improving the commercial availability of IBA tools and analyses, reducing the footprint and complexity of the required accelerator system and developing analysis software and quality of analyses. The actions and benefits of this work are presented for the ALD community.

- [1] S. Lepikko et al. Nat. Chem. (2023) DOI:10.1038/s41557-023-01346-3
- [2] J. Rosa et al. Materials 14 (2021) 5966
- [3] J. Yang et al. Adv. Electron. Mater. 8 (2022) 2101334
- [4] R. Ghiyasi et al. Chem. Mater. 34 (2022) 5241
- [5] S. Kinnunen et al. Surf. Coat. Tech. 441 (2022) 128456

AF-MoP-37 Atomic Layer Deposition of Ga_2O_3 from GaI_3 and O_3 : Effect of Substrates on the Film Growth and Structure, Aivar Tarre, L. Aarik, H. Mändar, J. Aarik, Institute of Physics, University of Tartu, Estonia

Gallium oxide (Ga_2O_3) has a marked application potential in high-voltage power electronic devices, solar-blind radiation detectors, ferroelectric and resistive switching memory devices and functional coatings. Hence, development of novel methods for deposition of Ga_2O_3 thin films is of significant interest.

In this work, Ga_2O_3 thin films were grown by atomic layer deposition (ALD) from GaI_3 and O_3 as precursors [1]. The films were grown on single crystalline Si and $\alpha\text{-Al}_2\text{O}_3$ substrates at temperatures (T_G) ranging from 200–650 °C applying 500–1100 ALD cycles, respectively. The Ga, O and I content in the films as well as a relative growth rate were determined by X-ray fluorescence (XRF). Crystal structure of the films and their thickness, density and roughness were characterized by X-ray diffraction (XRD) and X-ray reflection (XRR) methods.

The films deposited at lower temperatures were X-ray amorphous on all substrates while those grown at $T_G \geq 350$ °C on $\alpha\text{-Al}_2\text{O}_3$ (001) and at $T_G \geq 450$ °C on Si were crystalline consisting of ϵ - or $\kappa\text{-Ga}_2\text{O}_3$ phase. The $\alpha\text{-Ga}_2\text{O}_3$ phase was obtained at higher temperatures on $\alpha\text{-Al}_2\text{O}_3$ (012) but starting from as low as 275 °C when $\alpha\text{-Cr}_2\text{O}_3$ seed layers were used on Si substrates.

- [1] L. Aarik, H. Mändar, J. Kozlova, A. Tarre, and J. Aarik. Atomic Layer Deposition of Ga_2O_3 from GaI_3 and O_3 : Growth of High-Density Phases. Cryst. Growth Des. 2023, 23, 5899–5911. <https://doi.org/10.1021/acs.cgd.3c00502>.

AF-MoP-39 On the Trail Ancient Worlds: Comparative Study of Commercial Scandium and Yttrium Precursors, Asgard, Midgard, Vanaheim and Olympus, Martin Wilken, Ruhr Universität Bochum, Germany; T. Hepp, O. Briel, Dockweiler Chemicals GmbH, Germany; A. Muriqi, Tyndall National Institute, University College Cork, Ireland; C. Cho, Ruhr Universität Bochum, Germany; M. Nolan, Tyndall National Institute, University College Cork, Ireland; A. Devi, Leibniz Institute for Solid State and Materials Research, Germany

Scandium and Yttrium based materials such as their oxides (M_2O_3 M=Sc;Y) have garnered significant attention in recent years due to their unique properties and versatile applications. The unique combination of high melting point, wide bandgap, high refractive index, and excellent dielectric properties makes these oxides attractive candidates for advanced electronic and optoelectronic devices, such as memory devices, and photodetectors.^[1] In particular, the ability of these group 3 oxides to serve as a high-k dielectric material in thin film transistors (TFT's)^[2], highlights the need for versatile low temperature atomic layer deposition (ALD) processes. There are very few Sc and Y precursors suitable for ALD, which include the homoleptic cyclopentadienyl based compounds ($[\text{M}(\text{Cp})_3]$)^[3], substituted tris – R-cyclopentadienyl based compounds ($[\text{M}(\text{RCp})_3]$ (R=Me,Et,Pr))^[4] and the beta-diketonates ($[\text{M}(\text{thd})_3]$)^[5]. These compounds are associated with certain drawbacks such as low vapor pressure, short shelf life, limited thermal stability and low reactivity.

The search for suitable precursors and former studies^[6] on our highly promising structurally similar mixed ethylcyclopentadienyl, bdma and dbt (bdma=N,N'-bisdimethylaminoacetamidinato; dbt=1,3-bis(1,1-dimethylethyl)-1-triazenato) complexes ASGARD ($[\text{EtCp}_2\text{Sc}(\text{dbt})]$), MIDGARD ($[\text{EtCp}_2\text{Sc}(\text{bdma})]$), VANAHEIM ($[\text{EtCpSc}(\text{dbt})_2]$) and OLYMPUS ($[\text{EtCp}_2\text{Y}(\text{dbt})]$) motivated us to perform a comprehensive comparative study on these precursors. Following up on a thorough investigation on the spectroscopical, structural and thermal properties, we adopted a computational approach to evaluate their use in ALD applications (Figure 1). Structure and ligand dissociation energies were calculated and gave a first indication for its suitability as ALD precursor. Furthermore, the interaction towards oxygen and water was investigated, showing their degree of reactivity. The comparison of the most promising candidates in

proof-of-concept ALD experiments have given useful insights on their suitability as precursors.

AF-MoP-40 Design and Study of N-heterocyclic Carbenes as ALD Precursors, Mark Aloisio, E. Desroche, F. Tumino, C. Crudden, Queen's University, Canada

Several key characteristics must be considered when developing an atomic layer deposition (ALD) precursor. Among these considerations are the ability for the precursor to form a controlled and uniform monolayer. As well, afford benign byproducts of deposition to be considered for use at processing scales. N-heterocyclic carbenes (NHC) are an emerging molecular thin film due to the desired precursor characteristics. These ligand-based films show superior stability in chemical extremes and resistance to thermal treatments. The use of the ligands in organometallic chemistry lies with the tunability of the NHCs through synthetic preparations. Applying this molecular knowledge, a designer ligand can be developed for a specific ALD application. This study will explain the synthetic control of the NHCs and show film characterization via scanning tunneling microscopy to view film density on a crystalline metallic surface.

AF-MoP-41 ALD at 50: Collaborations, Topic Modeling, and Intersection with Atomic Layer Etching and Area Selective Deposition, E. Alvaro, Northwestern University; **Angel Yanguas-Gil,** Argonne National Laboratory

Over the past 50 years atomic layer deposition has experienced tremendous growth in terms of publications, authors, and topics. In a prior work, we conducted a longitudinal study exploring the evolution of ALD as a field as seen through the lens of scientific literature.[1] Using bibliometric and network analysis, we were able to observe the evolution of the field from three independent collaboration networks to one giant collaboration network spanning all countries and topics, a reflection of the maturity and increasing integration of the ALD community as a research field.

In this work, we extend this study to the present day and explore the interaction of the ALD community with two adjacent fields: atomic layer etching and area selective deposition. Leveraging more powerful analysis tools, we apply machine learning methods to understanding the different themes cutting across the ALD literature. Finally, we apply a similar methodology to the fields of atomic layer etching and area selective deposition and explore the overlap with ALD.

[1] E. Alvaro and A. Yanguas-Gil (2018) Characterizing the field of Atomic Layer Deposition: Authors, topics, and collaborations. PLoS ONE 13(1): e0189137. <https://doi.org/10.1371/journal.pone.0189137>

AF-MoP-42 MoO₂ DRAM Bottom Electrode by Thermal ALD Using a New Liquid Mo Precursor, Myeongho Kim, Y. Yi, I. Lee, J. Kim, H. Ryu, W. Koh, UP Chemical Co., Ltd., Republic of Korea; **C. Hwang, W. Jeon,** Kyung Hee University, Republic of Korea

Conducting MoO₂ was proposed as an oxide electrode for DRAM. Crystal structure of monoclinic MoO₂ matches well with rutile TiO₂. ALD of high-k rutile TiO₂ film was demonstrated on MoO₂ film formed by pulsed laser deposition [1]. In this study, MoO₂ films were formed by thermal ALD on TiN using a new liquid Mo precursor with O₃, followed by post-deposition annealing (PDA). A metal-insulator-metal (MIM) capacitor structure was created using RuO₂ top electrode, ALD TiO₂ dielectric, and ALD MoO₂ bottom electrode on TiN. The dielectric constant (k) was measured as high as 100, indicating formation of high-k rutile TiO₂. XRD patterns show that monoclinic MoO₂ phase and rutile TiO₂ phase are prominent in annealed films compared to an as-deposited film (Figure 2). XPS was used to investigate relative amount of molybdenum oxidation state (+4, +5 and +6).

[1] W. Lee et al. *J. Mater. Chem. C*, 2018,6, 13250-13256

AF-MoP-43 The Role of Substrate Temperature on the Self-limiting Growth of Highly (200) Oriented Cubic NiO Films via Hollow-cathode Plasma-assisted Atomic Layer Deposition, F. Bayansal, S. Allaby, H. Saleh, B. Willis, Necmi BIYIKLI, University of Connecticut

In contrast to the relative abundance of as-grown unintentionally doped n-type semiconductor materials, there are only a few alternative alloys showing p-type conduction without needing extra high-temperature doping processes. Among them, CuO, Bi₂O₃, SnO, and NiO represent the most widely studied metal oxides which exhibit native p-type properties. NiO is of particular interest mainly due to its relative stability and promising performance as hole-transport layers in emerging solar cell device structures. However, the transport properties of NiO still needs to be substantially improved for its use as reliable transistor channel layers. While low-temperature thermal, plasma, and ozone-assisted ALD efforts have

resulted in p-type NiO films, the hole mobility is far from being sufficient, typically lower than 1 cm²/Vs.

In an attempt to enhance the hole transport properties in low-temperature as-grown NiO layers, in this study we have carried out a systematic study on plasma-enhanced ALD (PEALD) of NiO films on Si, SiO₂/Si, and sapphire substrates using nickelocene (NiCp₂) and O₂ plasmas in a 4" plasma-ALD reactor with a stainless steel-based hollow-cathode plasma (HCP) source, equipped with an *in-situ* ellipsometer. Detailed saturation studies using *in-situ* ellipsometry monitoring were carried out, scanning for NiCp₂ pulse time, O₂ plasma exposure time, purge time, and plasma power. Optimal growth conditions were identified as 90 ms NiCp₂ pulse / 10 s purge / 20 s O₂-plasma at 100 W plasma exposure / 10 s purge. To check the growth linearity and obtain thicker films for materials characterization, 800 cycle long runs were conducted to evaluate the substrate temperature impact (100 - 250 °C) on growth-per-cycle (GPC) and film properties.

The resulting NiO films are characterized for their structural, chemical, optical, and electrical properties. Films grown at 200 °C exhibit higher refractive index values reaching 2.3, which is in good agreement with reported values for the best polycrystalline NiO films in the literature. NiO films deposited on both Si and SiO₂/Si substrates exhibit polycrystalline single-phase cubic structure (c-NiO). Furthermore, NiO films deposited on sapphire substrates showed weak grazing-incidence XRD signatures along with very strong and relatively sharp (200) peaks in the $\theta - 2\theta$ scans. An interesting observation is that the lowest substrate temperature sample (100 °C) displayed the strongest (200) peak. Hall measurements of the as-grown NiO layers on glass substrates, revealed film resistivity values about 40 ohm-cm.

AF-MoP-44 2D and 3D Growth Competition in ALD Super-cycles Process: Fe₃Ni₂O₇ and Fe₃Co₂O₇, Estelle Jozwiak, Humboldt University Berlin, Germany

Atomic layer deposition (ALD) is the technique of choice to produce ultra-thin films with a high reproducibility, thickness reliability, conformality and surface coverage. The super-cycle ALD enables the deposition of ternary compounds while maintaining the advantages of a traditional ALD. However, combining two metallic precursors with different growth mode in a super-cycle process can result in unexpected atomic ratios and morphologies. Indeed, when combining Fe(Cp)₂ (2D growth) with Ni(Cp)₂ or Co(Cp)₂ (3D growth), a minimum growth per cycle (GPC) is observed, which also correlates with the formation of a mixed morphology.

AF-MoP-45 Surface Morphology Analysis for WO_x Thin Film after Post-Sulfurization, C. Chang, B. Liu, H. Chen, K. Chiu, C. Su, Y. Lin, Yang-Yu Jhang, Y. Pu, Taiwan Instrument Research Institute, NARlabs, Taiwan

TMDs are layered materials that can exhibit semiconducting, metallic and even superconducting behavior. In the bulk formula, the semiconducting phases have an indirect band gap. Recently, these layered systems have attracted a great deal of attention mainly due to their complementary electronic properties when compared to other 2D materials. However, these bulk properties could be significantly modified when the system becomes monolayer: the indirect band gap becomes direct. Such changes in the band structure when reducing the thickness have important implications for the development of novel applications, such as high photoluminescence (PL) quantum yield.

Previous studies have demonstrated direct sulfurization of the metal precursor as an effective route to produce large-area TMDs. In this paper, we have produced WS₂ by depositing WO_x thin films directly onto sapphire followed by sulfurization process. However, ALD technique is well known for its thickness controllability, reproducibility, wafer-level thickness uniformity and high conformality. Here, we grow WO_x films by ALD method, and the synthesized WS₂ layer retains the inherent benefits of the ALD process. The overall experiments and measurement were carried out on our homemade 6" cluster systems, which include ALD, RTP, and XPS modules. The sample transfer inside are under 5x10⁻⁶ torr to avoid air pollution. WO_x films were deposited on sapphire at ALD module at ~230°C. After that, sulfurization process was progressed at RTP module, which connected the sulfurization equipment. This equipment heats TAA powder to ~130°C and makes it produce H₂S gas. Before Raman data indicated the WS₂ vibration signal appearing at 354 and 418 cm⁻¹ when post-sulfurization temperature achieved to 800°C. In this work, the AFM data show WS₂ flakes starting to appear at 900°C, and its size are small than 50nm² generally. In-plane grazing incidence diffraction (IPGID) measurements also discover crystalline in the (110) and (100) direction becoming stronger when process temperature is larger than 900°C. Finally, photoluminescence (PL) spectra reveal its stacking orientation conditions and bandgap.

AF-MoP-46 Low-Temperature Atomic Layer Deposition Process of SnSe₂ Thin Films, *Alejandra Ruiz-Clavijo*, Institute for Metallic Materials, Leibniz Institute for Solid State and Materials Research, Germany

SnSe₂ films are deposited via atomic layer deposition (ALD) using SnCl₄ and Se(SnMe₂)₃ as Sn Se reactants, respectively. The deposition temperature window is from 80 to 100 °C, observing almost no growth above 110 °C due to Se desorption from the films. The growth per cycle (GPC) is 0.11 nm/cc at 80 °C. The as deposit films are amorphous, and present a smooth surface and compact appearance. Post-annealing of the films at 250 °C for 30 min improves the crystallinity of the films, obtaining polycrystalline films with preferred crystal orientation along the 001 direction. The optical and electronic properties of the films were characterized employing a UV-VIS spectrophotometer, and high temperature hall system.

AF-MoP-47 Conformality Characterization of Al-Doped ZnO Films Grown by Atomic Layer Deposition on Lateral High-Aspect-Ratio Test Structures, *Eero Haimi*, Aalto University, Finland; *A. Philip*, Aalto University, India; *J. Velasco*, Aalto University, Bolivia (Plurinational State of); *M. Karpinen*, *R. Puurunen*, Aalto University, Finland

Zinc oxide (ZnO) is a wide band-gap semiconductor with variety of applications as thin film material. With formation of intrinsic donors, or extrinsic doping, electrical and optical material properties of ZnO can be tuned. Accordingly, aluminum doped ZnO (AZO) is a prominent transparent conductive oxide candidate. There are growing nano-application areas, where film deposition on high-aspect-ratio structures is of interest. In this work, set of AZO, ZnO and Al₂O₃ thin films were applied on PillarHall™ lateral high-aspect-ratio (LHAR) test structures using atomic layer deposition (ALD). Well established diethylzinc (DEZ) and water as well as trimethyl aluminum (TMA) and water processes were used for ZnO and Al₂O₃ depositions, respectively. AZO films were deposited by alternating DEZ/H₂O and TMA/H₂O exposures, resulting in nanolaminate structure with nominally 10 nm ZnO layers alternating with nominally 2 nm Al₂O₃ layers. All depositions were carried out at 125°C temperature applying long pulse/purge sequences. Conformality of the deposited films were characterized using energy dispersive electron probe X-ray microanalysis (ED-EPMA). In evaluation of targeted film thickness and structure, both X-ray reflectometry (XRR) and grazing incidence X-ray diffraction (GIXRD) were used for reference films deposited on silicon. Film penetration depth into the LHAR cavity and saturation profile shape along the cavity were analyzed. The results showed differences between saturation profiles of ZnO and Al₂O₃ as expected. In the case of AZO films, the higher proportion of ZnO deposition dominated the overall saturation profile shape. However, Al/Zn composition ratio of AZO films seemed to change along the LHAR cavity. This implies possible variation in material properties of AZO films along the cavity. Based on the results, high-aspect-ratio performance of the processes is discussed.

AF-MoP-48 Advancing Plasma Processes: Insights from Retarding Field Energy Analyzers in Ald/Ale Applications, *Angus McCarter*, *T. Gilmore*, *A. Verma*, Impedans Ltd., Ireland

Atomic layer deposition and etching (ALD/ALE) are important processes for creating nano scale patterns as they can deposit or remove layers with atomic-scale precision, excellent uniformity, and atomic level surface roughness. However, as structures become more spatially demanding and device dimensions shrink, the necessity for controllable and optimized plasma processes intensifies. To meet these challenges, careful selection of process parameters such as RF source power, bias power, pulsing frequency, and duty cycles is essential. Additionally, maintaining a damage-free surface is paramount due to ion-induced damage in plasma-assisted processes. Thus, spatial and time-resolved measurements of ion energy distribution functions and ion flux become imperative, providing valuable insights into the dynamics of energetic ions on wafers to control the process and facilitating the preservation of undamaged surfaces.

Impedans offers a comprehensive range of retarding field energy analyzers (RFEAs) designed to address the need for wafer-level measurements within plasma environments [1, 2]. Positioned at the substrate, these RFEAs offer insights into surface interactions within the plasma. The *Semion*RFEA measures the uniformity of positive and negative ion energies and flux hitting a surface, at multiple locations inside a plasma chamber using an array of integrated sensors. The *Quantum* is an advanced RFEA, that combines energy retarding grids with an integrated quartz crystal microbalance (QCM) allowing measurements of the ion energy and flux as well as the ion-neutral ratio and deposition rate. The ion-neutral ratio serves as a critical parameter for optimizing film properties. This talk will highlight the applications of these RFEAs in various ALD/ALE processes

ranging from laboratory grade experiments to industrial tools [3-7]. Topics will include measurement challenges, innovative solutions, and successful case studies, shedding light on the transformative potential of RFEA technology in advancing plasma-assisted processes.

References

- [1] Impedans Ltd, Dublin, Ireland [www.impedans.com]
- [2] S. Sharma *et al.*, Ph.D. Thesis, Dublin City University (2016)
- [3] J. Buitter, Master's Thesis, Eindhoven University of Technology (2018)
- [4] H. C. M. Knoop *et al.*, *J. Vac. Sci. Technol. A* 39, 062403 (2021)
- [5] K. Arts *et al.*, *Appl. Phys. Lett.* 117, 031602 (2020)
- [6] S. Dallorto, Ph.D. Thesis, Ilmenau University of Technology (2019)
- [7] H. B. Profijt *et al.*, *ECS Trans.* 33 61 (2010)

AF-MoP-49 Precision Interface Engineering of CuNi Alloys by Powder ALD Toward Better Thermoelectric Performance, *Amin Bahrami*, *S. He*, Leibniz-Institut für Festkörper- und Werkstofforschung Dresden, Germany; *C. Jung*, Max-Planck-Institut für Eisenforschung GmbH, Germany; *R. He*, Leibniz-Institut für Festkörper- und Werkstofforschung Dresden, Germany; *Z. Ren*, University of Houston; *S. Zhang*, Max-Planck-Institut für Eisenforschung GmbH, Germany; *K. Nielsch*, Leibniz-Institut für Festkörper- und Werkstofforschung Dresden, Germany

The main bottleneck in obtaining high-performance thermoelectric (TE) materials has been identified as how to decouple the strong interrelationship between electrical and thermal parameters. Herein, we present a precise interface modification approach based on the powder atomic layer deposition (ALD) technology to enhance the performance of CuNi alloys. ZnO and Al₂O₃ layers as well as their combinations have been deposited on the surface of powders, typically in 10–100 ALD cycles, and their effect on the TE performance of bulks has been thoroughly investigated. The enhancement of the Seebeck coefficient, caused by the energy filtering effect, compensates for the electrical conductivity deterioration due to the low electrical conductivity of oxide layers. Furthermore, the oxide layers may significantly increase the phonon scattering. Therefore, to reduce the resistivity of coating layers, a multilayer structure is deposited on the surface of powders by inserting Al₂O₃ into ZnO. The accurate microstructure characterization shows that the Al atoms diffused into ZnO and realized the doping effect after pressing. Al diffusion has the potential to increase the electrical conductivity and complexity of coating layers. Compared to pure CuNi, αT increased by 128% due to the decrease in resistivity and stronger phonon scattering in phase boundaries.

AF-MoP-50 Advances in Rare Earth Precursors for ALD, *Dominik Naglav-Hansen*, Ruhr Universität Bochum, Germany

Rare-earth (RE) containing materials are of significant importance for many fields of modern technology and environmental applications and have grown dramatically in diversity and importance over the past five decades.^[1,2]

The interest in RE containing materials can be attributed to their broad number of intrinsic functional properties. Especially RE oxides, nitrides and sulphides are currently of high interest for applications such as high- κ dielectrics (Y₂O₃, CeO₂), spintronics (EuS, GdN) and photovoltaics (Nd₂S₃).^[3-13] Reliable and scalable synthesis routes which yield high quality materials are required. Atomic layer deposition (ALD) is one such method that can meet the demands of modern device processing technologies. However, to develop ALD processes for RE-containing materials, suitable precursors are of utmost importance. There are very few precursors available for RE elements to choose from. Besides sufficient volatility and thermal stability at the operating conditions, the precursors need to exhibit a high reactivity towards the employed co-reactant.

A series of RE metal containing precursors with the formula [M(L)₃] (M = Sc, Y, Eu, Gd, Dy, Er); L = malonates, guanidates) were synthesized. The tunability of the structural and thermal properties via variation of the ligand side chains was demonstrated for these compounds with systematic thermogravimetric analysis studies (TGA). Proof-of-concept metal insulator semiconductor (MIS) capacitor structures with Gd₂O₃ resulted in promising electrical characteristics.

- [1] S. Cotton, *Lanthanide and Actinide Chemistry*, Wiley & Sons Ltd., West Sus., UK, 2006 [2] V. Balaran *Geos. Front.*, 10, 1285-1303 [3] A. Devi *et al Dalton Trans.*, 2022, 51, 5603-5611 [4] A. Devi *et al Dalton Trans.*, 2021, 50, 12944-12956 [5] A. Devi *et al Chem. Eur. J.*, 2021, 27, 4913-4926 [6] A. Devi *et al RSC Advances*, 2021, 11, 2565-2574. [7] A. Devi, M. Lastusaari *et al J. Lumin.*, 2019, 215, 310-315 [8] A. Devi *et al Dalton Trans.*,

2019, 48, 2926-2938 [9] A. Devi, R. B. M. Cross et al *Advances in Materials* 2018, 7(4), 137-143 [10] A. Devi, M. Karppinen et al *J. Mater. Sci.* 2017, 11, 6216-6224 [11] A. Devi et al *Chem. Vap. Dep.* 2015, 10-11-12, 335 [12] A. Devi et al *J. Nanosci. Nanotechnol.* 2014, 14(7), 5095 [13] A. Devi, S. T. Barry et al *Aust. J. Chem* 2014, 67(7), 989.

AF-MoP-51 New Non-pyrophoric Metalorganic Precursor for ALD of Ga₂O₃, Marcel Schmickler, F. Preischel, A. Devi, Ruhr University Bochum, Germany

The number of publications on Gallium oxide (Ga₂O₃) as a thin film material has risen considerably over the past five years. This can be attributed to the promising properties of this material system for various applications that include amongst others being a transparent conductive oxide (TCO) material with a wide bandgap of 4.5 – 4.9 eV.^[1] Paired with the high theoretical breakdown field strength of 7-8 MV/cm, the β-Ga₂O₃ phase is suitable for high-power applications.^[2] Additionally, Ga₂O₃ thin films selectively doped with specific rare-earths were demonstrated to make red, green, and blue LEDs.^[3]

The thin film deposition of group III element oxides via ALD is frequently done with the respective alkyls, which in the case of gallium is trimethylgallium (TMG). Although volatile, this precursor is highly pyrophoric and requires special precautions while handling. Additionally, it lacks the necessary reactivity towards water for thermal ALD.^[4]

Encouraged by the results of our previous studies regarding the development of non-pyrophoric aluminum precursors^[5,6] we extended the underlying concept of introducing intramolecularly stabilizing ligands to gallium with the scope of developing non-pyrophoric Ga precursors, yet being highly volatile and reactive. The new Ga compound is a low-melting solid with the thermal properties being very promising as depicted in the vaporization behavior illustrated in Figure 1. In this presentation, the focus is on tuning the physico-chemical properties of the Ga precursor and the subsequent ALD process development of high-quality Ga₂O₃ thin-films using this non-pyrophoric precursor.

[1]J. Wang, X. Ji, Z. Yan, S. Qi, X. Liu, A. Zhong, P. Li, *Journal of Alloys and Compounds*, 2024, 970, 172448.

[2]S. Wu, N. Liu, H. Li, J. Zhang, S. Shen, W. Wang, N. Xia, Y. Cao, Z. Zhong, W. Zhang et al., *Physica Rapid Research Ltrs.*, 2024, 18, 2300110.

[3]Q. Guo, K. Saito, T. Tanaka, *ACS Appl. Electron. Mater.*, 2023, 5, 4002.

[4]D. J. Comstock, J. W. Elam, *Chem. Mater.*, 2012, 24, 4011.

[5]L. Mai, M. Gebhard, T. de Los Arcos, I. Giner, F. Mitschker, M. Winter, H. Parala, P. Awakowicz, G. Grundmeier, A. Devi, *Chem. Eur. J.*, 2017, 23, 10768.

[6]L. Mai, N. Boysen, D. Zanders, T. de Los Arcos, F. Mitschker, B. Mallick, G. Grundmeier, P. Awakowicz, A. Devi, *Chem. Eur. J.*, 2019, 25, 7489.

AF-MoP-52 Novel Molybdenum Precursor for Chemical Vapor Deposition and Atomic Layer Deposition, Yuma Dote, A. Yao, A. Kikuchi, Central Glass Co., Ltd., Japan

The existing 3D-NAND memory uses materials such as Cu and W for word lines. However, as the memory width increases in the future, it becomes imperative to reduce the metal liner width, among other factors. Mo, with lower resistance than W in ultra-scaled dimensions^[1], exceptional processability, and being a barrierless material, emerges as a suitable candidate for next-generation interconnect materials.

Common Mo precursors for CVD and ALD include MoF₆, MoO₂Cl₂, and MoCl₅. Unfortunately, MoF₆ and MoCl₅ exhibit high reactivity, leading to substrate etching and loss during deposition. MoO₂Cl₂ is also prone to oxygen contamination^[2]. In this study, we address these issues by introducing a new Mo precursor, F4M.

Herein, Mo films were deposited on TiN and SiO₂ substrates using F4M, MoF₆, and MoO₂Cl₂. Various analysis methods, including SEM, XRD, and XPS, were employed to comparatively evaluate the Mo film quality. Results indicate that F4M does not show any the substrate loss due to etching during deposition (see supplemental document ; Fig. 1,2). Additionally, F4M also deposited Mo films on TiN and SiO₂ without a seed layer with a shorter incubation time than MoO₂Cl₂. The low substrate loss and short incubation time can be attributed to the low energy required for nucleation (see supplemental document ; Fig. 3). Furthermore, the electrical properties of the deposited Mo films were evaluated using four-terminal sensing. The electrical resistivity of the Mo film deposited by F4M was 6.9 μΩcm (electrical resistivity of bulk Mo: 5.2 μΩcm), lower than Mo films deposited with other precursors (see supplemental document ; Table 1)^[3]. The Mo film formed using F4M exhibited low electrical resistivity due to fewer impurities and larger Mo grain growth. Therefore, we believe that F4M is the most promising precursor for forming high-quality Mo films and is

suitable for both CVD and ALD.

[1] Daniel Gall, *J. Appl. Phys.*, 2020, 127, 050901.

[2] Baek-Ju Lee et al., *Coatings*, 2023, 13 1070.

[3] Kees van der Zouw et al., *J. Vac. Sci. Technol.* 2023, A41, 052402.

AF-MoP-53 Role of Indium and Tin Elements in Zinc-Based Ternary Oxide Thin Films Grown by Atomic Layer Deposition, Dong-Hyun Lim, I. Oh, A. Choi, Ajou University, Republic of Korea

Amorphous oxide semiconductors (AOSs) are highlighted for their potential as channel materials, attributed to high mobility and low off current [1], leading to the exploration of diverse transition metals and the proposal of various AOS materials. [2] Among these, the In-Zn-O (IZO) system, notably In-Ga-Zn-O, and the Zn-Sn-O (ZTO) system have shown superior electrical performance due to high mobility from overlapping In³⁺ and Sn⁴⁺ 5s orbitals. [3] However, intrinsic differences such as ionic radius, electronegativity, and metal-oxygen bond strength between In³⁺ and Sn⁴⁺ result in distinct properties for IZO and ZTO materials. [4] Given these differences, further research is crucial to deepen our understanding of the roles of In and Sn in AOS materials.

In this study, we investigate the effects of incorporating In and Sn into ZnO thin films via atomic layer deposition (ALD), analyzing the film properties. To examine the electrical properties in detail, bottom-gate thin film transistors (TFTs) with varying compositions of IZO and ZTO channels were fabricated to compare performance. We observe that while single ZnO films exhibit wurtzite crystallinity, incorporating In or Sn shifts the films to an amorphous state. This incorporation also leads to a negative shift in the threshold voltage (V_{th}) for TFT devices, indicating increased film conductivity with higher In or Sn content. We compare the electrical characteristics of TFT devices based on both IZO and ZTO channels, with intermediate ratios of Zn to In and Sn, respectively. As-deposited IZO TFT is too conductive, not displaying on/off characteristic; however, after annealing in air for 1 hour, it shows improved performance with a V_{th} of -7.4 V, field effect mobility (μ_{FE}) of 59 cm²/V s, and an I_{on} of 430 μA. Conversely, ZTO TFT displays on/off characteristic even before annealing with a V_{th} of -7.4 V, μ_{FE} of 14.8 cm²/V s, and an I_{on} of 110 μA. This suggests that incorporating In into ZnO films makes them more conductive compared to Sn.

References [1] T. Kim. et al., *Adv. Mater.*, 35, 2204663 (2023). [2] S. Lee., *Trans. Electr. Electron. Mater.*, 21, 235-248 (2020) [3] B. Lu et al., *Curr. Opin. Solid State Mater. Sci.*, 27, 101092 (2023) [4] S. Parthiban et al., *J. Mater. Res.*, 29, 1585–1596 (2014)

AF-MoP-54 Ultra-Low Electron Temperature Plasma for Damage-Free Atomic Layer Deposition of Titanium Nitride Films: Advancements in PEALD Process Applications, MINSEOK KIM, S. Kim, C. Lim, D. Kim, C. Chung, Hanyang University, Korea

The characteristics of Titanium Nitride (TiN) thin films have been improved by utilizing an ultra-low electron temperature (ULET, T_e < 1 eV) plasma in the plasma-enhanced atomic layer deposition (PEALD) process. The ULET plasma is produced by an inductively coupled plasma system with a DC grid system. Ultra-low electron temperature plasma can significantly reduce damage induced by the plasma. Due to its low ion energy, there is less damage from ion bombardment caused by self-bias voltage, and the absence of UV generation reduces damage from radiation. In the ULET-PEALD process, the resistivity of TiN films is reduced to 325 μΩcm, compared to 430 μΩcm in films deposited by the conventional PEALD method. Additionally, this method has reduced the surface roughness of TiN films to 0.3 nm from 0.78 nm, as measured by Atomic Force Microscopy (AFM). The deposition of TiN films at the atomic level is verified through Auger Electron Spectroscopy (AES) and X-ray diffraction (XRD) analyses. The film thickness, measured by Scanning Electron Microscopy (SEM), indicated a growth rate of about 1.5 Å per cycle. These enhanced characteristics of the TiN films can be explained through the physical mechanisms of ULET plasma

AF-MoP-56 Ultra Thin Diffusion Barrier Development by Utilizing Advanced Deposition Materials in ALD, Changbong Yeon, D. Cho, J. Jung, Soulbrain, Republic of Korea; K. Tan, Soulbrain, Malaysia; J. Lim, Y. Park, Soulbrain, Republic of Korea

As integrated circuits (IC) scaling continues to progress, both the transistor size and the gap between devices decrease, leading to various issues such as increased wiring resistance, quantum tunneling, and heat generation. Specifically, in terms of interconnect metallization, this reduction in

dimensions poses significant challenges including the resistivity size effect, electro migration, and insufficient conductor space [1]. Consequently, the performance of the device becomes highly dependent on the electrical resistance rather than the processing speed of the transistor. The resistance-capacitance (RC) delay of the circuit, which determines the quality of IC performance, is primarily influenced by the electrical resistivity (ρ) of the material [1]. In order to solve the RC delay issues, the adoption of new conducting materials such as Ru and Mo is attracting attention. However, it remains challenging due to the requirements for developing suitable processes and new precursors.

Another strategy to address these RC challenges is to reduce the thickness of the diffusion barrier and increase the volume of the conducting material [1]. Typically, TiN thin film is used as a barrier material for metal films. However, films with a thickness below 25 Å exhibit poor continuity and fail as diffusion barriers due to facile crystallization of TiN in a columnar structure, resulting in high surface roughness.

In this study, our objective was to increase the volume of the conducting material by reducing the critical thickness of the diffusion barrier while maintaining excellent diffusion barrier properties. To achieve this, we introduced a new deposition material known as advanced deposition material to control surface chemical reactions such as adsorption and reaction with the reactant gas [2]. Consequently, the deposition process and film properties were significantly improved. For instance, the film density increased from 4.3 g/cm³ to 5.2 g/cm³, eliminating nucleation delay in the ALD process. Additionally, the surface roughness was reduced from 0.33 nm to 0.15 nm. Even at an extremely thin thickness of approximately 1 nm, we observed a conformal thin film and conducted a pinhole formation test using HF dipping to confirm the diffusion barrier properties. Based on the experimental evidence, we believe that this research will contribute to the development of new strategies for next-generation interconnect process.

References

1. J. H. Moon, E. Jeong, S. Kim, T. Kim, E. Oh, K. Lee, H. Han, and Y. K. Kim, *Adv. Sci.* **10**, 23, 2207321 (2023)
2. C. Yeon, J. Jung, H. Byun, K. C. Tan, T. Song, J. H. Kim, S. J. Lee, and Y. -S. Park, *AIP Adv.* **11**, 015218 (2021)

AF-MoP-57 A Novel Liquid Ruthenium Precursor and Its Successful Implementation in ALD, Niklas Huster, Ruhr University Bochum, Germany; *I. Selvakumar*, Ruhr University Bochum, India; *F. Preischel*, *J. Obenluneschloß*, Ruhr University Bochum, Germany; *M. Gock*, *M. Unkrig-Bau*, *F. Eweiner*, Heraeus Precious Metals GmbH & Co. KG, Germany; *D. Rogalla*, RUBION - Ruhr University Bochum, Germany; *A. Devi*, Ruhr University Bochum, Germany

With the semiconductor industry reaching the 2 nm node and below, Copper (Cu) as a well-established interconnect material in integrated circuits (IC's) in the back-end-of-line (BEOL) process chain is reaching its limitations due to diffusion and electromigration under operating conditions.^[1] Next to Cobalt (Co), Ruthenium (Ru) is the most promising candidate to replace Cu in next generation microchips, due to higher chemical stability and shorter electron mean free path.^[2] To deposit thin films homogeneously over complexly structured substrates, as in next generation 2 nm and below gate-all-around field effect transistors (GAAFETs), atomic layer deposition (ALD) is the method of choice. However, finding suitable ALD Ru-precursors matching the requirements of high vapor pressure alongside thermal stability and high reactivity is a challenging task for researchers from academia and industry likewise.

In this presentation, we report on the synthesis of a novel liquid Ru precursor and its successful utilization in a Ru ALD process. The promising thermal properties as depicted in Figure 1, prompted us to employ it for Ru metal film deposition in combination with oxygen as co-reactant. This resulted in the growth of Ru films on Si and Cu substrates in the temperature range 250 – 300 °C with a GPC of 0.8 Å. The as-deposited films were analyzed by means of scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and X-ray reflectivity (XRR). The layer composition was determined by means of X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS) and nuclear reaction analysis (NRA) which revealed the high purity of the layers. The new findings on this newly developed precursor and associated ALD process can be rated as a significant step forward to meet the demands of the semiconductor industry for the 2 nm and beyond node.

[1]C. Adelman, *IEEE Int. Interconnect Technol. Conf. Proc.*, IEEE, San Jose, CA, USA **2016**, p. 38

[2]M. Popovici, B. Groven, K. Marcoen, Q. M. Phung, S. Dutta, J. Swerts, J. Meersschaut, J. A. van den Berg, A. Franquet, A. Moussa, K. Vanstreels, P. Lagrain, H. Bender, M. Jurczak, S. van Elshocht, A. Delabie, C. Adelman, *Chem. Mater.*, **2017**, 29, 4654

AF-MoP-58 Tailoring the Properties of Oxide Films by Doping Using Atomic Layer Deposition Method, Mahtab Salari Mehr, L. Aarik, T. Jõgiaas, H. Mändar, University of Tartu, Estonia

The complex ternary compound materials have received considerable attention in the last decades due to the exhibition of superior mechanical, optical, and chemical properties compared to their binary counterparts [1,2]. The programmable cycle formula of ALD enables control of the concentration of dopant elements in the composition of the thin films. Aluminum oxide and chromium (III) oxide are well-known ceramic materials showing interesting optical, and mechanical properties (hardness, elastic modulus, wear resistance). It has been reported previously that combining Cr₂O₃ and Al₂O₃ enables to tailor the properties of these oxide films for various applications [3]. In the current research study, ternary compound Cr-Al-O thin films (thickness from 50 to 80 nm) were deposited on Si (100) substrates using the ALD deposition formula of $n \times (\text{Cr}(\text{thd})_3\text{-O}_3) + m \times (\text{TMA-O}_3)$ at a deposition temperature of 275 °C. The enhancement in nanoindentation hardness values of (Cr, Al)₂O₃ films was observed compared with those of binary films. Furthermore, wear resistance measurements displayed less plastic deformation of the ternary (Cr, Al)₂O₃ films under applied wear load compared with binary Cr₂O₃ and Al₂O₃ films that exhibited ploughing-induced plastic deformation during wear. A decrease in the wear rate was observed for the ternary film with a higher hardness of 18.4 GPa and lower plasticity index value of 0.260 compared with binary oxide films (Fig. 1). Our findings showed that the deposition of multicomponent films paves the way for tailoring thin film materials with enhanced mechanical properties and wear durability for various industrial applications.

References:

[1] Salari Mehr, M.; Aarik, L.; Jõgiaas, T.; Tarre, A.; Kasikov, A.; Roosalu, K.; Mändar, H., *J. Alloys Compd.* **2023**, *968*, 172041. <https://doi.org/10.1016/j.jallcom.2023.172041>.

[2] Bahrami, A.; Delgado, A.; Onofre, C.; Muhl, S.; Rodil, S. E., *Surf. Coat. Technol.* **2019**, *374*, 690–699. <https://doi.org/10.1016/j.surfcoat.2019.06.061>.

[3] Koller, C. M.; Dalbauer, V.; Schmelz, A.; Raab, R.; Polcik, P.; Ramm, J.; Mayrhofer, P. H., *Surf. Coat. Technol.* **2018**, *342*, 37–47. <https://doi.org/10.1016/j.surfcoat.2018.02.077>

AF-MoP-59 Low-Temperature Atomic Layer Deposition of Vanadium Oxide: Unveiling the Nucleation and Growth Mechanism, Characterization, and Its Application in Perovskite Solar Cells, NIRANJAN SINGH BAGHEL, S. Sarkar, Indian Institute of Technology Bombay, India

Vanadium oxide (VO_x) thin films are pivotal in numerous applications ranging from smart windows to sensors, energy storage devices and solar photovoltaics. VO_x atomic layer deposition (ALD) is accomplished using sequential exposures of Vanadium (V) tri-*i*-propoxy oxide (VTIP) and H₂O for employed as a metal and oxygen sources, respectively, at low temperatures in a custom-built viscous flow reactor remains challenging, limiting their integration onto sensitive substrates. This study introduces the atomic layer deposition (ALD) technique for the growth of VO_x thin films at low temperatures, emphasising the enhancement of film uniformity, stoichiometry, and functional properties through precise process control where we explain the nucleation and growth mechanism of ALD VO_x in particular, hybrid halide perovskite surface aiming to utilize the process for photovoltaic devices in *n-i-p* configuration. We employ *in-situ* QCM to understand the deposition mechanism. Through this presentation, we reveal that not the thermodynamics but the kinetic of the deposition plays a pivotal role for the optimal photovoltaic performance employing ALD grown VO_x as the hole transport material.

AF-MoP-60 Fermi Level Tuning of ZnO Films through Mn Doping via Atomic Layer Deposition Supercycles, Carolina Bohórquez Martínez, Center of Nanoscience and Nanotechnology-UNAM, Mexico; *M. Domínguez de la Vega*, Institute for Research into Electronic Microscopy and Materials-UCA, Spain

The control of the electrical and mechanical properties of ZnO films is paramount for their diverse applications in electronic and optoelectronic

devices. Doping with various elements presents a versatile method to tailor these properties. In this work, we investigate the doping process of ZnO films with Mn using supercycles of atomic layer deposition (ALD), allowing for precise modulation of their electrical characteristics.

We employ scanning Kelvin probe force microscopy (KPFM) to measure the contact potential difference (V_{CPD}) directly, providing invaluable insights into the influence of the dopant on the Fermi level position within the bandgap. Our results reveal changes in the work function correlated with varying Mn dopant concentrations, offering significant insights into the doping mechanism.

Additionally, we confirm the piezoelectric nature of the material through surface potential measurements, both before and after mechanical force application with a cantilever. Subsequent evaluation of the film's polarization behavior involves comprehensive measurements, including pre-polarization assessments and post-polarization analyses up to 18 hours, demonstrating the temporal stability of the polarization. Furthermore, polarization is assessed using intermittent mode, allowing for purely electrical polarization, with data acquisition facilitated through DataCube technology. Our findings unveil a strain gradient induced by polarization, indicative of inverse flexoelectricity phenomena.

This study contributes comprehensive insights into the electrical and mechanical properties of Mn-doped ZnO films grown via ALD, providing crucial knowledge for utilizing these films in various electronic and optoelectronic applications.

AF-MoP-61 Atomic Layer Deposition of HfO₂ Thin Film Using a Novel Pyrrole Based Hf Precursor, Hyunwoo Jeong, C. Park, K. Park, H. Kim, K. Lee, J. Park, Hansol Chemical Co., Ltd., Republic of Korea

Group 4 metal oxide materials such as ZrO₂, TiO₂, and HfO₂ have attracted considerable attention for dielectric materials for microelectronic devices. HfO₂ films has an outstanding high-dielectric constant ($\kappa \sim 20$ -25, t-HfO₂), large band gap Energy ($E_g \sim 6.0$ eV) and good thermal stability. For these reason, the HfO₂ thin film applicate microelectronic devices such as the dynamic random access memory (DRAM) capacitors and central processing memory (CPU) gate dielectric application.

The most representative Hf precursor, CpTDMAHf (HAC), is known to exhibit excellent film properties when reacted with O₃ at 320°C. Recently, research is being conducted to develop precursors that can replace HAC under various conditions (temperature, reactant gas). We have developed precursors that can be used in either high or low temperature deposition and recently, we have designed new precursors for the application of various reaction gases.

In this study, we propose a novel pyrrole based Hf precursor namely HEP. The physical characteristic of HEP was investigated by NMR Spectroscopy. Also, we measure the properties of the HfO₂ thin film of HEP against usually used HAC by thermal atomic layer deposition (TALD). For both precursors HEP and HAC, the characteristic self-limiting ALD growth mode was confirmed. HAC reacts with O₃ at 320°C to form HfO₂ films, while HEP reacts with H₂O to form HfO₂ films.

Composition ratio of HfO₂ films were investigated by XPS. HfO₂ films deposited with HEP showed a comparable composition ratio to HAC at a lower temperature of 280°C. Also, C impurities in deposited film of HEP were 0.34%, which is lower than that of HAC (0.59%). Surface roughness of HfO₂ films were investigated by AFM. The deposited film of HEP represented comparable roughness compared to that of HAC.

From this study, The HEP is expected to be advantageous precursor for low temperature thin film deposition technique.

AF-MoP-62 Low-Carbon Silicon Oxynitride Films with Trisilylamine, Youngju Ko, H. Choi, J. Kim, N. Kim, H. Chae, Sungkyunkwan University (SKKU), Republic of Korea

Silicon oxynitride (SiON) has better barrier properties than silicon oxide (SiO_x) and better transmittance properties than silicon nitride (SiN_x). [1] Good SiON properties are required in various industrial fields such as semiconductors, organic light emitting diodes (OLEDs) and solar cells. One of the requirement for good SiON films is low carbon impurities. [2] However, most of conventional precursors are carbon-containing precursors such as hexa-methyldisilazane (HMDS), bis(tertiarybutylamino)-silane (BTBAS), tris(dimethyl-amino)silane (TDMAS), etc. [3] In this study, trisilylamine (TSA), a carbon free precursor, was used to deposit SiON by both plasma enhanced chemical vapor deposition (PECVD) and plasma enhanced atomic layer deposition (PEALD) with minimal carbon impurities. SiON with TSA had less than 3% carbon. Compared to the conventional precursors (BTBAS, TDMAS), there was a difference in carbon content of

more than 10% points. The carbon bonding state in the films was identified as C-H bonding mostly, or hydrocarbon (CxHy) functional groups contained in the conventional precursors. As the carbon content increased, the silicon and nitrogen contents decreased and Si-N bonds decreased. This study suggests that TSA, a carbon free precursor, may be a suitable precursor for the deposition of SiON films having improved film density.

AF-MoP-64 High-Temperature Atomic Layer Deposition of SiO₂ Using Metalorganic Si Precursor, Sojeong Eom, S. Lee, H. Yoon, S. Park, S. Na, J. Yoo, S. Jung, H. Kim, Yonsei University, Korea

Silicon dioxide (SiO₂) has been widely used in the semiconductor industry due to its good insulation properties such as wide bandgap, low leakage current, and good thermal stability. For example, high-quality SiO₂ films have been examined for use as tunneling oxide in NAND flash memory. The degradation of the device performance in 2D planar NAND was unavoidable as its integration density was increased solely through device scaling down. In this regard, vertically stacked NAND (3D V-NAND) was introduced, which could achieve a higher integration density by increasing the number of stacked layers. As a result, the device structure becomes more complex with high aspect ratio trenches. For these reasons, atomic layer deposition (ALD) is conducted for the deposition of the SiO₂ tunneling layer in 3D V-NAND. Furthermore, it requires thermal ALD rather than plasma-enhanced ALD because it usually suffers from non-conformal deposition in a high aspect ratio structure. Consequently, there has been attracted attention to the development of high-temperature thermal ALD to achieve a conformal deposition of high-quality SiO₂. For ALD SiO₂, aminosilane has been widely used, but thermal decomposition would occur at high temperatures (> 300 °C) due to its low thermal stability of the Si-H bond. SiCl₄ is known for good thermal stability, but it requires a large amount of exposure (> 10⁹ L) and the growth per cycle (GPC) is low due to its low reactivity. In this manner, we explored high-temperature thermal ALD using ozone and aminosilane, where the Si-H is replaced with the Si-CH₃ ligands, known for better thermal stability. The growth characteristics were investigated at deposition temperatures from 100 °C to 700 °C. The saturated GPC was 1.5 Å/cycle at 500 and 600 °C, while CVD-like growth was observed at 700 °C, revealing the thermal decomposition of the Si precursor. We also compared the film quality of SiO₂ deposited at 500, 600, and 700 °C by electrical characterization of metal-oxide silicon capacitor.

AF-MoP-65 Tailoring Crystal and Electrical Characteristics of Indium Oxide via Oxygen Reactants and Substrate Temperature Control in Atomic Layer Deposition, Seong-Hwan Ryu, T. Hong, S. Choi, Hanyang University, Korea; K. Yeom, D. Ryu, J. Seok, Hansol Chemical, Republic of Korea; J. Park, Hanyang University, Korea

In recent years, oxide semiconductors (OSs) have shown potential as an alternative to Si-based semiconductors due to certain advantageous properties such as high mobility, reduced off-current, and amenability to low-temperature fabrication. In addition, OSs have the advantage of being able to engineer the properties of materials by introducing various metal elements and controlling their composition, so multi-component materials such as InGaZnO, InSnGaO, InSnZnO, InGaO, and InZnO have been explored. In common, indium oxide (InO_x) is selected due to its favorable electron conduction attributes, so an in-depth understanding and controlling the factors affecting the properties of InO_x is a competitive technique for advanced engineering of its multi-component properties.

In our study, we developed a highly reactive liquid indium precursor named DMITN and controlled the energy of the surface reaction in the atomic layer deposition (ALD) process. We systematically observed the impact of various reactants (H₂O, O₃, or O₂ plasma) and substrate temperatures (100–250 °C) on the growth and characteristics of InO_x thin films. The growth characteristics (ALD window, growth per cycle, and step coverage) and film properties (impurities, stoichiometry, oxygen bonding state, crystallinity, film density, and electrical properties) differed based on the ALD process employed, ascribed to the distinct thermal energies and inherent reactivities of the chosen oxidants. Among the various factors, it was confirmed that the degree of crystal alignment has a dominantly effect on the charge carrier mobility. Furthermore, we observed disparities in step coverage for a 40:1 high aspect ratio structure based on the type of reactant used. Notably, the use of H₂O and O₃ reactants showed superior step coverage (~95%) in comparison to O₂ plasma (~74%). Our findings suggest that the growth and properties of InO_x can be tailored by judiciously choosing the reactants according to the application requirements. Moreover, we suggest that highly reactive DMITN precursors have advantages for a wide range of applications because they can select various reactants.

AF-MoP-67 Understanding Selectivity Loss in Area-Selective ALD - a DFT Investigation of the SMI Layer Disintegration Mechanisms, Philipp Wellmann, R. Tonner-Zech, Wilhelm-Ostwald-Institut, Universität Leipzig, Germany

The large-scale applicability of ALD in next-generation semiconductor device manufacturing depends on the capability of area-selective process management. Most commonly, area-selectivity is achieved by inhibitor molecules binding to the non-growth surface, thereby shielding it from the ALD precursors. By choosing molecules of low molecular masses, the small molecule inhibitor (SMI) approach aims at high inhibitor vaporability for versatile application in high-volume manufacturing. Currently, the biggest challenge for SMI systems is the sustained selectivity over a satisfactory amount of ALD cycles. In a recent hybrid experimental and DFT study surveying various alkoxy-silane inhibitors in blocking the deposition of Al_2O_3 on SiO_2 , the optimization of the SMI ligands for prolonged selectivity could benefit from a microscopic understanding of the chemical processes involved. [1] Yet, the diminishing selectivity over time - the processes disintegrating the SMI blocking layer and initializing the growth nucleation of Al_2O_3 - remains obscure.

This DFT modeling study investigates the possible disintegration reactions of common Al precursors with realistic SMI blocking layer models of the trimethoxypropylsilane (TMPS) SMI on amorphous SiO_2 substrates. The SMI blocking layer is not inert but subject to several chemical modifications through the ALD experiment. By systematic variation of the blocking layer density, starting from a single TMPS on the surface up to a theoretical SMI layer density maximum, the dependence of the disintegration reactions on the SMI layer density is disclosed. Based on these findings, proposals for improved process selectivity are derived. The results are substantiated by an energy decomposition analysis.

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AF-MoP-68 Nucleation of Copper ALD Films Studied with in Situ Synchrotron Measurements, Aleksandra Figura-Jagoda, S. Klejna, M. Marzec, AGH University of Krakow, Academic Centre for Materials and Nanotechnology, Poland; E. Kokkonen, Max IV Laboratory, Sweden; A. Kwiatkowski, AGH University of Krakow, Faculty of Physics and Applied Computer Science, Poland; K. Maćkosz, C. Minzoni, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; A. Szkuclarek, AGH University of Krakow, Academic Centre for Materials and Nanotechnology, Poland; I. Utke, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; M. Sikora, AGH University of Krakow, Academic Centre for Materials and Nanotechnology, Poland

Although atomic layer deposition of metal oxide films is well established process, fabrication of conductive metal layers still remains a great challenge. The main issue is non-uniform island growth, which leads to non-smooth and non-compact films. Furthermore, the process is highly surface-dependent [1]. In this study we used ambient pressure X-ray photoelectron spectroscopy (AP XPS) to investigate the mechanisms governing the ALD of copper thin films, taking advantage of surface and element sensitivity of the method along with its high sensitivity to the chemical state. With a few-nanometer penetration depth makes it possible to observe the reactions that occur on the surface and to distinguish bonds between different species involved, including the organic ones. Therefore, AP XPS allows for studying the nucleation stage of the ALD process and observation of the saturation of precursors on the surface during the half-cycles [2].

The investigated process was Cu ALD from copper hexafluoroacetylacetonate, $\text{Cu}(\text{hfac})_2$, and diethyl zinc, Et_2Zn , on two chemically different substrates: silicon dioxide and platinum. In-situ XPS cycle by cycle observations of the chemical state of the deposit and the surface showed substrate-dependent behaviour of precursors in the early nucleation stages. During the same phase of ALD process we observed higher copper signal of the platinum than on silicon dioxide. Zinc contamination was present on both surfaces after the full cycle. However, the Cu/Zn atomic ratio was significantly higher at the Pt substrate. Preliminary analysis does not seem to confirm the transmetalation reaction, proposed by [3]. Nevertheless, in-situ APXPS showed to be important method for better understanding of the mechanism of the nucleation and growth of copper.

[1] D. J. Hagen, M. E. Pemble, M. Karppinen, Appl. Phys. Rev. 2019, 6, 041309.

[2] E. Kokkonen, M. Kaipio, H.-E. Nieminen, F. Rehman, V. Miikkulainen, M. Putkonen, M. Ritala, S. Huotari, J. Schnadt, and S. Urpelainen, Review of Scientific Instruments 2022, 93, 013905.

[3] G. Dey & S.D. Elliott, J. Phys. Chem. C 2015, 119, 5914

AF-MoP-69 In-Situ Investigation of Oxidant Influence on Materials Properties of Ultrathin Cerium Oxide Films Using Novel $\text{Ce}(\text{Dpdmg})_3$ Precursor, Rudi Tschammer, J. Kosto, C. Morales, BTU Cottbus, Germany; M. Schmickler, Ruhr Universität Bochum, Germany; K. Henkel, BTU Cottbus, Germany; A. Devi, Ruhr Universität Bochum, Germany; J. Flege, BTU Cottbus, Germany

Atomic layer deposition (ALD) has been used extensively to grow homogeneous films with excellent coverage and atomic-scale thickness control for a variety of applications. However, remaining challenges include the investigation of novel precursor-oxidant combinations aiming for high growth rates, low-temperature deposition as well as unraveling the complex interplay between film stoichiometry and oxidant choice for reducible oxides. In this work, we present a detailed investigation of ultrathin cerium oxide films grown using the novel $\text{Ce}(\text{dpdmg})_3$ precursor with different oxidants (H_2O , O_2 , and O_3). Following a surface science-based approach, we have combined operando spectroscopic ellipsometry and in-situ X-ray photoelectron spectroscopy to allow rapid process optimization and determination of film properties such as stoichiometry, contaminations, and thickness under ultra-high vacuum conditions. This way, a distinct dependence of initial Ce^{3+} content on film thickness and choice of oxidant is revealed, paving the way for tailoring the deposit properties toward different applications, e.g., gas sensing, through optimization of deposition parameters and precursor-oxidant interplay.

AF-MoP-70 Impact of the Knudsen Number on the ALD Saturation Profile Characteristics – Extended Slope Method, C. Gonsalves, J. Velasco, J. Yim, J. Järvillehto, V. Vuorinen, Riikka L. Puurunen, Aalto University, Finland

Atomic layer deposition (ALD) is based on the self-terminating (i.e., saturating and irreversible) gas–solid reactions of at least two compatible compounds. Investigating the saturation profile of an ALD process inside a high aspect ratio (HAR) feature has emerged as a way to obtain information of the fundamental kinetics of the process. One-dimensional lateral HAR (LHAR) structures are especially suited for saturation profile analysis, and silicon-based microscopic LHAR structures have become available (PillarHall™, Chipmetrics). For a fingerprint saturation profile obtained under Knudsen diffusion conditions [1], a simple *slope method* relates a lumped sticking coefficient describing the kinetics of an ALD reaction (assuming single-site Langmuir adsorption) to the slope of the adsorption front inside a LHAR structure [2].

In this work, we present a systematic analysis of the ALD saturation profile characteristics at a wide range of Knudsen numbers, from free molecular flow ($\text{Kn} \gg 1$, Knudsen diffusion) via transition regime ($\text{Kn} \sim 1$) to continuum ($\text{Kn} \ll 1$, molecular diffusion) [3]. The simplest reaction case is considered, namely single-site Langmuir adsorption, with no generation of byproducts, and the simulations are made with the Ylilammi model [4]. We will show for example that the Knudsen number regime affects both (i) the penetration depth of the ALD film (free molecular flow resulting in the deepest penetration) and (ii) the slope of the adsorption front of the saturation profile (continuum resulting in steepest slope). On the basis of analysis of the slope of the adsorption front, we propose an extended method, where in addition to the square root relation with sticking coefficient at $\text{Kn} \gg 1$ [2], the slope has an inverse square root relation with the Knudsen number at $\text{Kn} \ll 1$.

[1] J. Yim, E. Verkama, J. A. Velasco, K. Arts, R.L. Puurunen, Phys. Chem. Chem. Phys. 24 (2022) 8645-8660. <https://doi.org/10.1039/D1CP04758B>

[2] K. Arts, V. Vandalon, R. L. Puurunen, M. Utriainen, F. Gao, W.M.M. Kessels, H.C.M. Knoop, J. Vac. Sci. Technol. A 37 (2019) 030908. <https://doi.org/10.1116/1.5093620>

[3] C. Gonsalves, J. A. Velasco, J. Yim, J. Järvillehto, V. Vuorinen, Riikka L. Puurunen, Submitted

[4] Re-implementation of the Ylilammi et al. model, E. Verkama, R.L. Puurunen, <https://github.com/Aalto-Puurunen/dream-ald>, accessed 2.2.2024

AF-MoP-71 Atomic Layer Deposition of Hafnium Oxide for Ferroelectric Devices, *Stijn van der Heijden, B. Macco, E. Kessels*, Eindhoven University of Technology, The Netherlands

Ferroelectric hafnium zirconium oxide (HZO) is a promising material which can be used for next-generation applications such as FeRAM and FeFET. To achieve this ferroelectric property, a solid understanding of the growth, annealing, and quenching of this alloy is required. This work focuses on the growth of hafnium oxide by atomic layer deposition. The aim is to understand the individual process first such that it can subsequently be used in conjunction with a ZrO₂ process for the creation of ferroelectric HZO.

The hafnium oxide films were deposited using the precursors CpHf(NMe₂)₃ and the co-reactant ozone. The films were deposited in an Oxford Instruments FlexAL™ ALD reactor on Si wafers with a native oxide. The process parameters were optimized, such that saturated growth was achieved (Fig. 1). Various material properties, such as thickness, density, stoichiometry, and crystal phase, are investigated for various deposition and annealing temperatures, as these parameters can play a significant role in the inducement of the ferroelectric orthorhombic crystal phase. Furthermore, the nucleation of HfO₂ on TiN is investigated, because the foreseen ferroelectric device structure utilizes HZO with TiN electrodes.

As the material is intended to be used in FeRAM devices, the conformality of the depositions is of profound importance. This conformality was investigated using lateral high-aspect ratio PillarHall™ chips (Fig. 2a), and an explorative HfO₂ deposition reached an aspect ratio of 55 (Fig. 2b). To reach this aspect ratio, a CpHf(NMe₂)₃ dose of 10 seconds, and an ozone dose of 1 minute was used. In future depositions, the recombination probability of ozone on HfO₂ is going to be determined, such that the achieved aspect ratio for various ozone doses can be accurately estimated.

These results provide a solid stepping-stone for the formation of ferroelectric HZO which can be used in ferroelectric devices.

AF-MoP-72 Analysing Growth Behaviour of Low Temperature ALD ZnO Films on Meso-porous Si Gr Battery Anodes for Improved Performance SEI, *Boris Hudec*, Institute of Electrical Engineering, Slovak Academy of Sciences, Slovakia; *P. Sahoo, A. Güneren, M. Precnerová*, Centre for Advanced Materials Application, Slovak Academy of Sciences, Slovakia; *M. Pecz*, Institute of Electrical Engineering, Slovak Academy of Sciences, Slovakia; *K. Fröhlich*, Centre for Advanced Materials Application, Slovak Academy of Sciences, Slovakia

Application of ultra-thin ALD coatings has been shown to greatly improve the properties of various cathode and anode materials of Li-Ion batteries [1]. ALD oxides SnO₂, Fe₂O₃ and ZnO have also been demonstrated as working anode materials [2,3]. In our recent work [4], we have shown that the electrochemical performance of the silicon/graphite (Si/Gr) anodes can be improved by ultra-thin ALD ZnO coating grown at 100 °C. We have shown that the ZnO surface coating effectively modified the SEI layer, lowering the SEI and charge-transfer resistances and thereby facilitating Li-ion transport to the anode volume. As a consequence, the rate capability became significantly improved for the ZnO-coated Si/Gr anodes. The ZnO-protected Si/Gr electrode minimized the amount of Li₂CO₃ formation during cell cycling. In the study we have experimented with ALD ZnO films grown by 5-40 ALD cycles, coating Si/Gr anodes of ~20 μm of thickness with estimated porosity of ~70%. Batteries prepared with the ZnO films grown by 20 ALD cycles has shown the highest improvement in the rate capability.

Tackling the ALD growth on battery electrodes, which are essentially thick substrates of meso-porous nature, is inherently challenging due to extreme values of effective surface area and equivalent aspect ratio. Rather low thermal stability of the binder in the electrode puts a constraint on the deposition temperature, which was kept at 100 °C in this study.

The major challenge of the process tuning lies in the evaluation of the penetration depth and thickness homogeneity of the films in the battery electrode. In this study we aim to correlate the ALD conditions to these properties, evaluated using a combination of non-invasive techniques. Selected experiments are evaluated using EDS scans on FIB-cut samples, and eventually correlated with the resulting electrochemical properties of fully assembled batteries.

The authors acknowledge support from VEGA Projects 2/0162/22 and projects APVV-19-0461 and APVV-20-0111. This study was performed during implementation of the project Building-up Centre for Advanced Materials Application of the Slovak Academy of Sciences, ITMS (Project 313021T081), supported by the Research & Innovation Operational Programme funded by the ERDF.

AF-MoP-73 Rapid ALD by Forced Flow Through 3-Dimensional Macroscopic Nanoporous Solids, *Austin Cendejas*, ASEE Postdoctoral Fellow Residing at U.S. Naval Research Laboratory; *B. Greenberg, K. Anderson, B. Feygelson*, U.S. Naval Research Laboratory

Coating the internal surface of macroscopic high-aspect-ratio nanostructures via ALD opens new possibilities to tune optoelectronic, electrical, and mechanical properties of nanocomposites. The most common approach to achieving uniform infills has thus far been to employ static dosing, allowing precursors to diffuse in, and byproducts out, of the tortuous porous networks.^{1,2} The timescales for individual ALD cycles are thus on the order of 10s of minutes, raising potential concerns about precursor stability and more practically, throughput.² In this work, we develop a new approach to infilling macroscopic nanoporous solids in which pressure gradients on the order 10-100 Torr are employed to force precursor flow directly through the nanoporous network. This method was utilized to deposit ZnO films on the internal surface of ~2mm thick nanoparticle compacts comprised of 200 nm SiO₂ nanoparticles. The effect of upstream backing pressure (i.e. pressure gradient across the compact) and precursor partial pressure on required saturation pulse times will be explored. The effluent composition downstream of the nanoporous solid is continuously monitored via *in situ* quadrupole mass spectrometry, allowing precise determination of precursor breakthrough. Additionally, the ALD coating on the internal surface is evaluated by X-ray diffraction, scanning electron microscopy and energy dispersive X-ray spectroscopy.

1. Gayle, A. J.; Berquist, Z. J.; Chen, Y.; Hill, A. J.; Hoffman, J. Y.; Bielinski, A. R.; Lenert, A.; Dasgupta, N. P. Tunable Atomic Layer Deposition into Ultra-High-Aspect-Ratio (>60000:1) Aerogel Monoliths Enabled by Transport Modeling. *Chem. Mater.* **2021**, *33* (14), 5572–5583.

2. Greenberg, B. L.; Anderson, K. P.; Jacobs, A. G.; Cendejas, A. J.; Hajzus, J. R.; Patterson, E. A.; Wollmershauser, J. A.; Feigelson, B. N. Conformal Coating of Macroscopic Nanoparticle Compacts with ZnO via Atomic Layer Deposition. *J. Vac. Sci. & Technol. A* **2023**, *42* (1), 012402.

AF-MoP-74 QCM the UiO Way, a Tutorial, *Ola Nilsen*, University of Oslo, Norway

Quartz Crystal Microbalances (QCM) do provide great insight into the growth dynamics of ALD and MLD processes, particularly when compared to their cost and ease of installation and operation. However, they can be misleading if you rely on the Sauerbrey equation alone. This talk will be a tutorial on how we perform QCM measurements at the University of Oslo (UiO), from hardware to software and dealing with effects like variations in temperature and evolution of surface roughness during growth, with examples of what to avoid and what works.

AF-MoP-75 Sticking Coefficients in Atomic Layer Deposition Processes, *Martin Knaut, O. Bieg, T. Mikolajick*, TU Dresden, Germany

The reaction probability of an Atomic Layer Deposition (ALD) process is often described as a sticking coefficient, yet this oversimplification disregards the existence of at least two distinct reactions arising from the separate half-cycles involved. This paper presents the impact of both reaction probabilities on film growth characteristics, dependent on the applied precursors and process parameters. Macroscopic and microscopic test structures with high aspect ratios served as the experimental setup to deposit and assess thickness profiles in undersaturated film growth regimes. Through this methodology, we analyzed the reaction probabilities with respect to specific process parameters and their effects on film growth, uniformity, and step coverage. In the case of Al₂O₃ ALD, our model process, significant differences in reaction probabilities were observed between the two half-cycles, illustrating variations in the required doses for achieving full surface saturation. Moreover, the utilization of uncoated, pre-treated, or pre-coated substrates facilitated the differentiation between heterogeneous and homogeneous film growth, unveiling the associated reaction probabilities and their impact on the necessary process parameters. This study aims to enhance understanding of the phenomena occurring during ALD film growth and to enable adaptations of processes and parameters accordingly.

AF-MoP-76 A Data-Driven Approach to Analyzing Chemical Reactions and Predicting Film Properties in SiO₂/N₂ ALD Processes, *Sung Kyu Jang, H. Kim, J. Jeon, H. Kim*, Korea Electronics Technology Institute, Republic of Korea; *H. Kim*, SurplusGLOBAL, Republic of Korea; *S. Kim, H. Kim, W. Lee, S. Kim*, Korea Electronics Technology Institute, Republic of Korea

Atomic Layer Deposition (ALD) is widely used in the semiconductor industry due to its ability to deposit materials uniformly on high aspect ratio structures. Accurate control and prediction of thin film properties, including

thickness, composition and optical properties, significantly affects the productivity of the ALD process. In this study, we equipped an ALD reactor with a time-of-flight mass spectrometer (ToF-MS) to monitor the process chemistry during film growth and to predict film properties. We performed SiOxNy ALD processes at different temperatures using hexachlorodisilane (HCDS) precursors. We investigated the degradation and depletion of precursors and by-products during the silicon SiOxNy ALD process using in-process ToF-MS. We successfully produced SiOxNy films with a controlled composition without oxidants. It is achieved by controlling the temperature, which influences the formation of the bond. In addition, we evaluated the growth rate, composition, and optical and electrical properties of the ALD synthesised SiOxNy films, including ellipsometry, X-ray photoelectron spectroscopy, and current-electric field and capacitance-voltage analysis. The results showed that the presence of Si-N bonds compared to Si-O and O-N bonds increased with increasing deposition temperature, and the dielectric constant of the film also increased. Finally, an artificial neural network (ANN) was used to build a predictive model trained on the properties of the ALD synthesised SiOxNy films and in-process ToF-MS data. The ToF-MS data, reflecting the precursor decomposition process, played a key role in predicting the final properties of the films. The data-driven modelling methodology developed in this study has the potential to be applied to other thermal and plasma deposition systems in the future. This research is expected to help improve the productivity of industrial manufacturing processes.

AF-MoP-78 In-situ Quartz Crystal Microbalance Measurement of Adsorption Equilibrium for Trimethylaluminum, Yuxuan Wu, J. Yamaguchi, N. Sato, A. Tsukune, Y. Shimogaki, The University of Tokyo, Japan

Atomic Layer Deposition (ALD) is a precise and high-quality thin film deposition method that achieves film thickness accuracy on an atomic scale owing to its unique and specific deposition mechanism. The adsorption equilibrium constant (K) of a precursor is a crucial parameter that determines the feasibility of ALD design to achieve uniformity and conformality. Aluminum oxide (Al_2O_3) deposited via ALD using trimethylaluminum (TMA) and water has been a promising ALD method for decades. However, less information was collected to demonstrate the intrinsic understanding of its feasibility for ALD design using K . Quartz Crystal Microbalance (QCM) is a powerful method for measuring the adsorbed mass of the precursor during ALD, which can be used to evaluate the adsorption equilibrium and kinetics. In this presentation, QCM was used to measure the adsorption behavior of TMA during Al_2O_3 ALD.

A homemade hot-wall ALD including a commercial ceramic tubular furnace heater, a quartz tube chamber, and a customized gas supply system was used for TMA ALD and adsorption measurement. TMA and H_2O served as the precursor and reactant, respectively in the bubbler, and He was used as the carrier and purge gases. TMA was vaporized in a bubbler at 20°C with 1200 Pa and the precursor line was maintained at 80°C to prevent condensation and the chamber temperature ranged from 140 to 180 Celsius. An in-suit QCM is installed at the center of the chamber to measure the adsorption and deposition of TMA. The quartz crystals (Piezo Parts Co., Ltd) are all in AT-cut with accurate measurements of different temperatures.

Fig. 1 shows the QCM measurement of TMA absorbed mass with the partial pressure of TMA from 140 to 180 Celsius. The adsorbed mass was recorded for evaluating the equilibrium constant K with Langmuir isotherm by using the following equation: $\theta = (KP)/(1+KP)$.

Several partial pressures (P) of TMA have been introduced and surface adsorption was recorded at certain temperatures to construct the adsorption isotherm of TMA, which is shown in Fig. 2. By obtaining the saturated adsorbed amount at high pressure, it is plausible to extrapolate equilibrium constant K from the relationship between surface coverage (θ) and partial pressure (P), which is the inverse of the slope as equations show following: $(1/\theta) = 1 + (1/K)(1/P)$.

The obtained K has the temperature dependency as shown in Fig.3. The ΔG of adsorption was obtained as -84.5 kJ/mol, which is close to the value reported by Quantum Computation (Density Functional Theory) calculations.

AF-MoP-79 Influence of N_2/Ar Plasma Exposure Time on the Growth Kinetics of Epitaxial InN Studied by *in Situ* Grazing Incidence Small-Angle X-Ray Scattering, Jeffrey Woodward, U.S. Naval Research Laboratory; S. Rosenberg, Lockheed Martin Advanced Technology Center; D. Boris, M. Johnson, U.S. Naval Research Laboratory; Z. Robinson, SUNY Brockport; S. Johnson, Honeywell; N. Nepal, U.S. Naval Research Laboratory; K. Ludwig, Boston University; S. Walton, C. Eddy, U.S. Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) has significant potential as an enabler of new InN-based electronics due to its inherently low process temperatures, self-limited growth, scalability, and ability to achieve alloy compositions within miscibility gaps.[1] However, while multiple groups have reported the successful growth of epitaxial InN films with promising characteristics, the realization of true device-quality material is hindered by insufficient fundamental understandings of the PEALD processes, especially as pertains to the role of the plasma. Previously, it was found that the InN growth mode and coarsening behavior are strongly influenced by the concentrations of reactive and energetic plasma species.[2] These results highlight the tremendous level of control over the growth process and resultant film properties that can arise from deliberate tuning of the plasma properties, and as such, motivate further investigation into the relationships between various plasma properties and the growth kinetics.

In this work, we investigate the influence of plasma exposure time on epitaxial InN PEALD on GaN using *in situ* grazing incidence small-angle x-ray scattering (GISAXS), a technique which can provide a detailed description of the nanoscale structure of a film as it evolves in real-time. The PEALD process uses trimethylindium and N_2/Ar plasma as metal precursor and reactant, respectively, and is performed at 250 °C. Plasma exposure time is varied from slightly undersaturated to optimized and excessive conditions. The relationship between plasma exposure time and the growth kinetics is discussed.

- [1] H. Pedersen et al., Cryst. Growth Des. **23**, 7010–7025 (2023)
[2] J. M. Woodward et al., J. Vac. Sci. Technol. A **40**, 062405 (2022)

AF-MoP-80 Theoretical Explorations of Vapour Phase Infiltration, Karl Rönby, Tyndall National Institute, University College Cork, Ireland; M. Perego, CNR-IMM, Unit of Agrate Brianza, Italy; M. Nolan, Tyndall National Institute, University College Cork, Ireland

Vapour Phase Infiltration (VPI) is a type of atomic layer deposition (ALD) in which the precursor is allowed to enter the substrate's matrix, typically a polymer, rather than depositing on top of it. Precursor infiltration opens avenues for crafting hybrid materials or achieving nanopatterning when using a patterned block copolymer with different infiltration properties. To fully utilise this deposition technique, a deeper understanding of the interaction between the precursor and polymer becomes crucial. Thus, theoretical modelling of VPI is necessary to develop the process.

To efficiently model VPI, we have developed a modelling framework employing both non-periodic and periodic density functional theory (DFT) calculations. The non-periodic model was utilised to rapidly screen interactions between precursor and a gas-phase oligomer chain of the polymer. This approach allowed us to find how the precursor can bind with the polymer, the interaction energies and possible decomposition of precursor or polymer upon infiltration. The periodic model was constructed by taking oligomer chains of the polymer in a computation cell with periodic boundary conditions, creating an infinite polymer matrix. This allowed us to investigate how the precursor can interact with multiple chains, the swelling of the matrix and saturation behaviour with increasing amount of precursor.

The modelling results were compared to experimental VPI of trimethyl aluminium (TMA) into poly(methyl methacrylate) (PMMA) and poly(lactic acid) (PLA). We could then expand upon this work and extend the modelling possibilities to other precursors or polymers, gaining valuable information on the VPI processes.

AF-MoP-81 Synthesis and Characterization of Group III Precursors for Atomic Layer Deposition, Dexter Dimova, S. Barry, Carleton University, Canada

As device size in microelectronic structures decrease, atomic layer deposition (ALD) can be relied on to provide high surface uniformity at Angstrom level precision. Architectures such as gate-all-around (GAA) can benefit from this (Figure 1). The requirement for electropositive metals like group III (scandium and yttrium) has become higher since these centres are excellent n-type dipole shifters,¹ and allow dipole tuning of the high-k/ SiO_x

interface layer and simultaneously take advantage of the higher current carrying capacity of GAA FETs.

Generally, scandium and yttrium complexes have not been well explored in ALD: precursors with the general formulae $M(\text{thd})_3$, $M(\text{PrAMD})_3$, and $M(\text{PrCp})_3$ being the most prominent published precursors.²⁻⁷ These three families of precursors are homoleptic and coordinatively saturated, with little opportunity to introduce other ligands to tune volatility or reactivity. This presentation will discuss Sc and Y compounds using our group's previously synthesized silicon-based ligand, geminal diaminosilane (gDAS).⁸ The versatility of this ligand arises from the simple modification of the alkyl functional groups, giving an excellent opportunity to elaborate the structure, as well as to select from mono- and di-anionic ligands using this framework. The monoanionic version of gDAS will chelate metals with +3 centers to form a 6-coordinate homoleptic geometry (Figure 2). Coordination may also be lowered to optimize the effects of steric bulk and metal center surface reactivity through synthesis of 3- or 4-coordinate heteroleptic yttrium and scandium precursors, where X will initially be amide ligands and L will be a simple, neutral base (Figure 3).

The complexes will be structurally characterized by proton and carbon nuclear magnetic resonance, and single crystal XRD. Thermal characterization by thermogravimetric analysis and differential scanning calorimetry will be used to investigate decomposition, evaporation, vapor pressure, and melting point. Analysis from these techniques and early deposition data will allow for comparison to known group III ALD precursors and inspire a family of potential complexes.

References

- [1] Huang, A. et al. *Chin. Sci. Bull.* 2012 57, 2872-2878.
- [2] Putkonen, M. et al. *Chem. Mater.* 2001, 13, 12, 4701-4707
- [3] Putkonen, M. et al. *Chem. Vap. Deposition.* 2001, 7, No. 1
- [4] De Rouffignac, P. et al. *Electrochemical and Solid-State Letters.* 2006, 9 (6) F45-F48
- [5] Boysen, N. et al. *RSC Adv.* 2021, 11, 2565-2574
- [6] Stafford, N. et al. *ECS Transactions.* 2009, 19 (2) 525-536
- [7] Xu, R. et al. *ECS Transactions.* 2012, 50 (13) 107-116
- [8] Griffiths, M. et al. *J. Vac. Sci. Technol. A* 2021 39, 032409.

AF-MoP-82 Suppression of Ru-loss and Crystallization of SrRuO₃ Films via Optimization of Initial RTA Steps, Donghyung Lee, Seoul National University, Republic of Korea

SrRuO₃ (SRO) is an auspicious electrode material for next-generation dynamic random access memory capacitors utilizing SrTiO₃ (STO) dielectric films due to their close lattice match.^[1] Precious studies reported growing the SRO films by combining atomic-layer deposition (ALD) of SrO and pulsed-chemical vapor deposition (CVD) of RuO₂, which generally results in amorphous as-deposited films.^[ref] However, after post-deposition annealing (PDA) for crystallizing the SRO film, Ru concentration decreased due to volatile RuO₄ formation, and the film morphology degraded by agglomeration. Therefore, these films could not serve as the optimum electrode layer. Recent studies investigated suppressing Ru-loss by ALD-doping and optimizing the gas flow conditions during PDA after the SRO film deposition.^[ref] Still, the genuine ALD process of the SRO film, i.e., both the SrO and RuO₂ component layers are grown by the ALD mechanism, which may improve the film quality even after the PDA, is desired.

Therefore, this work reports the SRO films growth via the combined ALD of SrO and RuO₂ layers using Sr(Pr₃Cp)₂ and Ru(ETCp)(η⁵-CH₂C(Me)CHC(Me)O) as the Sr- and Ru-precursors, respectively. The SRO film deposited on the Al₂O₃ substrate was crystallized by rapid thermal annealing (RTA) at 650°C under different gas environments. Even with the ALD SRO films, an O₂ gas environment was required for the SRO crystallization. When the RTA was conducted for 75s, a severe Ru loss (25% loss) was observed, which also degraded the film quality. However, when conducting RTA with O₂ for 25s followed by N₂ for 50s instead of O₂ for 75s, the Ru-loss rate was reduced from ~25% to ~5%. The crystallinity and surface roughness of the two films were similar. As a result of these process modifications, the resistivity of the 17nm-thick film was decreased from ~1000 for the ALD/CVD film to 112 Ohm-cm for the ALD film, suggesting the substantially enhanced film quality.

AF-MoP-83 Doped SnO₂ Thin Films Fabricated at Low Temperature by Atomic Layer Deposition with a Precise Incorporation of Niobium Atoms, G. Dirress Gessesse, Institut Photovoltaïque d'Île-de-France (IPVF), France; **Damien Coutancier**, UMR-IPVF 9006, CNRS, Institut Photovoltaïque d'Île-de-France (IPVF), France; *M. Al Katrib, F. Donsanti*, Institut Photovoltaïque d'Île-de-France (IPVF), France; *M. Bouttemy*, UMR 8180, CNRS, Institut Lavoisier de Versailles (ILV), France; *N. Schneider*, UMR-IPVF 9006, CNRS, Institut Photovoltaïque d'Île-de-France (IPVF), France

Doped SnO₂ thin films have emerged as a focus of interest to address the limitations of undoped SnO₂ in various applications. SnO₂ alone has garnered considerable interest in applications such as transparent conducting oxides (TCO), fuel cells, photocatalysis, dye-sensitized solar cells (DSSCs), and touch screens. However, the low doping level of SnO₂ hampers its performance in these applications. The incorporation of Nb(+V) into SnO₂ offers a solution to this challenge, enhancing carrier concentration and electrical conductivity. This is facilitated by the close ionic radii between Nb(+V) and Sn, enabling easy distribution within the SnO₂ lattice[1]. While there have been few studies on the properties and applications of atomic layer deposition (ALD)-fabricated SnO₂:Nb films[2,3], less attention has been paid to understanding the ALD growth process and its correlation with film properties. This work aims to bridge this gap by developing SnO₂:Nb thin films via ALD, investigating the growth process, and exploring various film properties.

Tetrakis(dimethylamido)tin(IV) and Tris(diethylamido)(tert-butylimido)niobium(V) precursors were used for Sn and Nb, respectively, with H₂O₂ and H₂O as reactants. Nb incorporation was studied using in-situ quartz crystal microbalance (QCM), manipulating the supercycle ratio for doping control. The sequence of precursor and reactant introduction was altered to explore its influence on doping efficiency.

Ellipsometry, SEM, and GI-XRD confirmed the successful synthesis of homogeneous SnO₂:Nb thin films by ALD. XPS analysis demonstrated variations in Nb atom concentration, indicating the tunability of doping efficiency through adjustments in precursor and reactant sequences.

The resulting films exhibited high optical transparency (>95% transmission over a wide UV-Vis-IR range) and tuned electrical properties, with resistivity decreasing upon Nb doping and reaching as low as 2.87x10⁻² Ω-cm with a carrier concentration of 5.23x10¹⁹ cm⁻³ and mobility of 4.11 cm²/Vs.

In summary, Nb-doped SnO₂ thin films synthesized at low temperatures (<100°C) via ALD demonstrated optimal Nb incorporation levels (<1 at.%) for enhanced electrical conductivity while maintaining high optical transparency. These findings pave the way for the integration of Nb-doped SnO₂ thin films into temperature-sensitive, nanostructured optoelectronic devices.

References:

1. Ramarajan, et al; *Ceramics International* 46 (2020) 12224-12231.
2. Stefik, et al; *Nano Lett.* 2012, 12, 5431-5435.
3. Hu, et al; *Adv. Energy Mater.* 2014, 4, 1400510.

AF-MoP-84 ALD Deposited Lanthanum Doped HfO₂ Thin Films on a Lateral High Aspect Ratio Structure (LHAR): Surface Characterization Using X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), J. Emara, A. Kia, **Sascha Bönhardt**, C. Mart, K. Kühnel, N. Haufe, Fraunhofer Institute for Photonic Microsystems Center Nanoelectronic Technologies, Germany; *R. Puurunen*, Aalto University, Finland; *M. Utriainen*, Chipmetrics Oy, Finland; *W. Weinreich*, Fraunhofer Institute for Photonic Microsystems Center Nanoelectronic Technologies, Germany

With the growing semiconductor industry and the need to miniaturize devices, the use of complex microscopic three-dimensional (3D) structures is on the rise. To develop and enhance these technologies, a comprehensive study of the materials involved is crucial. However, these 3D structures make surface characterization of deposited thin films challenging. To overcome this, two-dimensional (2D) PillarHall lateral high aspect ratio (LHAR) test structures are used in this work. These single-crystal silicon structures have lateral cavities with different lengths (1µm to 5 mm), aspect ratios (AR) of 2:1 to 10,000:1, and polysilicon pillars that hold up a membrane. This membrane can be easily peeled off with tape, exposing the area where the ALD thin films were deposited, and thereby facilitating surface analysis.

Thin film hafnium oxides (HfO₂) are used in micro- and opto-electronic devices due to their high-*k*- properties. When doped with lanthanum (La), HfO₂ becomes ferroelectric and can be used in technologies such as ferroelectric random-access memory (FRAM), tunnel junctions (FTJs) and

field-effect transistors (FeFETs). In this work, thin films of La doped HfO₂ were deposited on the LHAR structure using two different atomic layer deposition (ALD) processes: standard and three-step. To grow the doped films using standard ALD, the metal-organic precursors are injected into the process chamber alternately with an inert gas purging process in between. The three-step ALD process, where the precursors are subsequently introduced before the co-reactant (e.g. H₂O), has previously been proven to produce homogeneous aluminum (Al), silicon (Si) and La doped thin films with low defect densities and reduced internal bias fields. In this work we aim to advance the surface characterization of the La doped HfO₂ thin films prepared by using the two different ALD processes. To accomplish this, x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) were used to analyze the uniformity and composition of the doped thin film. Imaging and analysis of the structured surface of the LHAR was possible for both techniques. Uniquely, XPS analysis of such small structures was possible using secondary electron imaging (SEI) and micro area analysis with a tunable x-ray beam down to ~7.5 μm. Both techniques provide a complementary and in-depth analysis of material formation, travel length, elemental distribution, and composition, and thus a comprehensive comparison between the ALD processes can be presented.

AF-MoP-85 Investigating and Overcoming the Challenges of Coating sub-Micron Dielectric Powders by Thermal and Plasma ALD, Shagufta Batliwala, B. Peek, P. Chalker, A. Gardner, S. Gare, University of Liverpool, UK; J. Brindley, Gencoa, UK; R. Potter, University of Liverpool, UK

Over the past decade, ALD has emerged as a powerful technique for uniformly coating high surface area powders for a broad range of applications, including catalysts, battery electrodes, feedstocks for additive manufacturing and pharmaceuticals. The current work aims to investigate the process conditions required for precisely controlled uniform ALD on sub-micron dielectric powders using a home-built fluidised bed-style powder coating adapter in an Oxford Instruments OpAL reactor. The adapter has been designed to coat small-scale powder batches (100 mg to a few grams).

Initially, a recipe for the deposition of VO_x on flat silicon samples was developed using Vanadium oxy tri-isopropoxide oxide (VTIP) and H₂O. Transferring this recipe to coat powders proved to be a significant challenge. Hence, this work offers an opportunity to share insights into problems associated with powder ALD such as powder outgassing, powder agglomeration, longer resident times, and parasitic CVD reactions. A Gencoa Optix remote plasma optical emissions spectrometer sensor was used on the reactor foreline to provide insights into the initial powder outgassing and optimal reactants dose and purge times.

A range of bulk particles was investigated as substrates. Extended outgassing was observed when the powders were heated under vacuum resulting in VO_x deposition when VTIP was dosed without any co-reactant doses. To address this, we investigated using pre-doses of Trimethylaluminium (TMA) before ALD of the target material. These doses resulted in the deposition of Al₂O₃ on the powder, which was an effective way to passivate the powder through gettering mechanisms. The outgassing was seen to be suppressed completely for non-porous substrates but persisted for the high surface area (~200 m²/g) powders with nanopores. A non-porous SiO₂ powder with a nominal particle size of 0.5 μm was chosen as the substrate to achieve controlled ALD.

To speed up the process and enhance the control, H₂O was switched with a Meaglow hollow cathode plasma system with O₂/Ar gas to generate oxidant species. There was strong evidence for a self-limiting ALD using the PEALD approach, but uneven deposition due to caking was observed in the powder bed for higher numbers of ALD cycles. It has been hypothesised that the static charge build-up during the longer runs was responsible for this caking. Introducing an H₂O dose after every 20 PEALD cycles significantly enhanced uniformity and minimised the caking.

Mixed metals oxide ALD using the approach developed is now being explored as a route to nano-engineer core-shell heterogeneous catalysts.

AF-MoP-86 Indium Precursors with Improved Thermal Stability for Atomic Layer Deposition of Indium Oxide, Lukas Mai, P. Mehlmann, Merck Electronics KGaA, Germany; R. Higuchi, Intermolecular, Inc.; H. Heil, Merck Electronics KGaA, Germany

Atomic Layer Deposition (ALD) is a critical process for fabricating semiconductor thin films with atomic precision. Indium gallium zinc oxide (IGZO) is particularly important for thin-film transistors (TFTs) due to its excellent electrical and optical properties. Precursor thermal compatibility is crucial for ALD, as indium, gallium, and zinc precursors must be deposited

at the same deposition temperature. Weak point in terms of precursors was found to be trimethylindium (TMI). Despite its excellent volatility and good reactivity suitable for ALD, it is limited by its solid state at room temperature, pyrophoric nature, and low thermal stability, with a maximum deposition temperature of 250°C.

Addressing these limitations, new indium precursors have been developed with enhanced thermal stability and a melting point below 50°C to ensure consistent vapor pressure in ALD processes. Through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), we evaluated melting points, vapor pressures, and decomposition temperatures, identifying two promising candidates surpassing TMI in performance.

Both precursors show a high volatility suitable for ALD experiments. Moreover, they are designed to withstand ALD processes above 250°C, potentially matching the thermal properties of gallium and zinc precursors and enabling their use at the same deposition temperature. This was confirmed by initial ALD testing, indicating that these novel indium precursors exhibit improved thermal stability.

In conclusion, the introduction of new indium precursors with better thermal properties and handling ease marks a considerable advancement in ALD technology. This progress promises to refine the production of IGZO films, pushing the boundaries of TFT performance and the development of flexible and transparent electronic devices.

AF-MoP-87 DFT Study of Metal Precursor Pulse in Atomic Layer Deposition of Pt, Sylwia Klejna, AGH University of Krakow, Poland

Atomic layer deposition of metals relies on sequential pulses of metal precursor – metal-organic complex and co-reagent that removes the organic ligands to yield nanometre thin metallic target film. The chemisorption of the metal precursor on the substrate material is a crucial step in ALD process. It determines the efficiency of the deposition, setting the length of the incubation period and the nucleation delay. In this study, density functional theory (DFT) is utilized to investigate the metal precursor pulse in the MeCpPtMe₃-based Pt ALD (MeCp – methylcyclopentadienyl ligand, CH₃C₅H₄; Me – methyl group, CH₃). Adsorption, decomposition and dehydrogenation pathways during metal precursor pulse are computed. Volatile by-products are identified: CH₄, C₂H₄ and MeCpH and the thermodynamics of these reactions are studied. The discussed processes are investigated on different surfaces: during nucleation on SiO₂ and during steady-state on the Pt substrate.

AF-MoP-88 Analytical Factors in High-Resolution Mapping of Low Leakage Current Detection in High-K Materials Deposited by Atomic Layer Deposition, James J.Y. Su, B. Liu, C. Kei, C. Hsiao, F. Chen, Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan

High-resolution mapping of physical and electrical properties has been shown good spatial correlation results by adopting current sensing atomic force microscopy (CS-AFM). However, precision analysis such as low leakage current detection in the pA range could be altered by external factors. In this work, key factors have been optimized in order to improve the resolution and repeatability of low leakage current mapping in high-k materials including HfO₂ stacks in different thickness. Moreover, this method could be further applied to identify the minimum required thickness of high-k materials. HfO₂ is a known material with insulating properties, high refractive index and low absorption. But there are tremendous differences in the large number of processing factors as reported, such as precursor temperature, flow rate, flow distribution, container geometry, chamber volume, pressure, carrier gas, etc. Low leakage current mapping provides statistical results to ensure high-k material quality. Our results indicate that the key factors in low current sensing measurements must be taken into account when performing CS-AFM analysis. Especially when comparing results obtained in different requirements.

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Room Hall 3A - Session AF1-TuM

Precursors and Chemistry: Precursor Design, New Precursors, Process Development II

Moderators: Hyungjun Kim, Yonsei University, Korea, Atsushi Sakurai, ADEKA CORPORATION

8:00am **AF1-TuM-1 Navigating the Semiconductor Market for ALD Precursors - in the Past and in the Future, Jonas Sundqvist**, TECHCET LLC CA, Germany

The semiconductor industry has been witnessing more than two decades of high volume scale up in the production and application of ALD and CVD precursors, particularly within Advanced Logic, DRAM, and 3DNAND sectors. Recent research by TECHCET reveals a nuanced landscape where the ALD/CVD precursor market, after a period of stagnation in 2023 due to declining memory pricing, is poised for a significant resurgence. This expected revival is attributed to the recovery in memory pricing and a robust demand for metal, high- κ and low- κ dielectric precursors, essential for the fabrication of advanced semiconductor devices.

The research underscores a dynamic growth trajectory for ALD/CVD precursors, driven by the expansion of leading-edge logic devices and the transition of DRAM to more sophisticated Multi Patterning and Extreme Ultraviolet (EUV) technologies. Moreover, the ongoing scaling of 3DNAND architectures to beyond 500 layers heralds an increased demand for several high volume precursors, essential for high aspect ratio etch and deposition processes. This demand is further amplified by the full implementation of High- κ /Metal Gate technologies also in DRAM, necessitating a steady supply of hafnium precursors despite existing supply chain challenges.

Notably, the supply dynamics of critical materials like tungsten, derived from WF6 precursors, integral to the vertical scaling of 3DNAND, indicate a balanced supply-demand scenario through 2023, with potential constraints anticipated by 2026. This looming shortage underscores the semiconductor industry's relentless pursuit of alternative materials and processes, such as the potential adoption of molybdenum solid precursors, to ensure the sustainable growth of ALD/CVD precursor markets.

This research encapsulates the resilience and adaptability of the semiconductor industry, highlighting the critical role of ALD/CVD technologies in meeting the ever-increasing demands for higher performance and more compact semiconductor devices. The anticipated growth in the ALD/CVD precursor market not only reflects the industry's response to current challenges but also its proactive stance towards future technological advancements. A deeper dive into historical IAP filing by Fabricators, Equipment companies and precursor suppliers will be given.

8:15am **AF1-TuM-2 Improvement of COSMO-SAC Method for Estimating Vapor Pressure of ALD Precursors, Noboru Sato**, The University of Tokyo, Japan; Y. Wu, The University of Tokyo, Japan, China; J. Yamaguchi, A. Tsukune, Y. Shimogaki, The University of Tokyo, Japan

In ALD, metal complexes (MCs) are mostly used as precursors. Because a sufficient concentration of the precursor is necessary for saturated adsorption, MCs with high vapor pressures are required. Therefore, a method to accurately predict vapor pressure is required when designing new precursors for ALD. In this study, the vapor pressure prediction of MC using COnductor-like Screening MOdel Segment Activity Coefficient (COSMO-SAC) method¹ was investigated.

Vapor pressure calculations using COSMO-SAC method were performed using Amsterdam Modeling Suite². The existing COSMO-SAC method can predict the vapor pressure of MCs with CO or cyclopentadienyl groups with double or half the accuracy of COSMO-SAC method, which is sufficient for precursor selection. However, the vapor pressures of MCs with β -diketonate, amidinate, and alkoxide groups were underestimated by a factor of 100–1000. Therefore, the conventional COSMO-SAC method cannot be applied to a wide range of precursor selection methods.

To improve the accuracy of vapor pressure estimation, we added three procedures to the conventional COSMO-SAC method. Figure 1 shows a schematic of the conventional COSMO-SAC method (black arrows) and improved COSMO-SAC method (colored arrows). As there are no ϵ_{dsp} (empirical parameters to calculate dispersive interactions) data for metal

atoms, we investigated the non-regressive method to calculate ϵ_{dsp} (blue arrows in Fig 1). Because the dispersion force is known to be correlated with polarizability, we predicted that ϵ_{dsp} would also be correlated with polarizability. We found a correlation between ϵ_{dsp} and polarizability, expressed by the following equation:

$$\epsilon_{\text{dsp}} = 1035 \times \alpha^{1.34},$$

where α is the polarizability of the atoms in the molecule. By calculating the α of the metal atom in the MC and substituting it into this equation, we estimated the ϵ_{dsp} of the respective metal atoms. Then, we modified the activity coefficient due to dispersion interactions (γ_{dsp}) based on the polarizability of molecules (red arrows in Fig 1) and branching in the molecules (green arrows in Fig 1).

Figure 2 shows the measured vapor pressure of titanium tetraisopropoxide (TTIP) and those estimated using our method and the conventional method. Our method reproduced the experimental values more accurately than the conventional method did.

Figure 3 shows a comparison between the experimental and estimated vapor pressures of various MCs. As shown in Fig 3, our method reproduces the vapor pressure with an accuracy of approximately 50–200%, which is sufficient to determine whether the MC is suitable for ALD.

8:30am **AF1-TuM-3 Development of Precursors and Reactivity for Thermal Atomic Layer Deposition (ALD) of Main Group Elements, Majeda Al Hareri, D. Emslie**, McMaster University, Canada

The majority of the developments in elemental ALD have involved transition metals. However, interest in main group ALD has increased in recent years due to potential applications in a variety of technologies.¹⁻³ Research in the Emslie group is focused on the design, synthesis, and characterization of new precursor molecules, and investigations into their use as thermal ALD precursors through a combination of solution-state reactivity studies and ALD reactor studies. Through modification of the precursor design of a previously reported elemental antimony ALD process,⁴ we recently developed the first example of room-temperature thermal ALD of a pure element, using Sb(SiMe₃)₃ in combination with SbCl₃ to grow pure antimony films on H-terminated Si and SiO₂ substrates.⁵ Efforts to expand this research to elemental boron ALD will be described, including synthesis of the potential precursors, (R₃E)₂B(NR'₂) (E = Si or Ge), spectroscopic and crystallographic characterization of these compounds, and attempted boron deposition using a boron trihalide (BX₃; X = Cl, Br) co-reactant; anticipated byproducts in this reactivity are R₃EX and B(NR'₂)₂X₂, where the formation of strong E–X bonds provides a thermodynamic driving force. Development of a thermal ALD process for elemental germanium will also be described, achieving self-limiting growth at relatively low temperatures, and exhibiting substrate selectivity for deposition on H-terminated Si rather than SiO₂.

References

1. Salinga, M; Kersting, B.; Ronneberger, I.; Jonnalagadda, V. P.; Vu, X. T.; Le Gallo, M.; Giannopoulos, I.; Cojocaru-Mirédin, O.; Mazzarello, R.; Sebastian, A. Monatomic Phase Change Memory. *Nat. Mater.* **2018**, *17*, 681-685.
2. Glavin, N. R.; Rao, R.; Varshney, V.; Bianco, E.; Apte, A.; Roy, A.; Ringe, E.; Ajayan, M. Emerging Applications of Elemental 2D Materials. *Adv. Mater.* **2020**, *32*, 1904302.
3. Pillarisetty, R. Academic and Industry Research Progress in Germanium Nanodevices. *Nature* **2011**, *479*, 324-328.
4. Pore, V.; Knapas, K.; Hatanpää, T.; Sarnet, T.; Kemell, M.; Ritala, M.; Leskelä, M.; Mizohata, K. Atomic Layer Deposition of Antimony and its Compounds Using Dechlorosilylation Reactions of Tris(triethylsilyl)antimony. *Chem. Mater.* **2011**, *23*, 247-254.
5. Al Hareri, M.; Emslie, D. J. H. Room-Temperature Atomic Layer Deposition of Elemental Antimony. *Chem. Mater.* **2022**, *34*, 2400-2409.

8:45am **AF1-TuM-4 A New ALD Process for Elemental Tellurium, Paavo Porri, T. Hatanpää, H. Nieminen, K. Mizohata, M. Putkonen, M. Ritala**, University of Helsinki, Finland

Research on ALD of metal tellurides has been focused on phase-change memory materials. Owing to their electrical switching behaviour, binary and ternary compounds and alloys of germanium, antimony and tellurium have become an important area of development for memory and selector devices. Elemental tellurium has also garnered interest in materials research due to its thickness-dependent electrical properties, air stability and high hole mobility. Thus, it has been found to be a potential candidate to ensure continuing the miniaturization of transistors. However, process

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studies for depositing tellurium films are quite scarce. This study aims to illuminate a new ALD chemistry route for elemental Te films by combining an alkylsilyl telluride precursor with tellurium dichloride. In addition to elemental Te films, the new ALD process can be used for tuning the composition of metal telluride compounds such as GeTe.

The depositions were done in a commercial flow type ALD reactor using $(\text{EtSi})_2\text{Te}(\text{bis}(\text{triethylsilyl})\text{telluride})$ and TeCl_2 as precursors. The process is expected to involve a dechlorosilylation reaction, which follows the Lewis hard-soft acid-base principle. Film morphology was studied with SEM, film crystallinity and crystallization temperature with XRD, and elemental composition with ToF-ERDA. Tellurium growth was observed at a temperature range of 90–110 °C. Film morphology and growth rate were highly dependent on the substrate. On native silicon oxide, the nucleation was sparse, and morphology of the deposited material initially resembled nanowires that subsequently coalesced with further deposition cycles. On Au the film morphology was smoother and continuous already at low cycle numbers. The considerable difference in the growth rates between native SiO_2 and Au is leveraged to attain area selective growth on Au. The films deposited in mild conditions are crystalline exhibiting hexagonal crystalline structure, and of high purity. A GeTe ALD process was modified with the studied Te process to yield tellurium-rich Ge_xTe_y films with enhanced phase transition temperature.

9:00am **AF1-TuM-5 Development of an Innovative Method to Find New Efficient Gallium ALD Precursors**, *Eva Pugliese, D. Coutancier, J. Hervochon, P. Pavard, CNRS-IPVF, France; C. Gosmini, Ecole Polytechnique - CNRS, France; V. Lair, Cimie ParisTech PSL, France; A. Ringuede, Chimie ParisTech PSL, France; M. Bouttemy, Institut Lavoisier de Versailles, France; A. Auffrant, Ecole Polytechnique - CNRS, France; N. Schneider, CNRS-IPVF, France*

Atomic Layer Deposition (ALD) is a booming technology to deposit thin films and it has been applied in several fields. This technique is based on surface-chemical reactions, and relies on the gas phase transport of metal containing molecules into a reaction chamber. However, not any molecule is suitable to be used as precursor, as they must be thermally robust while being sufficiently volatile and chemically labile to react with the surface functional groups. Organometallic chemistry offers a nearly infinite set of options to design new efficient precursors, though predicting their volatility and reactivity in the ALD chamber remains a challenge.^[1] Establishing an efficient method to assess the physical and chemical properties of complexes would grant access to new ALD precursors and a better understanding of surface reactions.

This communication focuses on the development of new efficient gallium precursors to be used in the ALD of oxygen-free gallium-containing sulfide thin films.^[2] A series of gallium complexes with chelating nitrogen based ligands (guanidinate, amidinate and triazenides) were synthesized and characterized (NMR, XRD) thanks to modular procedures.^[3,4] To assess the thermal stability of the reagents and shed light on their transport in ALD, thermal analysis (TGA, DSC) were realized under N_2 and vacuum to mimic transport conditions. Finally, reactivity studies in solution of established ALD precursors and synthesized complexes provide an insight of surface reactions, which might take place in an ALD chamber. Having selected the most promising candidates, they were tested for film growth in an ALD apparatus using QCM setup. Interestingly, it was possible to highlight the crucial role of the non-chelating ligands in the film growth. Complexes with methyl ligands lose their surface reactivity after few cycles, whereas their substitution with amino groups can give a constant GPC over the whole range of the study. Gallium sulfide thin film could be prepared and their chemical fine composition was analyzed by XPS.

These results display the challenges that we may encounter in the targeting of new precursors and the importance of establishing a precise method to predict reactivity in ALD conditions.

References:

- [1] S. E. Koponen, P. G. Gordon, S. T. Barry, *Polyhedron* **2016**, *108*, 59–66.
- [2] N. Schneider, M. Frégnaux, M. Bouttemy, F. Donsanti, A. Etcheberry, D. Lincot, *Materials Today Chemistry* **2018**, *10*, 142–152.
- [3] A. P. Kenney, G. P. A. Yap, D. S. Richeson, S. T. Barry, *Inorganic Chemistry* **2005**, *44*, 2926–2933.
- [4] S. Dagorne, R. F. Jordan, V. G. Young, *Organometallics* **1999**, *18*, 4619–4623.

9:15am **AF1-TuM-6 Insights into Reactive Oxygen Species and Film Properties of Atomic Layer Deposited Al_2O_3 using Different Plasma-Activated Waters as Co-reactant**, *J. Karnopp, Aeronautics Institute of Technology, Brazil; F. Miranda, Universidade Estadual Paulista (UNESP), Brazil; N. Azevedo Neto, Aeronautics Institute of Technology, Brazil; L. Daiane Pereira Leite, Universidade Estadual Paulista (UNESP), Brazil; D. Marcel Leite, C. Alves Junior, A. da Silva Sobrinho, Rodrigo Sávio Pessoa, Aeronautics Institute of Technology, Brazil*

This investigation focuses on harnessing the unique reactive properties of plasma-activated water (PAW) as an innovative oxidant within the atomic layer deposition (ALD) process, specifically targeting the synthesis of aluminum oxide (Al_2O_3) films. The study is premised on the hypothesis that PAW, enriched with reactive oxygen species (ROS) such as ozone (O_3) and hydrogen peroxide (H_2O_2), could significantly enhance the efficiency of the ALD process, thereby improving the growth rate and quality of Al_2O_3 films. Our experimental approach involved the generation of PAW with varied ROS concentrations, achieved through atmospheric air plasma in three distinct reactor configurations: a coaxial dielectric barrier discharge reactor focusing on high O_3 concentrations, a pin-to-water reactor yielding H_2O_2 -rich PAW, and a hybrid DBD+gliding arc reactor producing a balanced mix of O_3 and H_2O_2 . The impact of these different PAW types on the ALD process was meticulously evaluated through a series of ALD runs conducted at substrate temperatures of 100°C, 150°C, and 200°C, with the process spanning 1000 reaction cycles on Si(100) substrates. The study's findings were profound, revealing that the incorporation of PAW, particularly those with elevated H_2O_2 and O_3 levels, led to a marked increase in the growth per cycle (GPC) of Al_2O_3 films at 100°C, with the most significant enhancement observed with the hybrid PAW. This improvement in GPC was accompanied by notable changes in the films' uniformity and chemical composition, which were thoroughly analyzed using FTIR and AFM. These analyses highlighted a shift in the chemical bonds present within the films, with an increase in hydroxyl and carbon-related groups, and a corresponding rise in surface roughness compared to films grown using deionized water. Additionally, the study ventured into examining the PAWs' evaporation behavior under vacuum conditions, revealing an accelerated evaporation rate compared to standard deionized water. This observation, coupled with the detailed ROS analysis, provides a compelling explanation for the heightened reactivity and efficacy of PAW in the ALD process. The practical implications of these findings are vast, extending beyond the field of material synthesis. Notably, the application of PAW-generated Al_2O_3 films on polymeric substrates like PMMA demonstrated a significant total reflection effect in the infrared spectrum, suggesting potential uses in passive cooling technologies. This aspect of the research opens up new avenues for the application of PAW-enhanced ALD films in advanced engineering and environmental management.

9:30am **AF1-TuM-7 The Effect of Co-Reactants on Interfacial Oxidation in Atomic Layer Deposition of Oxides on Metal Surfaces**, *J. Swarup, H. Chuang, A. You, James Engstrom, Cornell University*

We have examined the ALD of Al_2O_3 using TMA as the precursor and *t*-BuOH and H_2O as the co-reactants, focusing on the effects of the latter on both the ALD process and the possible modification of the underlying substrate. We have employed a quartz-crystal microbalance (QCM) to monitor ALD *in situ* and in real-time, and the deposited thin films have been characterized using X-ray photoelectron spectroscopy, spectroscopic ellipsometry, and X-ray reflectivity. Growth of thin films of Al_2O_3 using TMA and either *t*-BuOH or H_2O as the co-reactant at $T = 285$ °C produces thin films of similar physical properties (density, stoichiometry, minimal carbon incorporation), and the growth rate per cycle is similar for the two co-reactants at this temperature. At a lower temperature of $T = 120$ °C, the behavior is starkly different, where growth occurs with H_2O but not with *t*-BuOH. At either process temperature, we find no evidence for significant coverages of a long-lived *tert*-butoxy species from the reaction of *t*-BuOH. Deposition of thin films of Al_2O_3 on metal surfaces of Cu and Co has been examined for evidence of interfacial oxidation. While growth with either co-reactant does not lead to the oxidation of the underlying Cu substrate, use of H_2O leads to the oxidation of Co, while use of *t*-BuOH as the co-reactant does not. Thermodynamic factors may affect early stages of growth as Al species will likely scavenge all free O species. In contrast, at later times diffusion of species through the deposited Al_2O_3 thin film could result in oxidation at the Al_2O_3 |metal interface, a process that is strongly hindered in the case of *t*-BuOH due to its size. This observation highlights the importance of the choice of the co-reactant concerning ALD of oxides on metal surfaces.

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9:45am **AF1-TuM-8 Atomic Layer Deposition of Co₂P Thin Films**, *Elisa Aatosuo*, P. Deminskyi, ASM Microchemistry Ltd., Finland; K. Mizohata, T. Hatampää, M. Ritala, University of Helsinki, Finland

In this work we have deposited cobalt phosphide (Co₂P) by thermal ALD. Co₂P is a metallic material that has potential in a variety of applications such as hydrogen evolution reaction and lithium-ion batteries.

In general, the ALD processes for metal phosphides are scarce and mostly use the highly toxic PH₃ gas as the phosphide source. To our knowledge, only two ALD processes for transition metal phosphides has been reported. CoP_x has been deposited using Co(AMD)₂ with PH₃ plasma and H₂ plasma as precursors.[1] MoP was deposited by using MoCl₅ and PH₃. [2]

In this work Co₂P was deposited by using CoCl₂TMEDA (TMEDA = N,N,N',N'-tetramethylethylenediamine) and tris(trimethylsilyl)phosphine (P(SiMe₃)₃) as precursors. Alternatively, Co₂P can be deposited by using a three-precursor process: CoCl₂(TMEDA), NH₄F and P(SiMe₃)₃. The advantages of our processes are that we avoid the use of toxic PH₃ but also the possible damage caused by plasma.

Co₂P films were deposited with the CoCl₂(TMEDA) + P(SiMe₃)₃ process at 225–250 °C. The GPC was approximately 0.65 Å at 250 °C. Saturation of the GPC with respect to both precursors was verified at 250 °C. The films consist of orthorhombic Co₂P as measured by XRD, and the Co/P ratio is close to 2 as measured by ToF-ERDA. The main impurity is carbon, decreasing with the decreasing deposition temperature from 9.5 at-% at 250 °C to 6.7 at-% at 225 °C. However, with the three-precursor process lower deposition temperatures can be used and the C content is lower, e.g., ~ 3.3 at-% at 215 °C. In addition, only a small F content (e.g. ~0.4 at-%) was found in the films.

[1] H. Zhang, D. J. Hagen, X. Li, A. Graff, F. Heyroth, B. Fuhrmann, I. Kostanovskiy, S. L. Schweizer, F. Caddeo, A. W. Majjenburg, S. Parkin, R. B. Wehrspohn, *Angew. Chem. Int. Ed.* **2020**, *59*, 17172

[2] R. Browning, P. Plachinda, R. Solanki, *Appl. Nano* **2023**, *4*, 38–44

ALD Fundamentals

Room Hall 3A - Session AF2-TuM

Growth and Characterization: Plasma Enhanced ALD I

Moderators: Prof. Dr. Hyeontag Jeon, Hanyang University, Erwin Kessels, Eindhoven University of Technology, Netherlands

10:45am **AF2-TuM-12 Plasma-Enhanced ALD of Ga₂O₃ and GaN with Remote CCP-Plasma, Short Cycle Times, and Substrate Biasing**, *Roel Theeuwes*, Eindhoven University of Technology, Netherlands; *L. Gutmann*, Eindhoven University of Technology, Germany; *H. Knoops*, Oxford Instruments Plasma Technology, Eindhoven University of Technology, Netherlands; *E. Kessels*, Eindhoven University of Technology, Netherlands
The unique merits of atomic layer deposition (ALD), including high uniformity, high conformality, and excellent thickness control, often come with the caveat of relatively long processing times. Therefore, there is a demand for faster ALD processing, which has driven innovations in terms of ALD reactor and plasma source design.¹ In this work, we investigate plasma-enhanced ALD (PE-ALD) of gallium oxide (Ga₂O₃) and gallium nitride (GaN) on a new ALD system, designed for ultrafast and low-damage PE-ALD processing with rf substrate biasing capabilities. Ga₂O₃ and GaN are materials with highly suitable properties for use in various applications, including power devices.^{2,3}

The PE-ALD processes for Ga₂O₃ and GaN were developed on an Oxford Instruments PlasmaPro ASP and serve to further explore the capabilities of this new system, and compare differences between processing of Ga₂O₃ and GaN on the same tool. Triethylgallium ([C₂H₅)₃Ga; TEG) and Ar/O₂ or Ar/N₂/H₂ plasmas are used to deposit Ga₂O₃ and GaN (*T*_{dep} = 200 °C), respectively. The Ga₂O₃ process has a short cycle time of 2 seconds, a growth-per-cycle (GPC) of 0.73 Å/cycle, and 3.8 % thickness non-uniformity on an 8 inch wafer. The GaN process has a cycle time of 6 seconds, a GPC of 0.33 Å/cycle, and a 15.6 % thickness non-uniformity on an 8 inch wafer. The films are close to stoichiometric, with carbon impurities <1 at. %, which confirms the deposition of high-quality films. The oxygen content in GaN is quite low at around 4 at. %. The material properties of GaN and Ga₂O₃ can be tuned using deposition temperature and rf substrate biasing. A higher deposition temperature leads to a higher density for GaN, while for Ga₂O₃ density does not change significantly for deposition temperatures between 100-200 °C. Furthermore, rf substrate biasing with DC bias voltages between 0 and -70 V affected both GPC and refractive index of GaN, which

show the importance of precise ion energy control. This research has allowed for insights in the behaviour of this new ALD system, and shows that high-quality Ga₂O₃ and GaN films with short cycle times and controllable properties can be obtained.

References

¹H. Knoops *et al. J. Vac. Sci. Technol. A*, **39** (2021).

²A. Mahmoodinezhad *et al. J. Vac. Sci. Technol. A*, **38** (2020).

³P. Motamedi *et al. J. Mater. Chem. C*, **3** (2015).

11:00am **AF2-TuM-13 Y_xC Thin Films Prepared by Plasma Enhanced Atomic Layer Deposition as a Diffusion Barrier and Glue Layer for Cu & Ru Interconnects**, *Minjeong Kweon*, C. Park, S. Kim, S. Kim, Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Transition metal carbides (TMC) and nitrides (TMN) are widely used materials in industrial applications due to their exceptional hardness, high melting temperatures, and chemical stability [1]. In particular, transition metal carbides are stable at high temperatures with a higher phase transition temperature than other nitrides and oxides. Additionally, they possess excellent resistances to the oxidation and corrosion, making them valuable in various technological applications, including mechanical structures, the chemical industry, and nuclear power [2]. However, researches regarding both the processes of yttrium carbide (YC_x) thin film, one of the transition metal carbides, and their properties are still in the very early stages and pioneering studies exploring the deposition possibility of YC_x thin film and its potential applications based on the characteristics of the deposited YC_x thin film are necessary. In this study, YC_x films were deposited by plasma enhanced atomic layer deposition (PEALD) (IOV dX1 PEALD reactor, ISAC Research, Korea) using a new Y metalorganic precursor and H₂ plasma as the reactant, at the deposition temperature ranged from 150 to 350 °C. With an increase in precursor pulse time and reactant pulse time, self-limited film growth, which is the typical characteristics of ideal ALD, was observed. Moreover, under the optimal pulsing conditions, a clear linear dependence of film growth on the number of ALD cycles was evident. The saturated growth per cycle (GPC) was approximately 1.3 Å/cycle. The ALD–YC_x films with the formation of nanocrystalline structures and a rhombohedral Y₂C phase were confirmed by XRD and XPS, with optimized deposition condition at 250 °C. STEM-EDS analysis showed that the composition was YC_x (C/Y = 0.47). Additionally, experiments on the thermal stability of YC_x films at high temperatures were conducted alongside XRD analysis. The step coverage of the film deposited at 250 °C was approximately 85% on the trench structures (bottom width of 120nm and aspect ratio of approximately 4.3). Finally, the PEALD–YC_x deposited under optimized conditions is applied as a diffusion barrier for the Cu & Ru interconnects. The detailed results will be presented in the conference.

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[1] Aliakbari, A., & Amiri, P., Structural, elastic, electronic, thermal, and photonic properties of yttrium carbide: First-principles calculations, *Materials Chemistry and Physics*, 2021, **270**, 124744.

[2] Pierson, H. O., Chapter 4, in *Handbook of Refractory Carbides and Nitrides*, William Andrew Publishing, 1996, Pages 55-80.

11:15am **AF2-TuM-14 Plasma Enhanced Atomic Layer Deposition of Boron Nitride**, *Marc Reynaud*, University of Texas at Austin; *J. Zhao*, *J. Carroll*, *G. Blankemeyer*, *P. Ventzek*, Tokyo Electron America, Inc.; *J. Warner*, *J. Ekerdt*, University of Texas at Austin

The International Roadmap for Devices and Systems has identified challenges with continued device scaling and for future device architectures. With respect to interconnect technology requirements for logic devices, the challenges include “the introduction of new materials that meet the wire connectivity requirements, reduce dielectric permittivity and meet reliability requirements. The interlayer dielectric constant is projected to range from 3.2 to 2.2 for inorganic materials. Reaching these dielectric constants poses significant challenges. Conventional silicon dioxide based (SiCOH-based) dielectrics cannot reach these levels without introducing porosity that compromises the reliability of the film. Thin dielectric layers will be needed to serve as liners and etch stop layers along with the interlayer dielectric. Boron nitride (BN)-based thin films are promising materials for these applications as they possess attractive chemical, mechanical and electrical properties for the low-k environment integrated with Cu/Ru and Mo. Indeed reports have shown amorphous BN (a-BN) films with dielectric constants less than 3.0.

Here, we use PEALD to deposit boron nitride on Si(001) native oxide by alternating a thermal exposure of borazine (triazatriborinane), a single

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source precursor, at 25 and 100 °C, and a nitrogen-based plasma step. An experimental capacitively coupled radio frequency plasma source is used to understand how different plasmas, including ammonia, hydrogen, nitrogen, and pure argon, different frequencies, and plasma power impact the nature of chemisorption, film growth and film properties. Films are characterized using *in situ* X-ray photoelectron spectroscopy and *ex situ* using Raman spectroscopy, transmission electron microscopy and time of flight secondary ion mass spectroscopy.

ALD is realized at 25 °C using 300 mTorr exposures of borazine and converting adsorbed borazine into a-BN using a N₂/Ar plasma operating 100 MHz and 400 W power. Lower exposure pressures at the same Torr-s exposure result in undersaturation of the adsorbed layer and lower growth per cycle. Films are slightly N-rich and essentially carbon-free (0-2% carbon) with B:N compositions averaging B_{0.46}N_{0.54}. SiO₂/(SiO₂) pretreatment with a H₂/Ar plasma is required to create reactive sites for film nucleation on the native oxide. This talk will address the role of different plasma conditions on borazine adsorption and transformation into a-BN.

11:30am AF2-TuM-15 Time-Resolved Study of OH Radicals During PEALD of Al₂O₃ by Advanced Laser Spectroscopy, Antoine Salden, TU / Eindhoven, Netherlands; M. Ceppelli, L. Martini, University of Trento, Italy; R. Engeln, H. Knoops, E. Kessels, TU / Eindhoven, Netherlands

Radicals play an important role in PE-ALD due to their highly reactive nature, meaning that understanding their role in reaction mechanisms is crucial for subsequent process optimization. However, their interaction with the surface can be challenging to investigate due to their short lifetimes, given their reactive nature. While excited states can be readily detected by optical emission spectroscopy (OES), the radicals in the ground state — generally the bulk of radicals — are invisible to this technique. Furthermore, OES provides line-of-sight integrated measurements that make it arduous to decouple processes in the surface–environment from those in the plasma bulk.

To overcome aforementioned challenges, this study implements *in situ* active laser spectroscopy, in the form of laser induced fluorescence (LIF), to investigate the ground state of the OH radical during PE-ALD of Al₂O₃ using Al(CH₃)₃ and O₂ plasma. By resonantly exciting ground state OH with a laser, the observed induced fluorescence from the A²Σ⁺, v=0,1 manifold is a measure of the ground state density. Owing to the high spatiotemporal resolution of the technique, we were able to measure the time-resolved, relative density of the ground state at different distances from the substrate surface, during the plasma step of the process. At the start of the plasma step, we observe a brief high density of OH in the plasma, which is caused by surface reaction products diffusing away from the surface. Close to the surface, however, in the plasma (pre)sheath, OH formation by electron impact is inhibited. Not only does this cause a decrease in density, it also changes the evolution in time of the density: OH close to the surface appears to originate from diffusion from the plasma. These trends are strikingly more intricate than the evolution that is observed by OES for characteristic emissions associated with surface reaction products — such as OH and CO from methyl-group combustion — as those signals are dominated by contributions from the plasma bulk. While different, the results between LIF and OES appear compatible with each other when accounting for diffusive transport. All in all, these results demonstrate the deeper insights gained from well-localized diagnostics, capable of probing the radical ground state with high time resolution, to further investigate the environment at the plasma–surface boundary during PE-ALD.

11:45am AF2-TuM-16 Engineering of VO_x Properties Through Control of Plasma Characteristics During Plasma-Enhanced Atomic Layer Deposition, Peter Litwin, U.S. Naval Research Laboratory; M. Currie, N. Nepal, M. Sales, D. Boris, S. Walton, V. Wheeler, US Naval Research Laboratory

Crystalline VO₂ (c-VO₂) undergoes a phase transformation between two crystalline states at ≈ 68 °C, which is accompanied by a metal-to-insulator transition (MIT). Below the critical transition temperature (T_c), c-VO₂ exists in the monoclinic crystal structure and is a semiconductor with a band gap of ~0.7 eV that is transparent to infrared light. Above the transition temperature c-VO₂ exists in a tetragonal crystal structure and behaves as a metal that is reflective to infrared light. The MIT in c-VO₂ is of interest for numerous applications such as passive thermal regulation (e.g. energy efficient windows), thermal sensors, and passive radio frequency components.

VO₂ films deposited by traditional (thermal) atomic layer deposition (ALD) processes are amorphous (a-VO₂) and thus do not exhibit a MIT. While the

a-VO₂ films can be crystallized by a post-deposition annealing step, this limits the application space of ALD VO₂ due to thermal budget constraints. Plasma-enhanced ALD (PEALD) has been shown as a route to deposit crystalline materials by offering increased kinetics without the use of high substrate temperatures. This is made possible by the simultaneous delivery of a flux of both energetic and reactive plasma species to the growth surface. However, the enhanced reactivity of oxidizing-plasma sources poses challenges not present in thermal ALD processes. For example, control of the V oxidation state in thermal ALD is often dictated by the oxidation state of the V in the metal-organic precursor used during growth. For that reason, a V⁴⁺ oxidation state precursor is commonly used to promote the deposition of VO₂ in thermal ALD. Conversely, the strong oxidation characteristics of oxidizing-plasma sources used in PEALD typically result in the growth of V₂O₅, i.e., V⁵⁺, regardless of the metal-organic precursor used.

Here we present studies investigating the role of O₂-plasma characteristics on the stoichiometry and crystallinity of VO_x thin films deposited by PEALD. A focal point of these studies is correlating plasma properties, including plasma power, Ar/O₂ ratio, system pressure, and total gas flow during the plasma step with the control of the V⁴⁺/V⁵⁺ ratio and crystallinity, as probed by x-ray photoelectron spectroscopy and Raman spectroscopy. Initial results, based on a typical Ar/O₂ plasma used for ALD Al₂O₃ films, show a mix of the V⁴⁺ and V⁵⁺ oxidation states with evidence for the crystalline forms of each. Further optimization will be discussed and, where applicable, hysteretic characteristics of the MIT in PEALD VO₂ films are benchmarked against traditional annealed, thermal ALD films using optical transmittance.

ALD Fundamentals

Room Hall 3A - Session AF1-TuA

Precursors and Chemistry: Precursor Design, New Precursors, Process Development III

Moderators: Prof. Anjana Devi, Ruhr University Bochum, Paul Williams, Pegasus Chemicals

1:30pm **AF1-TuA-1 New Class of Tin Precursors Targeting Low Temperature ALD Processing**, *Jean-Pierre Glauber, A. Devi*, Ruhr University Bochum, Germany

Motivated by the ever-increasing interest for low temperature atomic layer deposition (ALD) processes of tin-based nanomaterials to implement them in flexible devices or sensitive material stacks, new precursors with prerequisites for ALD are of key interest. Although several tin precursors have been reported, low temperature processing require a distinct reactivity to ensure a clean ligand cleavage at the targeted moderate process conditions.[1-4]

All-nitrogen coordinated chelating ligands with several metals have garnered increasing scientific attention while they impart reactivity and suitable thermal stability because of the chelating effect. Among them, amidinate based complexes such as tin(II)amidinates and tin(II)formamidinates have been in the focus, but their strong binding nature can lead to insufficient ligand cleavage leading to impurities in the thin films.[1-4] This can be attributed to their delocalized electron ligand-metal system that significantly increases their stability, but could make complete ligand cleavage difficult, especially when moderate process conditions are targeted.

To tackle this issue, alternative chelating ligand systems such as geminal diaminosilane (gDAS) are promising alternatives as demonstrated for several metals including Co, V, Ni and Mg.[1,5] In this study, a systematic variation of the gDAS ligand side chains resulted in tin compounds [Sn(*t*Bu-gDAS)₂] (**1**) and [Sn(gDAS)₂] (**2**) which were characterized thoroughly by complementary analytical methods including NMR, FTIR, EA, SCXRD, EI-MS and LIFDI-MS. The monomeric nature of the complexes was confirmed by LIFDI-MS measurements and SCXRD. Thermal analysis and vapor pressure determination revealed favorable volatility. This study reveals, that the distinct changes in the ligand side chain can have significant influence on their respective thermal behavior. The encouraging thermal properties of the complexes makes them appealing for application in low temperature ALD processes of tin-based nanomaterials which is exemplified with ALD of SnO_x.

[1]: M. B. E. Griffiths, *et al.*, *J. Vac. Sci. Technol. A*, **2021**, 39, 32409.

[2]: B. S. Lim, *et al. Nat. Mater.* **2003**, 2, 749.

[3]: H.-B.-R. Lee, *et al. J. Electrochem. Soc.* **2010**, 157, D10.

[4]: P. Rouf, *et al.*, *J. Phys. Chem. C*, **2019**, 123, 25691.

[5]: D. Zanders, *et al.*, *Angew. Chem., Int. Ed. Engl.*, **2020**, 59, 14138.

1:45pm **AF1-TuA-2 Novel Synthesis Route for Atomic Layer Epitaxy of BaSnO₃**, *Andreas Alstad, H. Sønsteby*, University of Oslo, Norway

Since 1965 Moore's law has predicted the development of transistor density for decades, but silicon-based devices are reaching their physical limits. Even HfO₂, a high-κ dielectric which replaced the SiO₂ gate oxide in 2007, will soon meet the same fate. New materials are thus needed to further evolve electronic devices with regards to performance and industrial feasibility. An emerging class of materials that may bring about a new paradigm of device design are complex oxides. Their cations can easily be substituted via doping to alter and tune their electronic properties. The research on these materials in the context of microelectronics has barely scratched the surface, as there are numerous atomic configurations of ternary oxides yet to be explored. If one considers quaternary oxides and beyond, then the possibilities border on countless. Nanoscale electronic devices are extremely sensitive to impurities and defects, which is why atomic layer deposition (ALD) is increasingly being used in manufacturing to ensure uniformity and conformality. One promising candidate in this paradigm shift is the perovskite BaSnO₃ (BSO). BSO is a transparent wide-bandgap n-type semiconductor that has gotten attention for its excellent charge carrier mobility, especially when doped with lanthanum, making it a promising candidate for high-frequency electronics and other applications where good charge carrier transport is important. It also shows excellent thermal stability.

Designing an ALD process for BSO and characterizing it is the topic of this work. The ALD processes for SnO₂ and BaO have been optimized separately both at a deposition temperature of 300 °C. X-ray fluorescence spectroscopy of our SnO₂ films using Sn(IV)Cl₂(*acac*)₂ found no chlorine impurities in the film. Additionally, we have demonstrated gas sensing capabilities of our SnO₂ thin films. The deposited barium films using Ba(Pr₃Cp)₂ contain both BaCO₃ and BaO, confirmed by Fourier-transform IR spectroscopy. The next step is to tune the stoichiometry of the ternary ALD process. Combining these into BSO thin films likely requires post-deposition annealing to decompose and remove the carbonate. The last deposition will attempt epitaxial growth of BSO on a SrTiO₃ substrate. Finally, we will investigate the electronic properties of BSO as function of its thickness, such as charge carrier mobility.

BaSnO₃ sees potential uses in microelectronics as a transistor channel material for its mobility, but also in photovoltaics as an electron transport layer (ETL) to reduce the probability of electron-hole recombination, and as a transparent conducting oxide (TCO) for displays and touch screens.

2:00pm **AF1-TuA-3 Microwave Enhanced ALD of Al₂O₃**, *B. Kupp, A. Schraner, John Conley*, Oregon State University

While advantageous for many applications, the low deposition temperature characteristic of ALD can allow incorporation of -OH groups or residual impurities from unreacted ligands leading to non-ideal stoichiometry and sub-optimal physical, optical, and electrical properties. Although increasing deposition temperature and post deposition annealing can help drive off impurities, increase density, improve stoichiometry, adjust morphology, and improve properties of ALD films, these strategies can move a process out of the ALD regime or exceed the thermal budget of sensitive substrates or devices, respectively. To maintain the low thermal budget of ALD while maximizing film properties, annealing or adding energy *during* each (or every few) ALD cycle or supercycle can help drive/speed reactions and reduce impurity/ligand incorporation. Energy enhanced (EE)-ALD methods to date include in-situ rapid thermal (MTA, DADA, etc.) annealing, flash lamp, plasma exposure, and UV, and electric field [1-15].

Here, we introduce microwave enhanced (MWE) ALD using an MKS SG 1024 solid state microwave (MW) generator with a custom antenna integrated into a Picosun R200 PEALD. Al₂O₃ films were deposited at 300 °C using TMA and H₂O. Thickness was measured using a Film Sense FS-1 mapping ellipsometer. Adding a 30 s in-situ 400 W MW exposure (without plasma generation) during the TMA purge part of each ALD cycle reduced film thickness by ~2% across a 150 mm Si wafer (Fig. 1). Preliminary leakage measurements on MOS devices suggest an associated reduction in low field leakage (1 MV/cm) and decrease in the onset-voltage for Fowler-Nordheim conduction. Additional results to be presented include placement of MW exposure step within ALD cycle, temperature, electrical data, morphology, and other materials. MWE-ALD merits further investigation as an EE-ALD technique.

1. Conley, Jr. *et al.*, *Appl. Phys. Lett.* **84**, 1913 (2004).
2. Conley, Jr. *et al.*, *MRS Proc. Vol.* **811**, 5 (2004).
3. Conley, Jr., *et al.*, in *Physics and Technology of High-k Gate Dielectrics II*, ECS Proc. Vol. 2003-22.
4. Holden *et al. J. Vac. Sci. Technol. A*, **40**, 040401 (2022).
5. Henke *et al.*, *ECS J. Sol. Sta. Sci. Tech.* 4(7), 277 (2015)
6. Clark *et al.*, *ECS Transactions*, 41(2), 79 (2011)
7. Miikkulainen *et al.*, *ECS Tran.* 80(3), 49 (2017)
8. Chalker *et al.*, *ECS Tran.* 69, 139 (2015)
9. Kim *et al.*, *Electrochemical and Solid-State Lett.* 14(4), H146 (2011)
10. No *et al.*, *J. ECS* 153, F87 (2006)
11. Shih *et al.*, *Sci. Rep.* 7, 39717 (2017)
12. Österlund *et al. J. Vac. Sci. Tech. A* 39, 032403 (2021)
13. Ueda *et al.*, *Appl. Surf. Sci.* 554, 149656 (2021)
14. Liu and Chang. *J. Chem. Phys.* 116, (2002)
15. Becher *et al.*, *Adv. Eng. Mater.* 2300677 (2023)

2:15pm **AF1-TuA-4 Atomic Layer Deposition of SnO Film Using Liquid Sn(EtCp)₂ Precursor and Combinations of H₂O and H₂ Plasma**, *Fumikazu Mizutani, N. Takahashi*, Kojundo Chemical Laboratory Co., Ltd., Japan; *T. Nabatame*, National Institute for Materials Science, Japan

The SnO₂ (Sn⁴⁺) and SnO (Sn²⁺) films have been widely investigated as n-type and p-type oxide semiconductors, respectively, for oxide TFTs. We previously reported characteristics of SnO₂ films deposited by ALD using a new Sn precursor (bis(ethylcyclopentadienyl) tin; Sn(EtCp)₂) and O₂ plasma [1]. In this study we investigated SnO films formation by ALD with the same

$\text{Sn}(\text{EtCp})_2$ and combination of a weak oxidant H_2O and a strong reduction H_2 plasma gases.

At first, the usefulness of H_2O gas on formation of the SnO film during ALD with $\text{Sn}(\text{EtCp})_2$ was studied. The growth temperature was 200 °C and ALD cycle was 100. Surprisingly, no growth of SnO film was observed because the thickness of the SnO film was less than 1 nm regardless of the number of ALD cycle. This was quite different results from our previous research of ALD of ZnO using a similar two-coordinated cyclopentadienyl complex and H_2O [2]. This was thought to be due to insufficient adsorption of $\text{Sn}(\text{EtCp})_2$ on the SnO surface.

To solve this problem, we investigated ABC type ALD in which H_2 plasma treatment is applied to the SnO surface so that $\text{Sn}(\text{EtCp})_2$ is well adsorbed. ALD process was conducted by using $\text{Sn}(\text{EtCp})_2$ as a precursor and H_2O followed by H_2 plasma as co-reactants. SnO films were deposited on 150 mm Si wafers with native oxide films at a growth temperature of 200 °C. Saturation of reaction was confirmed when 0.2 s of $\text{Sn}(\text{EtCp})_2$, 3 s of H_2O , and 5 s of H_2 plasma pulse times were applied. At this condition, linear growth of SnO film was observed, and the growth per cycle (GPC) was approximately 0.05 nm/cycle. This GPC is relatively high compared to the previously reported values for ALD of SnO [3]. Note that the high GPC shown in Ref. [3] is the value under low growth temperature conditions, and the GPC at a growth temperature of 200 °C is quite low at about 0.01 nm/cycle.

SnO thin films were deposited by ALD using a new cyclopentadienyl-based precursor and combinations of H_2O and H_2 plasma. Linear growth with high GPC of SnO thin film was confirmed.

Reference

- [1] M. Mizui, N. Takahashi, F. Mizutani, and T. Nabatame, AF1-TuM-8, 23rd International Conference on Atomic Layer Deposition (2023).
- [2] F. Mizutani, M. Mizui, N. Takahashi, M. Inoue, and T. Nabatame, J. Vac. Sci. Technol. A 42, 022403 (2024).
- [3] A. Mameli, J. D. Parish, T. Dogan, G. Gelinck, M. W. Snook, A. J. Straiton, A. L. Johnson, and A. J. Kronemeijer, Adv. Mater. Interfaces 9, 2101278 (2022)

2:30pm **AF1-TuA-5 A New Water Assisted ALD Process for Sc_2O_3 Using a Volatile Liquid Precursor**, **Martin Wilken**, Ruhr Universität Bochum, Germany; *T. Hepp*, *O. Briel*, Dockweiler Chemicals GmbH, Germany; *A. Muriqi*, Tyndall National Institute, University College Cork, Ireland; *C. Cho*, Ruhr Universität Bochum, Germany; *M. Nolan*, Tyndall National Institute, University College Cork, Ireland; *A. Devi*, Leibniz Institute for Solid State and Materials Research, Dresden (IFW), Germany

Scandium oxide (Sc_2O_3) thin films have garnered significant attention in recent years due to their unique properties and versatile applications. The unique combination of high melting point, wide bandgap, high refractive index, and excellent dielectric properties makes scandium oxide an attractive candidate for advanced electronic and optoelectronic devices, such as memory devices, and photodetectors.^[1] In particular, the ability of scandium oxide to serve as a high-k dielectric material in thin film transistors (TFTs)^[2], highlights the need for versatile low temperature atomic layer deposition (ALD) processes. Although ALD is beneficial to form highly uniform, pure and homogeneous layers of Sc_2O_3 on nanostructured surfaces, there are very few Sc precursors that include the tris-cyclopentadienyl scandium ($[\text{ScCp}_3]$)^[3], substituted tris-R-cyclopentadienyl scandium ($[\text{Sc}(\text{RCp})_3](\text{R}=\text{Me},\text{Et},\text{Pr})$)^[4] and scandium betadiketonates ($[\text{Sc}(\text{thd})_3]$)^[5]. These compounds are associated with certain drawbacks such as low vapor pressure, short shelf life, limited thermal stability and low reactivity. The homoleptic scandium amidinates such as scandium tris-(N,N'-diisopropylacetamidinate)^[6] have limited volatility as well.

In our study, we targeted the commercially available new liquid scandium precursor ASGAR $[(\text{EtCp})_3\text{Sc}(\text{dbt})]$ (dbt=1,3-bis(1,1-dimethylethyl)-1-triazenato) (Figure 1). Following up on a thorough investigation of the spectroscopical, structural and thermal properties, we adopted a computational approach to evaluate its use in ALD applications. Structure and ligand dissociation energies were calculated and gave a first indication for its suitability as ALD precursor. Furthermore, the interaction towards oxygen and water was investigated, showing its high degree of reactivity. Finally, the promising attributes of this precursor were proven by the development of a water-based ALD process in the temperature range between 220°C and 275°C. Apart from the ALD characteristics like linearity and saturated growth, the high purity of the Sc_2O_3 films could be proven by compositional analysis employing RBS/NRA (Figure 1). These results unveil the favorable characteristics of the new Sc precursor for Sc_2O_3 thin film growth.

2:45pm **AF1-TuA-6 Atomic Layer Deposition of Crystalline Molybdenum Trioxide and Suboxide Thin Films**, **Alexey Ganzhinov**, *M. Putkonen*, *M. Ritala*, University of Helsinki, Finland

Molybdenum oxides (MoO_x) have a range of different oxidation states and crystal structures which affect material properties significantly, leading to a wide range of applications. In addition to the most common stoichiometric molybdenum oxides, such as dioxide (MoO_2) and trioxide (MoO_3), there are multiple nonstoichiometric MoO_x suboxides where x is between 2.75 and 3. Additionally, molybdenum oxides can change oxidation states relatively easily between Mo^{4+} , Mo^{5+} , and Mo^{6+} . This wide range of possible oxidation states and structures allows the control of optical, electrical, and catalytic properties of the material. For example, the resistivity of molybdenum oxide changes from almost metallic for MoO_2 and Mo_3O_{11} , to semiconducting Mo_3O_{26} , and insulating MoO_3 . Emerging applications of MoO_x thin films are (organic) semiconductors, organic and perovskite solar cells, catalytic surfaces, and gas sensors.

Due to the plethora of possible different oxides with varying material properties, many new atomic layer deposition (ALD) processes are needed to cover them all. We developed a new ALD process for crystalline MoO_x thin films and deposited first crystalline ALD MoO_x thin films at 200 °C. Molybdenum acetate dimer ($\text{Mo}_2(\text{OAc})_4$) and ozone (O_3) were used as precursors at 200 --- 300 °C in a flow type F120 ALD reactor. Films deposited at low temperatures consist purely of unidentified suboxide phase while higher temperatures show $\alpha\text{-MoO}_3$ phase in the GIXRD measurements. The growth rate of the process ranges from $\sim 0.4 \text{ \AA}/\text{cycle}$ at low temperatures to $\sim 3 \text{ \AA}/\text{cycle}$ at 300 °C.

In-depth composition characterization of the films will be made with X-ray photoelectron spectroscopy (XPS) and time-of-flight elastic recoil detection analysis (TOF-ERDA). Further deposition parameters, such as oxidant type and dose, will be investigated to tune the oxidation state of the thin films from suboxide to trioxide and vice versa during the deposition. Lastly, optical differences between the oxides will be investigated with UV-VIS spectroscopy.

3:00pm **AF1-TuA-7 Promising Precursor Chemistry for ALD of Lithium-Based Thin Films**, **Jorit Obenluneschoß**, Inorganic Materials Chemistry, Ruhr University Bochum, Bochum, Germany; *N. Boysen*, Fraunhofer Institute for Microelectronic Circuits and Systems, Duisburg, Germany; *U. Brokmann*, Inorganic Non-metallic Materials, Technische Universität Ilmenau, Ilmenau, Germany; *D. Rogalla*, RUBION, Ruhr University Bochum, Bochum, Germany; *E. Rädlein*, Inorganic Non-metallic Materials, Technische Universität Ilmenau, Ilmenau, Germany; *A. Devi*, Inorganic Materials Chemistry, Ruhr University Bochum, Bochum, Germany

Lithium-containing materials have been particularly difficult to be realized by ALD. This has been mostly attributed to the unavailability of suitable precursor chemistry.^[1] That is in stark contrast to the desire to incorporate lithium-containing thin films for battery applications on the large scale.^[2] Efforts to utilize oxygen-based precursors such as diketonates (THDs) with low volatility or alkoxides with low thermal stabilities and reactivities are not really promising. Progress has been made with the trimeric lithium hexamethyldisilazane $[\text{Li}(\text{HMDS})_3]$ in the past as a more reactive precursor, but this trimeric compound only provides mild reactivities compared to unstable but highly reactive monomeric Li complexes. Most thin films that have been fabricated via ALD so far were prone to the formation of carbonates, which is often observed for Li containing films.^[3]

In our present work we aim at opening pathways to solve the challenges with ALD of lithium containing materials. We propose a highly reactive heteroleptic and monomeric lithium precursor making use of the stabilizing effect of N-heterocyclic carbenes (NHC).

Identifying the stability of monomeric lithium complexes as generally troublesome, we adopted the proven technique of introducing a stabilizing ligand. When employing a NHC with its unique dative abilities due to the free electron pair, electron density can be provided to the electropositive lithium to decrease the strong polarization of the bond between Li and the HMDS ligand. When utilizing NHCs, a monomeric linear $\text{Li}(\text{I})$ complex $[\text{Li}(\text{NHC})(\text{HMDS})]$ was successfully synthesized. This new complex has been characterized thoroughly by means of NMR, SC-XRD, and LIFDI-MS. Further, it shows excellent thermal properties as evidenced by the TGA (Fig. 1) as desired for ALD.

To prove its utility we set out to develop an ALD process and could successfully fabricate lithium silicate layers when the $[\text{Li}(\text{NHC})(\text{HMDS})]$ is reacted with ozone as co-reactant. Self-limiting growth could be confirmed and XPS together with RBS/NRA were employed to prove the presence of both lithium and silicon oxide species, confirming the lithium silicate

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material. Making use of the specifically designed precursor, a new and valuable process for lithium-based materials could be realized. The present results set a new pathway in finding highly reactive and yet stable precursor chemistries to deposit Li-containing films by ALD.

[1] M. Madadi, et al., *ACS Appl. Mater. Interfaces* **2021**, *13*, 56793–56811.

[2] O. Nilsen, et al., *Phys. Status Solidi A* **2014**, *211*, 357–367.

[3] M. Putkonen, et al., *J. Mater. Chem.* **2009**, *19*, 8767.

3:15pm AF1-TuA-8 Benchmarking 4 Different Cobalt Precursors for Atomic Layer Deposition of Complex Cobalt Oxides, Yani Amedjokou, H. Sønsteby, University of Oslo, Norway

The world is in an energy crisis. In ICT, the demand for electricity is expected to jump up to 20% of today's production by 2030, mainly due to the rapid expansion of data centers and device networks. The main cause is the inefficiency of modern silicon technology in electronic devices. These devices are so inefficient in fact that 40% of the power use in a typical data center is spent on cooling. Moore's law has held true for over 50 years now but is beginning to fail. Silicon transistors cannot be much smaller than they already are, and therefore we need new materials with new functionalities. Oxides seem to be fit the bill for this purpose, as they host a wide variety of functional properties that have great potential for applications in electronics. The main issue holding these materials back is the lack of viable production methods at an industrial scale. This is where atomic layer deposition comes in. The big chipmakers already use ALD in their production lines, but what's missing are reliable ALD systems for complex oxides for the manufacturers to utilize. To achieve this, research into how different ALD precursors affect the systems is required.

The work we have done aims to serve as a benchmark for four cobalt precursors in a ternary cobalt oxide ALD system. The precursors in question are $\text{Co}(\text{acac})_2$, $\text{Co}(\text{acac})_3$, $\text{Co}(\text{thd})_2$ and $\text{Co}(\text{thd})_3$. We have chosen these four as they let us examine the difference between Co(II)- and Co(III)-precursors and the difference between having the larger thd-ligand and the smaller acac-ligand.

We have attempted to grow thin films of both binary cobalt oxide and the ternary LaCoO_3 to examine if the difference in precursor affects things as crystallinity, conformity, consistency, and growth rate as these things normally play an important role for the properties of the film material.

We have found that the crystal orientation of binary cobalt oxide deposited on $\alpha\text{-Al}_2\text{O}_3$ substrates are affected by the choice of precursor. With the acac-precursors, we observe an additional set of reflections that are not present in films grown with the thd-precursors. Our belief is that the structure relaxes during growth only with the thd-precursors, and therefore we only observe one set of reflections. Furthermore, we have also observed that films grown with $\text{Co}(\text{thd})_2$ have a lower growth rate than the rest, but virtually no thickness gradients in the reaction chamber.

It is our belief that the results we find will facilitate the development of novel ALD systems for complex cobalt oxides, as these materials exhibit both electric and magnetic properties.

ALD Fundamentals

Room Hall 3A - Session AF2-TuA

Precursors and Chemistry: Simulation, Modeling, and Machine Learning for ALD

Moderators: Prof. Dr. Michael Nolan, University College Cork, Prof. Dr. Ralf Tonner-Zech, Leipzig University

4:00pm AF2-TuA-11 Machine Learning Assisted Surface Reaction Study of Al(Me)₃ and Water on OH/Si(111), H. Nakata, Cheol Ho Choi, Kyungpook National University, Republic of Korea

INVITED

Knowledge of the detailed mechanism behind the atomic layer deposition (ALD) can greatly facilitate the optimization of the manufacturing process. Computational modeling can potentially foster the understanding; however, the presently available capabilities of the accurate *ab initio* computational techniques preclude their application to modeling surface processes occurring on a long time scale, such as ALD. In this talk, we propose an iterative protocol for optimizing machine learning (ML) training data sets and apply ML-assisted *ab initio* calculations to model surface reactions occurring during the ALD process on the semiconductor surfaces. The protocol uses a recently developed low-dimensional projection technique, greatly reducing the amount of information required to achieve high accuracy (1 kcal/mol or less) of the developed ML models. Hence, the

proposed protocol furnishes a very effective tool to study complex chemical reaction dynamics at a much-reduced computational cost.

4:30pm AF2-TuA-13 Quantum Chemical Investigation on the Reaction Mechanism of Atomic Layer Deposition of ZrO_2 from Heteroleptic $\text{CpZr}(\text{N}(\text{CH}_3)_2)_3$ Precursor and Ozone, Rabi Khanal, R. Joe, A. Dip, Tokyo Electron America, Inc.

High-k oxides, such as ZrO_2 , are being studied as alternatives to SiO_2 due to their advantageous properties for scaling down semiconductor devices. They have lower leakage current, consume less power, switch faster, and are thermally stable. Moreover, they can maintain a high capacitance at thinner film thickness, which is ideal for achieving higher packaging density and increasing memory cell integration on a single chip.

Heteroleptic precursors containing amido and cyclopentadienyl (Cp) ligands exhibit adequate thermal stability for the atomic layer deposition (ALD) of ZrO_2 . In ALD, ozone (O_3) can be used as an oxidizer instead of water (H_2O). Ozone has a higher oxidation potential than H_2O . This higher oxidation potential allows for more surface reactions, faster growth, uniform deposition, and reduced impurities. It is worth noting that different ligands in heteroleptic precursors have unique reaction paths depending on their ligand exchange reactions, unlike homoleptic precursors. It is crucial to understand the detailed surface reaction mechanism of ALD to enhance the quality and performance of thin films by reducing impurities incorporated during film growth.

In this study, we have employed quantum chemical calculations at the density functional theory (DFT) level and *ab initio* molecular dynamics (AIMD) to investigate the detailed reaction mechanism of ZrO_2 ALD with the precursor $\text{CpZr}(\text{N}(\text{CH}_3)_2)_3$, and O_3 as an oxidizer. Our findings suggest that when the precursor is adsorbed onto a hydroxylated Si surface, the elimination of the amido ligand is preferred over that of the Cp ligand. During the oxidation process, all remaining ligands on the adsorbed precursor are eliminated through the adsorption of O_3 in two subsequent processes, each consisting of multiple intermediate reaction mechanisms.

In addition, the energy barriers associated with the oxidation of Zr-Cp bonds are higher (about 12 kcal/mol) than those of the Zr-N bonds. The higher energy barrier indicates that the release of the Cp ligand occurs after the amido ligand. When the Cp ligand remains on the surface during the ALD cycle, it increases the adsorption energy for incoming molecules and acts as a blocking group to reduce impurity incorporation during film growth. Our study provides a fundamental understanding of the reaction mechanism of various ligands with O_3 at the Si surface, which has yet to be reported. We believe this knowledge can be extended to the deposition of other high-k oxides, such as HfO_2 . Also, it can serve as a basis for tuning film properties using feature and reactor scale simulations.

4:45pm AF2-TuA-14 Microkinetic Modelling to Reveal How the Atomic-Scale Mechanism of Deposition or Etch Plays Out at Feature and Reactor Scale, Simon D. Elliott, Schrödinger, Ireland; T. Hughes, T. Ludwig, Schrödinger; J. Gavartin, Schrödinger, UK

Microkinetic modelling is a technique for determining the turnover of a gas-surface process by solving the coupled kinetic rate equations of its constituent elementary reaction steps [1]. It is widely used in the field of heterogeneous catalysis. Here we present a microkinetic model of the atomic layer deposition (ALD) of alumina from trimethylaluminium (TMA) and water and discuss its utility in investigating growth at macroscopic length and time scales.

We first outline the computational scheme, where elementary steps and their activation energies have been computed with density functional theory (DFT), averaging across a wide variety of geometries. We emphasize the importance of converting the DFT energies to free energies at the temperatures and pressures of interest. The resulting microkinetic model for alumina-on-alumina growth yields measurable quantities (relative growth per cycle and sticking coefficients) as a function of temperature and pressure, which are validated against experiment. For instance, the values of sticking coefficient from the model, $s_0(\text{TMA}) = 7 \times 10^{-3}$ and $s_0(\text{H}_2\text{O}) = 3 \times 10^{-4}$ at 1 Torr and 300°C, compare well with experiment [2]. Sticking coefficients are crucial inputs for computational fluid dynamics simulations at feature-scale and reactor-scale.

We then show results for how microkinetic modelling can be used in specific scenarios. By adding appropriate elementary steps, the model can reveal the contribution from continuous CVD-style growth under given conditions, or under what conditions ALD can be flipped over into ALE. Alternatively, activation energies can be modified to account for the different chemistry that may exist during nucleation on a substrate, without

Tuesday Afternoon, August 6, 2024

explicitly modelling any one substrate at the atomic scale. This can be used to test which chemistries are effective in tuning area-selectivity of a process towards various substrates. Finally, we show how a microkinetic model can be used to study the variation of sticking coefficient with pressure and thus account for penetration depth and conformality within high aspect ratio features.

These examples illustrate how existing mechanistic data from atomic-scale DFT can be leveraged in computationally-inexpensive higher-scale models to allow 'what-if' experiments to be carried out that link directly to measurements.

[1] Iwao, T.; Yang, T.-H.; Hwang, G. S.; Ventzek, P. L. G.; *J. Vac. Sci. Technol. A* **2023**41, 032410

[2] Arts, K.; Vandalon, V.; Puurunen, R. L.; Utriainen, M.; Gao, F.; Kessels, W. M. M.; Knoop, H. C. M.; *J. Vac. Sci. Technol. A* **2019**37, 030908

5:00pm **AF2-TuA-15 First-Principles Based Comprehensive Surface Kinetic Modeling for Molybdenum ALD Film Growth**, *Toshihiko Iwao, K. Lee, J. Cha, J. Hong, J. Son, S. Kang*, Etch/CLN Equipment R&D Team, Samsung Electronics, Republic of Korea

As a design rule of semiconductor device fabrication reaches near tens of angstrom scale, interconnect metallic materials require not only lower bulk resistivity but also smaller electron mean free paths which cause an increase in the effective resistivity of nanometer-scale structures due to interface electron scattering phenomena. Consequently, there is an increasing demand for nanoscale wiring formation using materials with short electron mean free paths, such as molybdenum (Mo), ruthenium (Ru), and cobalt (Co). Among them, the development of Mo micro-wiring formation technology using atomic layer deposition (ALD) is being actively pursued, but further acceleration of productivity is required. In this study we have established a surface reaction model using first-principles analysis to identify the rate-limiting factors of Mo growth mechanism. The construction of reaction models consists of three elements: calculating the activation energy through first-principles surface reaction analysis, determining the reaction pathway, and analyzing real-time coverage using the activation energy. This analysis demonstrates that the temperature dependency of Mo growth-per-cycle (GPC) is caused by the 1.27 eV of desorption energy of surface adsorbed hydrogen site Mo-H(s) desorption. During the molybdenum dichloride dioxide (MoO_2Cl_2) precursor dose step, decomposed chlorine and oxygen atoms from the precursor molecule remain on the molybdenum surface and inhibit further precursor molecule adsorption by creating Mo-O-Mo(s), and Mo-Cl(s) surface. This phenomenon describes the monolayer saturated adsorption of the precursor and reveals the necessity of hydrogen flux to remove these inhibitors from the surface. We also analyzed the reaction barrier of removing surface inhibitor by both molecular hydrogen and surface stuck hydrogen site Mo-H(s). By combining these reaction paths into surface kinetic model we have successfully reproduced the GPC tendency with over 90% accuracy on various process parameters based on these reaction barrier energy and surface kinetic model, which analyzes the surface coverage in actual process timescale. This film growth analysis scheme provides the detailed and quantitative film growth mechanism for various novel materials and processes.

5:15pm **AF2-TuA-16 Modelling the Ligand Exchange Process for the Atomic Layer Deposition of Metal and Metal Oxide Thin Films**, *Ji Liu*, Tyndall National Institute, University College Cork, Ireland; *H. Sønsteby*, University of Oslo, Norway; *M. Nolan*, Tyndall National Institute, University College Cork, Ireland

Atomic layer deposition (ALD) is widely used in microelectronics and semiconductor industry to deposit metal and its oxide and nitride thin films as part of device fabrication in nano- or subnano-dimensions. The key advantages of ALD are the conformality and precise thickness control at the atomic scale, which are difficult for physical or chemical vapor deposition methods. The atomic scale understanding of ALD is vital and essential to design and optimize the deposition process, and density functional theory (DFT) calculations play an important role in providing detailed reaction mechanism, theoretical screening of suitable precursors and estimated growth-per-cycle (GPC).

In this presentation, I discuss our recent work on the detailed first principles simulation of ligand exchange process for thermal ALD of a range of technologically relevant deposition chemistries. 1) Co thin film deposition using $\text{CoCl}_2(\text{TMEDA})$ and reducing agent $\text{Zn}(\text{DMP})_2$; 2) FeZn thin film deposition using FeCl_3 and $\text{Zn}(\text{Et})_2$; and 3) BaO/Ba(OH)₂ using $\text{Ba}(\text{acac})_2$ and oxygen-containing reactants as part of depositing BaTiO_3 (BTO). We first focus on gas-phase precursor chemistry and apply DFT calculations to

identify plausible ligand elimination pathways, which allow us to assess the most favourable chemistry for each film deposition. Then we explore the surface chemistry in the two half reactions for the ALD process. For Co deposition we show that a pathway involving initial ligand exchange of DMP and Cl on Co(111) surface with CoCl_2 termination and Zn is removed via $\text{ZnCl}(\text{DMP})$ formation and desorption, resulting $\text{Co}(\text{DMP})_2$ termination on the surface. The two DMP ligands are removed via C-C bond formation in a straightforward way. In intermetallic alloy deposition we show that the FeCl_3 precursor is found on the surface as an FeCl_2 and -Cl fragment and the reaction with DEZ follows mixture of butane and subsequent EtCl formation and desorption. Finally, for BaO/Ba(OH)₂ ALD, we explore how the $\text{Ba}(\text{acac})_2$ precursor reacts on Bi-O terminated surfaces and how this can impact on the preferred deposition chemistry. These works showcase how we can apply DFT calculations to elucidate the ligand exchange mechanism during metal or metal oxide thin film growth and give some insights on how the selection of precursors and reducing agent or co-reactant affects the growth behavior.

ALD Fundamentals

Room Hall 3A - Session AF1-WeM

Growth and Characterization: High Aspect Ratio/High Surface Area/Powder ALD and Characterization of ALD Films

Moderators: Mr. Nouredine Adjeroud, Luxembourg Institute of Science and Technology (LIST), Viljami Pore, ASM

8:00am AF1-WeM-1 Conformality of Ternary Oxides by Spatial ALD: Monte Carlo Simulations and Experimental Study, Mike van de Poll, S. van der Heijden, P. Poodt, E. Kessels, B. Macco, Eindhoven University of Technology, Netherlands

Conformal film growth is one of the key merits of ALD and essential for many applications. The conformality of binary oxide depositions using a simple AB-process has been thoroughly examined in the past and is well understood. Although materials containing three or more elements have been conformally deposited before in 3D-structures, fundamental understanding is still limited. This is especially the case for spatial ALD (s-ALD), which is promising for high-volume low-cost applications. In this work, we investigate the conformality of atmospheric-pressure s-ALD deposited ternary oxides, both through modeling and experiments.

A significant influence of the precursor dosing method (i.e., dosing the metal precursors in separate cycles within a supercycle versus co-injecting both metal precursors simultaneously) on the conformality was demonstrated using a Monte Carlo model. The supercycle method generally grants a large degree of control over the film stoichiometry because of the fact that the precursor doses can be tuned separately. To obtain films with invariable stoichiometry with respect to position in the trench, the doses should be tuned either such that either full step coverage is reached, or such that the penetration fronts of both precursors overlap. Controlling the composition is more challenging for Co-injection. Modeling results highlight the importance of many different aspects, such as precursor partial pressure, diffusivity, and sticking probability.

The modeling results were confirmed experimentally for both dosing methods by spectroscopic ellipsometry and XPS. Additionally, experimental results show the importance of precursor-precursor interactions at the surface during co-dosing. Al-doped ZnO and AlZnO were deposited in lateral high-aspect-ratio (LHAR) test chips (PillarHall™ by Chipmetrics Ltd) using DMAI, DEZ, and water. Co-injection resulted in two distinct regions: an Al-rich region at the start of the trench, followed by a Zn-rich region deeper in the trench. A detailed study revealed that DMAI displaces DEZ molecules bound to the surface, resulting initially in primarily AlO_x growth, followed by ZnO growth deeper in the trench where DMAI is depleted. Precursor displacement can potentially play a role for many other co-injection processes depending on the reactivity of the precursors.

This study into the different dosing methods of s-ALD has shown which aspects are important for conformal deposition and enables the deposition of high-quality ternary oxides in high-aspect-ratio structures.

8:15am AF1-WeM-2 Reusable Macroscopic HAR Test Kit Enabling Fast, Routine Characterization of Film Conformality, Jesse Kalliomaki, I. Manninen, J. Järvillehto, Applied Materials, Finland

A defining feature of atomic layer deposition (ALD) is conformality, which has made it an invaluable tool in several industries. However, the testing film growth in high-aspect-ratio (HAR) structures has thus far been a laborious, slow, and costly endeavor, involving manual analysis of specialized nanostructures [1]. This limits the conformality studies during ALD process development.

This approach also neglects another strength ALD offers, scalability. ALD can coat macroscopic objects conformally as well as the microscopic. However, conformality tests carried out on a microscopic scale often led to overestimation of the film penetration depth at half-thickness (PD50) on macroscopic HAR objects [2], failing at the intended purpose of the ALD film.

Our work introduces a novel approach to tackle the issue of cost and scalability: a reusable HAR-test device comprising a wafer-sized annular metal disk with radial grooves of varying height (50-900 μm) extending outwards (Fig 1a). When placed on a wafer, closed lateral tunnels with varying aspect ratios are formed. After deposition, growth pattern is revealed by removing the disk (Fig 1b), easily accessible using wafer-scale instruments. Due to the macroscopic size of the pattern, low resolution

techniques, such as ellipsometry or even measurement using a ruler, can be used to obtain useful results. This feature was leveraged to boost process development efficiency by varying a process parameter in steps during a deposition. This resulted in a staircase profile, comprised of characteristic PD50s of the varied parameter (Fig. 1c). For example, a TEMAHF-H₂O deposition using TEMAHF pulse times of 1.0, 2.0, 2.7 & 3.0 s, resulted in PD50s of 16, 20, 22 & 23 mm, respectively, in a tunnel with a height of 240 μm. Data from 12 tunnels was combined to form the HAR Growth Constant (HGC), describing how the process scales to HAR features with any hydraulic diameter within the same flow regime.

This invention (patent pending) enables routine conformality testing during process development in a cost-effective and timely manner - facilitating further exploration of experimental conditions.

[1] Appl. Phys. Rev. 6, 021302 (2019); doi: 10.1063/1.5060967
[2] Manninen, I., Aalto University, Espoo, Finland, 2022. <https://aaltodoc.aalto.fi/handle/123456789/113671> (accessed 2022-02-01).

8:30am AF1-WeM-3 Superconformal ALD Using a Heavy Inert Diffusion Additive, Arun Haridas Choolakkal, P. Mpofo, P. Niiranen, J. Birch, H. Pedersen, Linköping University, Sweden

The self-limiting surface chemistry of ALD routinely allows perfectly conformal, i.e., a step coverage of 1, film deposition. However, achieving superconformal deposition, i.e., a step coverage above one, with thicker film in the bottom of a recessed feature than in the top, has remained elusive in ALD, we will here show that it is possible. We recently showed how a CVD process for boron carbide using triethyl boron as single source precursor can be perfectly conformal by adding a co-flow of Xe.¹ Here, we expand on this concept by using Kr as diffusion additive in thermal ALD of AlN from trimethyl aluminum (TMA) and ammonia (NH₃).

We observe that the step coverage in 16:1 aspect ratio feature increased from 1 to 1.4 with the addition of Kr to the ALD process. The deposition depth observed from initial depositions conducted in lateral high-aspect-ratio (LHAR) chips with 500 nm gap height shows no significant change with Kr addition, and it remained at 42 μm.

The rationale behind this is the competitive co-diffusion of mainly the lighter NH₃ (17 amu) and Kr (83.8 amu) during every other half-cycle. The higher sticking probability of TMA ensures a chemisorbed layer up to 42 μm depth in the LHAR structure, limited by the influx of the given TMA dose. Kr, with a lesser mass difference with TMA (72 amu), does not provide a notable competitive advantage during co-diffusion. This means that NH₃ molecules are pushed down to the trench bottom, resulting in dilution at the openings of the high-aspect-ratio feature. This dilution prevents the surface saturated half-reaction at the openings while achieving an excess NH₃ concentration at the trench bottom, ensures surface saturated half-reactions at the bottom surfaces.

Reference:

A. H. Choolakkal et al. Competitive co-diffusion as a route to enhanced step coverage in chemical vapor deposition. *ChemRxiv*2024: doi:10.26434/chemrxiv-2024-nlf00

8:45am AF1-WeM-4 Ald of Alumina-Silica Multilayers on Carbon Microfiber Fabrics: Microstructure and Potential as Refractory Oxygen Diffusion Barriers, Elise des Ligneris, D. Samélor, CIRIMAT-INPT, France; A. Sekkat, CNRS, France; C. Vahlas, CIRIMAT-INPT, France; B. Caussat, CNRS, France

Provided that the sensitivity of carbon fibers (CFs) to thermal oxidation above 400 °C is tackled, CFs could then be used as reinforcement in high temperature composites, microwave absorption materials or thermal insulators in extreme environments [1, 2]. Indeed, CFs are not subjected to creep with increasing temperature, and exhibit even higher elongation modulus, contrary to ceramic microfibers such as SiC or boron-doped alumina [1, 2]. Rather than protecting a carbon macro-object, this study makes use of ALD for the deposition of a refractory oxygen diffusion barrier layer (OBL) on the surface of CFs (7 μm diameter) entangled within a woven fabric [1, 2]. While ALD of alumina-silica barrier layers was previously reported [3], the deposition of silica-based thin films on CFs have long been considered a challenge. Indeed, the oxidation-sensitive nature of CFs does not bode well with the thermal oxidative conditions associated with common protocols of silica ALD [3]. Nonetheless, the use of a catalytic ALD process illustrated in Scheme 1 enabled for the deposition of amorphous alumina-silica bilayers from 445 K using trimethylaluminium (TMA) and tris(*tert*-pentoxy)silanol (TPS) [2]. Amorphous alumina ALD was achieved below 120 °C using TMA and water [1]. The sequence of alumina low

temperature ALD and alumina-silica catalytic ALD allowed for the deposition of alumina-silica laminates of tunable thicknesses on CFs, as presented in Figure 1[1, 2]. A CF-alumina interface prevented from carbon diffusion within the coating, while the fluid phase of silica could fill voids induced in part by alumina crystallisation. This study then focused on the compounds formed at the alumina-silica interface, in a trial to reach a three-dimensional structured coating, containing a crystalline mullite structure oriented parallel to the carbon substrate, and thus limiting events of intra-delamination.

1. des Ligneris, E., et al., Amorphous Alumina Thin Films Deposited on Carbon Microfibers As Interface Layer for Thermal Oxidation Barriers. *ACS Applied Engineering Materials*, 2023. 1(10): p. 2707-2722.
2. des Ligneris, E., et al., *Catalytic ALD of alumina of amorphous alumina-silica thin films on carbon microfibers*. *AVS Journal of Vacuum Science and Technology A*, 2024.
3. Putkonen, M., et al., *Low-temperature atomic layer deposition of SiO₂/Al₂O₃ multilayer structures constructed on self-standing films of cellulose nanofibrils*. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 2018. 376(2112): p. 20170037

9:00am **AF1-WeM-5 Pillarhall Lateral High Aspect Ratio Assisted Unveiling of Secondary Growth Front and Background Reaction Mechanism in Atomic Layer Deposition**, *Anish Philip*, Chipmetrics Ltd, Finland; *S. Elliott*, Schrödinger, Germany; *J. Kinnunen*, Chipmetrics Ltd, Finland; *A. Mirhamed*, Park Systems GmbH, Germany; *M. Zaheer*, *M. Utriainen*, Chipmetrics Ltd, Finland

The 3D vertical scaling trend in nanoelectronics necessitates high-aspect ratio (HAR) features and conformal ultra-thin films, crucial for the semiconductor industry today. The lateral high aspect ratio (LHAR) test structure and measurement method is a unique test vehicle for characterizing the conformality for the 3D thin films. The unique feature of LHAR is the ability to quantify the conformality for both ALD and CVD processes. PillarHall® LHAR4 test chips enable accurate and repeatable film penetration depth (PD) profile measurements which help to predict and quantify the step coverage in any HAR features. In the current research we are showing another important aspect of these LHAR beyond the already existing applications. Utilization of LHAR in understanding the reaction mechanism of ALD process especially in 3D structures is the major highlight of the current research. We reveal a secondary reaction front (ultra-thin layers, Figure 1) for the TMA+H₂O thermal ALD process with the support of LHAR, contrast SEM and imaging ellipsometry techniques. The merit of using imaging ellipsometer is that beyond visualizing the second front, it also facilitates the measurement of film thickness within the second front region. We checked the process at two different deposition temperatures (125°C and 300°C) and with different combinations of pulsing and purging lengths to investigate the influence of these parameters on the observed secondary growth front. The observation of secondary growth front for both temperatures unambiguously ruled out the deposition temperature influence on the observed feature. To investigate the possible mechanistic reasons for the secondary growth front, we have carried out microkinetic modelling of ALD cycles over a range of combinations of precursor pressures, simulating the situation at various cavity depths. As expected, high pressure of both precursors leads to high growth rates up to the primary growth front. At the lower pressures that are present further into the cavity, the model predicts much lower growth rates, along with an increase in the sticking coefficient of TMA (Figure 2). As the depth of a growth front scales with the square root of the sticking coefficient [1], the low-pressure growth front should therefore be deeper than the high pressure one, which matches the experimental observation. Our results indicate that the formation of the second front results from the presence of multiple reaction mechanisms, which are otherwise challenging to distinguish.

Reference

- [1] K. Arts, V. Vandalon, R.L. Puurunen, M. Utriainen, F. Gao, W.M.M. Kessels, H.C.M. Knoop, *J. Vac. Sci. Technol. A* 37, 030908 (2019).

9:15am **AF1-WeM-6 Helium Ion Microscopy on ALD Thin Films**, *Sami Kinnunen*, University of Jyväskylä, Finland; *E. Alakoski*, *T. Laine*, JAMK University of Applied Sciences, Finland; *T. Sajavaara*, University of Jyväskylä, Finland

Scanning electron microscopy (SEM) is routinely used to image thin nanoscale features such as thin films. Helium ion microscopy (HIM) is in many ways a very similar imaging method with few key differences. In HIM helium ion beam is used to scan the sample and back scattered electrons

are detected. In addition to excellent resolution and depth-of-field, charging of insulating samples is easily counteracted with electron flood gun and no extra conductive coating is needed. It is also possible to use neon beam to mill material or fabricate patterns. On the other hand, the minimal generation of x-rays makes elemental analysis more complicated compared to SEM.

In this work we present examples of HIM at the University of Jyväskylä related to ALD and thin film research. For example, imaging insulating cellulose fibers (Fig. 1 a) or packaging materials coated with non-conducting thin films are regularly studied without any special sample preparation. We also show how HIM has been used as a focused ion beam (FIB) tool by changing the incident beam from helium to neon. This can be used, for example, to reveal the cross-section of the ALD film on a substrate (Fig. 1 b). We also show how HIM-based ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) can be used for elemental imaging with high spatial resolution and discuss the limitations of the technique at its current state.

9:30am **AF1-WeM-7 Understanding the Amorphous Structure of Al- and Zn- Doped TiO₂ with an Automated 4D-STEM Analysis Pipeline**, *Andreas Werbrouck*, *N. Paranamana*, *X. He*, *M. Young*, University of Missouri-Columbia

Titanium oxide is an ALD staple. It finds uses in microelectronics, (photo) catalysis and lithium-ion-based energy storage. One of the reasons for its attractiveness is the possibility to tune the functional properties by means of the structure: e.g. the conductivity of the material changes by means of doping and/or phase selection through annealing (anatase or rutile).

Amorphous TiO₂ is subject to similar effects. Small concentrations of impurities (e.g. dopants or precursor ligands) may have a large impact on the final structure. Similarly, subtly different structures may arise at the substrate-film or film-vacuum interface. This will affect the functional properties of the films. Due to the difficulty characterizing the nature of the amorphous phase, such differences are easily overlooked. Hence, it is necessary to develop spatially resolved, structural characterization techniques for both crystalline and amorphous materials.

In this work, we report on a 4D-scanning transmission electron microscopy (4D-STEM) investigation of the amorphous structure of undoped and doped TiO₂ as deposited with TiCl₄ and water, with AlMe₃ and ZnEt₂ as precursors for the doping. 4D-STEM measurements allow to investigate and map material structure at the nanoscale in a TEM: 2D diffraction data is available for every recorded pixel and can be combined with co-located Energy-Dispersive X-ray Spectroscopy (EDS) data to match structures and compositions.

The large volume of data and the complexity of diffraction analysis makes manual processing of 4D-STEM data prohibitively slow. To address this, we developed an automated workflow for analyzing 4D-STEM data. This workflow is cast as a Directional Acyclic Graph (DAG). First, the 4D data is split into spatially mapped crystalline and amorphous components. Then, non-local averaging and non-negative matrix factorization distill the amorphous data into a low number of higher-quality pair distribution functions (PDFs). Finally, these can be structurally refined using reverse Monte Carlo (RMC) fitting and molecular dynamics (MD).

This automated approach greatly reduces the amount of time and effort necessary to interpret the data in a meaningful way. Specifically for TiO₂, we clearly observe how even a low level of Zn, Al and Cl impurities profoundly alter the amorphous structure. Through this effort, a better understanding of the as-deposited, amorphous material is gained, which can then serve as a stepping stone to study and engineer more advanced dielectrics, catalysts and electrode interfaces.

9:45am **AF1-WeM-8 Non-Destructive Characterization of ALD Thin Films Using Angle-resolved XPS and Structure Modeling**, *K. Artyushkova*, *N. Biderman*, *Wolfgang Betz*, Physical Electronics USA

A powerful tool for surface and interface analysis: X-ray photoelectron spectroscopy (XPS) has long been a trusted technique for analyzing the chemical composition of thin layers and interfaces, offering a non-destructive approach to unlocking valuable information. Angle-resolved XPS (AR-XPS) builds upon this foundation, leveraging the power of tilted measurements to determine the composition and thickness of multilayered films, reaching depths of up to 5-10 nanometers below the surface.

Conventional structure modeling algorithms applied to AR-XPS data rely on the assumption of uniform, discrete thin film growth. This approach presents significant limitations for accurate thickness determination when analyzing films with complex morphologies: pinholes, island growth, and

non-uniform coverage which are particularly observed in atomic layer deposition (ALD) processes.

Structure modeling package *StrataPHI* goes beyond the limitations of conventional ARXPS data modeling for multilayered films. Its fractional coverage mode tackles non-uniform island morphologies typically seen in early ALD stages. This talk highlights *StrataPHI*'s capabilities, including layer coverage and accurate thickness even for non-uniform layers.

By employing the microprobe X-ray spot of PHI XPS instruments, capable of analyzing areas ranging from as small as 5 μm in diameter and as large as 1mm x 200 μm , AR-XPS measurements can be used to assess thickness and coverage variations across multiple length scales providing deeper insights into growth mechanisms.

ALD Fundamentals

Room Hall 3A - Session AF2-WeM

Growth and Characterization: Low Temperature ALD

Moderators: Prof. Dr. John Conley, Oregon State University, Prof. Henrik Pedersen, Linköping University, Sweden

10:45am **AF2-WeM-12 Low-Temperature ALD of Metallic Cobalt for 3D Structures**, *Mathias Franz*, L. *KaBner*, Fraunhofer ENAS, Germany; C. *Thurm*, University of Technology Chemnitz, Germany; X. *Hu*, Fraunhofer ENAS, University of Technology Chemnitz, Germany; M. *Daniel*, scia systems GmbH, Germany; F. *Stahr*, Forschungs- und Applikationslabor Plasmatechnik GmbH, Germany; S. *Schulz*, Fraunhofer ENAS, Center for Microtechnologies (ZfM), University of Technology Chemnitz, Germany

Atomic Layer Deposition (ALD) of metallic films is a broad and ongoing topic of research. The conformal deposition of metallic cobalt is relevant for modern interconnects¹, seed layers for electroplating², and antibacterial coatings³. One of the essential process parameters is the deposition temperature. Here, we present the development of a low temperature ALD process for the deposition of metallic cobalt on integrated 3D structures in silicon substrates.

We base our process development on a set of previously developed precursors of the form $[\text{Co}_2(\text{CO})_6(\text{RC}\equiv\text{CR}')]^+$ published by Georgi et al.⁴. We evaluated a set of these precursors for ALD using density functional theory (DFT) calculations. According to these calculations the precursor $[\text{Co}_2(\text{CO})_6(\text{HC}\equiv\text{CC}_5\text{H}_{11})]^+$ was identified as the most favourable precursor for deposition via ALD. It adsorbs with remaining $(\text{HC}\equiv\text{CC}_5\text{H}_{11})$ group which can be easily removed by use of activated hydrogen. The process development was done on a novel *scia Atol 200* reactor. The depositions took place on 200 mm Si wafers with a preliminary SiO_2 layer of 100 nm thickness. The precursor was evaporated via the bubbling method. A full ALD cycle consists of a cobalt precursor pulse, an Ar purge, an H_2 plasma pulse, and a second Ar purge. The deposited cobalt films were analysed by *in-vacuo* ellipsometry to determine in-line the film growth rates. Figure 1 shows the growth per cycle in the temperature range from 35 °C to 125 °C showing the ALD window for this process within the range of 50 °C to 110 °C.⁵ The process was optimised regarding pulse and purge duration times to ensure stable saturation conditions. *Ex situ* measurements with XPS confirm that cobalt is in metallic state. The optimised ALD process has been applied to silicon trench structures. Figure 2 shows a SEM image of cobalt deposited to the sidewalls of a silicon trench.

We demonstrated the successful development of a low temperature ALD process for metallic cobalt. This process was successfully applied to 3D structures.

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References

- ¹ Lanzillo *et al.*, doi: <https://doi.org/10.1109/TVLSI.2021.3126541>
- ² Liu *et al.*, doi: <https://doi.org/10.1149/1945-7111/ac862d>
- ³ Jeong *et al.*, doi: <https://doi.org/10.1016/j.tsf.2008.10.063>
- ⁴ Georgi *et al.*, doi: <https://doi.org/10.1039/c4tc00288a>
- ⁵ Franz *et al.*, doi: <https://doi.org/10.3762/bjnano.14.78>

11:00am **AF2-WeM-13 Towards Deposition of Metallic Molybdenum Films from Molybdenum Hexacarbonyl in a Process Involving an Intermediate ALD Step and Subsequent Reduction**, *Kees van der Zouw*, M. *Sturm*, T. *Aarnink*, A. *Kovalgin*, University of Twente, the Netherlands

Atomic layer deposition (ALD) is expected to be essential for future CMOS back-end-of-line (BEOL) applications. Due to its electrical and thermal properties, molybdenum (Mo) is among the metals that have gained significant interest [1]. The research into ALD of metallic Mo has been limited to halide-based processes [2-5], in which corrosive byproducts like hydrogen fluoride or hydrogen chloride can be formed. A process for Mo ALD from a metalorganic precursor remains to be identified. This work investigates the feasibility of Mo ALD using molybdenum hexacarbonyl $[\text{Mo}(\text{CO})_6]$ as the precursor.

Films of metallic Mo were produced by the atomic hydrogen (at-H) reduction of ALD MoO_3 films obtained from $\text{Mo}(\text{CO})_6$ and ozone (O_3). The reduction of MoO_3 with molecular hydrogen (H_2) at temperatures beyond the BEOL limit is well-known and commercially utilized [6]. This work investigated the feasibility of bringing the temperature well below the BEOL limit by replacing H_2 with at-H.

First, a reliable ALD process for MoO_3 growth was developed by determining an appropriate ALD cycle (Fig. 1) and process temperature (Fig. 2). According to spectroscopic ellipsometry, the resulting films showed a 2-3% film thickness non-uniformity across the 100 mm wafer (Fig. 3). X-ray photoelectron spectroscopy (XPS) confirmed the MoO_3 stoichiometry (Fig. 4a). The as-deposited MoO_3 films were then exposed in situ to a steady supply of (hot wire generated) at-H for 30 min at 150 °C. A shift in the peak position of the $\text{Mo}3d$ doublet from 234/237 eV to 228/231 eV showed a transition from an oxidized to a metallic state of Mo (Fig. 4b). The existence of satellite peaks corresponding to Mo in a non-zero oxidation state indicated the need to increase the reduction temperature. Another sample was reduced for 30 min at 350 °C, significantly lowering the satellite peak intensity (Fig. 4c). Performing angle-resolved XPS measurements on the samples revealed a gradual increase of the metallic Mo phase at the surface compared to that in the bulk (Fig. 5).

Implementing super cycles by introducing an at-H pulse during each ALD cycle resulted in highly oxidized films, indicating the importance of applying a final at-H reduction step to obtain metallic Mo films. Similarly, an ALD cycle that excluded O_3 oxidation but solely included at-H reduction resulted in a non-self-limiting deposition of Mo films with significant shares of carbon (15-25 at%) and oxygen (10-20 at%). Based on these findings, we conclude that the formation of pure Mo from $\text{Mo}(\text{CO})_6$ below the BEOL limit requires an oxidation route to remove carbon efficiently; the intermediately formed MoO_3 can then be reduced in at-H to metallic Mo.

11:15am **AF2-WeM-14 Growth of Metallic Ru Film by Oxidant-Free Atomic Layer Deposition Below 100 °C**, *Kyeongmin Min*, H. *Lee*, Incheon National University, Republic of Korea; C. *Nguyen*, Incheon National University, Viet Nam

Ru is one of the very well-known metals in atomic layer deposition (ALD) researches because of its potential applications in the interconnect technology of Si devices. The main drawback of Ru ALD processes reported so far, however, is the oxidant counter reactants, such as O_2 , O_3 , and H_2O . In ALD, most of the noble metals, including Pt, Ir, and Ru, could be deposited by using oxygen counter reactant through their combustion reactions, so the oxidation of substrate underneath of the noble metal films could not be avoidable. The oxidation of substrate increases contact resistance of Ru, so it is not desirable in the interconnect applications. In this study, we deposited a high purity Ru film through thermal H_2 plasma ALD at low deposition temperature below 100 °C without any oxidant counter reactants. The thermal plasma was generated by exposing the H_2 counter reactant gas to a filament with high temperature over 1600 °C. By the high thermal energy of the filament, the H_2 gas molecules are dissociated into high energy radicals, and the radicals play an important role as a reactant in the thermal plasma ALD process. A high purity and conformal Ru film was obtained, and the resistivity of Ru film was 25 $\mu\Omega\text{cm}$. The metallic Ru films could be formed even at the low temperature, 80 °C. The resistivities of Ru films were X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES) showed very low impurity levels below 5% in carbon and oxygen spectra. From the results of this work, we believe that the thermal plasma ALD could be widely applied to many applications which have critical issues in the oxidation of bottom layer and increase of contact resistance.

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11:30am **AF2-WeM-15 Unveiling the Effect of the Starting Precursor on Ge₂Sb₂Te₅ Atomic Layer Deposition**, *Jyoti Sinha*, KU Leuven, IMEC Belgium; *J. Innocent, A. Illiberi, M. Givens*, ASM, Belgium; *L. Nyns, A. Delabie*, IMEC Belgium

Chalcogenide materials like Ge₂Sb₂Te₅ (GST) are widely studied for application in memory devices [1]. To address the material needs resulting from the architectural device challenges within storage class memory (SCM), atomic layer deposition (ALD) has emerged as a prominent solution. Pore et al. have demonstrated a low temperature ALD process for GST using GeCl₂.C₄H₈O₂, SbCl₃, and Te[(CH₃)₃Si]₂ as precursors [2]. This process comprises the two binary ALD processes of GeTe and Sb₂Te₃ in a specific ratio to target the desired Ge₂Sb₂Te₅ composition, using either GeCl₂.C₄H₈O₂ or SbCl₃ as the first precursor pulse. This first pulse could affect the final film composition, and as such affect device performance.

In this work, we therefore study how the starting precursor influences the GST growth behavior and layer composition when deposited on SiO₂. The deposition on the SiO₂ substrate is initially Ge-rich, irrespective of the starting precursor, and gradually evolves to the desired 2:2:5 Ge:Sb:Te ratio when the thickness increases. The ideal composition is reached after 36 cycles. The interfacial Ge content is slightly higher when the GST ALD process starts with a GeCl₂.C₄H₈O₂ reaction as compared to starting with a SbCl₃ reaction, according to X-ray Fluorescence (XRF).

The chemical reactions at the GST/SiO₂ interface are investigated more thoroughly through chemisorption experiments, where we apply a single precursor reaction and measure the surface concentration of either Ge, Te or Sb ex-situ by means of total reflection XRF (TXRF). The results indicate that GeCl₂.C₄H₈O₂ has a higher reactivity towards SiO₂ than SbCl₃, as the concentration of Ge is ~4 times higher than the concentration of Sb. Almost no Te was observed after a single Te[(CH₃)₃Si]₂ reaction, indicating very low reactivity. We also investigate the subsequent Ge, Te, and Sb precursor reactions after a first Sb, Te, or Ge precursor reaction on SiO₂ and analyze the results assuming that only ligand exchange reactions take place, according to the model in [3]. Based on the concentration of Ge, Te, and Sb, we propose that Ge could react with two surface hydroxyl groups on the SiO₂ surface. On the other hand, due to the lower reactivity of SbCl₃, we propose that there are still unreacted surface hydroxyl groups after the SbCl₃ reaction that can react with GeCl₂.C₄H₈O₂ during the next pulse. This model leads to an overall Ge-rich GST at the interface, irrespective of the starting precursor.

References:

1. T. Kim et al., IEEE Trans Electron Devices 67, 1394 (2020).
2. V. Pore et al., J Am Chem Soc 131, 3478 (2009).
3. R. L. Puurunen, Chemical Vapor Deposition 11, 79 (2005).

11:45am **AF2-WeM-16 Atomic Layer Deposition Equipment Vendors Market and Technology**, *Taguhi Yeghoyan*, Yole Group, France

From many years, Atomic Layer Deposition (ALD) and Atomic Layer Etch (ALE) have enabled subsequent generations of logic and memory. In 2024, ALD and ALE is again indispensable to drive innovation across patterning approaches, architecture change for transistor (FinFET to Gate All Around) and memory (DRAM to 3D DRAM or 3D NAND layer increase) as well as improve the performance of specialty devices (CMOS Image Sensors, BCD Power Si devices, SiC devices, integrated RF devices).

These advancements are enabled by ALD and ALE equipment vendors who provide complete solutions that consider precursors, substrates, and processing problematics. Their efforts generate a collective 2023 market size of 3.3USDB for thermal and plasma equipment, representing 13% of the total deposition Wafer Fab Equipment (WFE) market. With further ALD and ALE needs, we expect this number to grow to 4.9USDB in 2029 with a 4.9% CAGR23-29, outperforming the overall WFE.

Via the market research, we aim to lay out the landscape of the industrial ALD and ALE equipment providers worldwide and highlight their innovative solutions proposed, which lead to specific market shares. Moreover, we draw a market forecast driven by mentioned CapEx hungry devices. Finally, we breakdown the market size to different device applications, wafer size, thermal and plasma ALD technologies.

ALD Fundamentals

Room Hall 3A - Session AF1-WeA

Growth and Characterization: *In-situ* and *in-vacuo* Analysis, Surface Science of ALD I

Moderators: Prof. Seán Barry, Carleton University, Canada, Dr. Simon D. Elliott, Schrödinger

1:30pm **AF1-WeA-1 Triggering Nucleation of Pt ALD through UV-illumination**, *J. Santo Domingo Peñaranda, Jolien Dendooven*, Ghent University, Belgium; *V. Miikkulainen*, Aalto University, Finland; *S. Klejna*, AGH University of Science and Technology, Poland; *E. Solano*, ALBA synchrotron, Spain; *M. Rosenthal*, ESRF, Grenoble, France; *Z. Hens*, C. Detavernier, Ghent University, Belgium

ALD of noble metals on oxides is marked by the growth of 3D islands rather than a uniform 2D layer in the initial growth stages. A relatively large number of ALD cycles is often required to achieve coalescence of the growing islands into a continuous layer, posing limits to the deposition of thin metal films. To obtain layer closure at lower thicknesses, a larger density of nuclei formed on the substrate surface (#nuclei/cm²) is desired.

For MeCpPtMe₃-based Pt ALD, strategies to enhance the nucleation include using N₂-plasma as reactant instead of O₂ [1], exposing the substrate to alkylated precursors prior to Pt deposition [2], and using electron excitation of the Pt precursor [3]. Here, we implement UV-illumination as an external trigger during MeCpPtMe₃-O₂ ALD and study the Pt uptake and nucleation process *in situ* via X-ray fluorescence (XRF) and grazing incidence small angle X-ray scattering (GISAXS) at the ESRF synchrotron.

With 365 nm illumination turned on continuously during the ALD process, *in situ* growth curves (Fig. 1) reveal a significant increase in Pt deposition during the incubation period at all temperatures tested. Depositions in which a number of Photo-ALD cycles is followed by thermal ALD (Fig. 2) also show a drastic increase in Pt uptake, even if only few Photo-ALD cycles are carried out, confirming a crucial role for the UV-light in the nucleation. The size and areal density of the nuclei is extracted for samples with the same Pt loading (#Pt atoms/cm²) (Fig. 3). Remarkably, a larger amount of smaller islands is formed with Photo-ALD, indicative of an increased nucleation density.

Next, the timing of the UV-illumination in the ALD cycle is varied to understand the effect of light-assistance during each ALD step. UV-illumination during the MeCpPtMe₃ exposure is required to achieve growth enhancement, suggesting that the precursor is activated in the gas phase prior to adsorption. We hypothesize that the UV-light assists in the dissociation of the Pt-Me bonds [5], enabling a larger Pt uptake on the surface.

In summary, UV-light can trigger the nucleation of Pt ALD, leading to a larger nucleation density and faster layer closure compared to conventional thermal ALD. While this in itself offers great opportunities for ALD of thin metal films, the Photo-ALD approach also holds promises towards selective deposition for micropatterning.

- [1] Dendooven et al. Nat. Commun. 2017, 8, 1074.
- [2] de Paula et al. Chem. Mater. 2020, 32, 315.
- [3] Lien et al. J. Phys. Chem. Letters 2018, 9, 4602.
- [4] Engmann et al. PCCP 2012, 14, 14611. Egger et al. J. Organomet. Chem. 1970, 24, 501.

1:45pm **AF1-WeA-2 Reaction Pathway of Copper Atomic Layer Deposition via Time-of-Flight Mass Spectrometry**, *Camilla Minzoni, K. Mackosz, C. Hain*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *C. Frege*, TOFWERK AG, Switzerland; *I. Utke, P. Hoffmann*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Atomic Layer Deposition (ALD) has emerged as one of the most promising technique for depositing conformal and uniform copper thin film, especially for application in electronic devices [1].

Despite a comprehensive understanding of ALD mechanisms in metal oxides, limited theoretical and *in situ* experimental work has been dedicated to unraveling the reaction mechanisms of copper and related metals. The extension of ALD to elemental metals presents distinctive challenges, primarily attributed to the lack of the mechanistic understanding of the ongoing surface reactions [2].

Time-of-Flight Mass Spectrometry (ToFMS) has become a powerful tool for addressing these issues, providing unique advantages in terms of high

sensitivity and resolving power, rapid data acquisition, ability to detect species over a wide mass range and real-time tracking of surface reactions and volatile byproducts.

This study presents *in situ* ToFMS monitoring to investigate the gas-phase mechanism involved in the ALD process of copper through transmetalation, using dehydrated Cu(hfac)₂ (CuC10H2F12O4) with diethylzinc DEZ (Et₂Zn) being the reducing agent.

Lee et al. [3] previously proposed a transmetalation reaction mechanism using an analogous copper complex and DEZ. The mechanism involves a ligand exchange step between the copper complex and DEZ, leading to the formation of the volatile byproduct Zn(hfac)₂ (ZnC10H2F12O4), along with the generation of copper alkyl surface species. These copper alkyl species rapidly undergo reductive elimination, producing copper metal and butane (C₄H₁₀) [4] (Fig. 1).

During the monitoring of the ALD cycles with ToFMS, the theoretically anticipated byproducts from the transmetalation reaction were detected (Fig. 2). The results identifying these byproducts are the first of their kind under vacuum ALD conditions, supporting also the theoretical calculations and solution-based of analogous reactions [5-6].

The combination of ALD and ToFMS is therefore proving to be a powerful method for a depth understanding of complex ALD reaction mechanisms at molecular level that would be challenging by other means.

References

1. K. Venkatraman, A. Joi, Y. Dordi, R. Akolkar, Electrochemistry Communications 91, 2018
2. D. Hagen, M. Pemble, M. Karppinen, Appl. Phys. Rev. 6,041309, 2019
3. B. Lee, J. Hwang, J. Nam, S. Lee, J. Kim, S. Koo, A. Baunemann, R. Fischer, M. Sung, Angew. Chem. Int. Ed., 48, 2009
4. P. Gordon, A. Kurek and S. Barry, ECS Journ. of Solid State Science and Technology 4, 2015
5. Y. Maimaiti, S. Elliott, Chem. Mater. 28, 17, 2016
6. B. Vidjayacoumar, D. Emslie, S. Clendenning, J. Blackwell, J. Britten, A. Rheingold, Chem. Mater. 22, 17, 2010

2:00pm **AF1-WeA-3 *in vacuo* Cluster Tool for Studying Reaction Mechanisms in ALD and ALE Processes**, *Marko Vehkamäki, M. Chundak, H. Nieminen, M. Putkonen, M. Ritala*, University of Helsinki, Finland

ALD and ALE processes are solely dependent on the chemical reactions occurring on the substrate surface. These surface reactions define the outcome of each process and can set critical challenges on the process development and integration. Studying the chemical reactions is hence of utmost importance to fully understand the growth and etch processes and exploit the advantages ALD and ALE have to offer.

The best ways to study reaction mechanisms in ALD and ALE processes is to do the measurements without exposing the film to air, that is, either *in situ* or *in vacuo*. A cluster tool which allows a variety of ways to study reaction mechanisms in nearly all kinds of process chemistries has been set up in HelsinkiALD laboratory. In this tool, a commercial flow-type ALD reactor is connected directly to a set of ultra-high vacuum analysis chambers. After interrupting the process at selected point the substrate can be transferred *in vacuo* straight from the ALD reactor to surface analysis. The chemical composition of the surface, including also reaction intermediates on the film, can be investigated after each precursor pulse individually. With this information, the overall film growth mechanism can be resolved.

The newest addition to the cluster tool is a low-energy ion scattering (LEIS) instrument. LEIS has the ultimate surface sensitivity as it distinguishes the outermost atom layer from the others. This resolution is important in distinguishing reaction intermediates from the rest of the surface and in analyzing the closure of the thinnest films. X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD) and *in situ* quartz crystal microbalance (QCM) have already been utilized effectively in reaction mechanism studies on ALD of Al₂O₃, noble metals Pt and Ru, and ALE of Ta and Mo. Additionally, the cluster tool contains *in vacuo* ion scattering spectroscopy (ISS), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), low-energy electron diffraction (LEED), and ultraviolet photoelectron spectroscopy (UPS). There is also an ellipsometer for *quasi in situ* measurements in the ALD chamber. As the system contains genuine flow-type ALD reactor, reaction mechanisms can be solved without compromising true ALD conditions.

Wednesday Afternoon, August 7, 2024

2:15pm **AF1-WeA-4 Understanding the Dual-Source Behavior of LiHMDS for Si-Free Li-Containing Films**, *Meike Pieters, L. Bartel, C. van Helvoirt, M. Creator*, Eindhoven University of Technology, The Netherlands

The electrochemical stability of interfaces is key to long-lasting and safe Li-ion batteries. To study these interface processes, ALD can deliver thin film model systems of electrodes. For example, the behavior of Ni-rich $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ cathodes can be understood by investigating LiNiO_2 thin films due to the similar electrochemical properties. Moreover, the control that ALD provides over film composition and crystal orientation allows to study how those material properties influence the interface stability. To grow LiNiO_2 by ALD, lithium hexamethyldisilazide (LiHMDS) is preferred over the widely-used LiO^tBu because of its lower melting point of 70°C, but the presence of silyl groups can result in the undesired incorporation of Si. Previous work proposes that Si is incorporated during both precursor and O_2 plasma steps in the ALD cycle [1]. However, processes in which the LiHMDS dose is followed by a H_2O pulse can yield Si-free films [2,3], indicating that the co-reactant plays a major role in the Si incorporation.

To shed light on the reaction mechanisms of LiHMDS and the two co-reactants, we carry out in-situ growth studies by spectroscopic ellipsometry and mass spectrometry (QMS) [4]. The O_2 plasma process shows linear growth and the film contains 16 at.% Si according to XPS, but the H_2O process results in bulk-driven growth and Si-free films. QMS shows that the difference between the processes lies in the reaction products during the co-reactant step: H_2O removes the HMDS ligands of physisorbed LiHMDS via a proton exchange reaction, whereas the O_2 plasma combusts HMDS. The redeposition of Si-containing combustion products during the plasma step is presumably the origin of the dual-source behavior of LiHMDS.

We also include a H_2 plasma step following the O_2 plasma step, with the hypothesis that H radicals can etch the incorporated Si. This process exhibits bulk-driven growth and the grown films are, as expected, Si-free and have a Li_2O composition. QMS confirms the release of SiH_x -species during the H_2 plasma step. Interestingly, the growth behavior and film composition remain the same when the order of the O_2 and H_2 plasmas is reversed. The QMS results in this case indicate that H_2 plasma removes the HMDS ligands and thereby prevents Si incorporation in the subsequent O_2 plasma step.

Overall, this work shows that the co-reactant controls the reaction mechanism, and therefore the dual-source behavior, of LiHMDS. These insights can aid the fabrication of Si-free LiNiO_2 films.

- [1] Werbrouck et al., J. Phys. Chem. C, 2020, 124
- [2] Østreng et al., RSC Adv., 2012, 2
- [3] Østreng et al., J. Mater. Chem. C, 2013, 1
- [4] Pieters et al., to be submitted

2:30pm **AF1-WeA-5 ALD of Two-Dimensional Gallium Sulfide: Understanding the Nucleation and Strain Evolution During Growth**, *O. Massmeyer, R. Günkel, S. Kachel*, Philipps Universität, Germany; *P. Klement*, Justus Liebig University Giessen, Germany; *J. Belz*, Philipps Universität, Germany; *S. Chatterjee*, Justus Liebig University Giessen, Germany; *M. Gottfried, Kerstin Volz*, Philipps Universität, Germany

Two-dimensional (2D) materials are gaining great attention due to their extraordinary thickness-dependent properties. The layered III-VI semiconductors such as GaS and GaSe show a unique band structure. Furthermore, 2D GaS and GaSe have a bandgap in the UV region, which makes them candidates for several LED and detector concepts. Moreover, the composition tuning of multilayer $\text{GaS}_x\text{Se}_{1-x}$ alloys allows for establishing bandgaps between 2.0 and 2.5 eV.

Hence, group III-chalcogenides are promising materials for next-generation optoelectronic applications, as they even reach these properties with comparably little use of material. Typical preparation routine for 2D materials, however, is the mechanical exfoliation, which is no suitable technique when applications are aimed for. Hence, we establish a pulsed growth regime using metal organic precursors to find suitable growth routines for 2D materials using a well-accepted growth technique. The samples are characterized by means of Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), Raman spectroscopy, X-ray reflectometry (XRR), X-ray photoelectron spectroscopy (XPS) and

Transmission Electron Microscopy (TEM) as well as several optical spectroscopy techniques.

The ALD (Atomic Layer Deposition) scheme is needed due to prereactions of the di-*tert*-butyl-sulphide (DTBS) and tri-*tert*-butyl-gallium (TTBGa) precursors on the surface. This results in the formation of 2D, closed films instead of 3D structures containing liquid Ga on the surface. The growth of a 2D film is enabled by a specific interface reconstruction between the sapphire and the GaS.

The presentation will summarize our current understanding of the nucleation and ALD growth of group III-chalcogenides by systematic variation of different growth parameters such as temperature, chalcogen/group III gas phase ratio and deposition sequences and correlate the findings to optoelectronic properties of the layers.

2:45pm **AF1-WeA-6 Self-Limiting Deposition of Copper from Copper Beta-Diketonates and Plasma Electrons**, *Premrudee Promdet, P. Niiranen, A. Haridas Choolakkal, D. Lundin, H. Pedersen*, Linköping University, IFM, Sweden

We have recently demonstrated how films of elemental metals can be deposited using free electrons from a plasma discharge as reducing agents.¹ We refer to this process as electron CVD (e-CVD). We will here demonstrate e-CVD of Cu using plasma electrons and copper beta-diketonates precursor; we will also show that the deposition chemistry appears to be self-limiting. Hence, we suggest that this might be an e-ALD process.

In this study, a positive bias is applied to the substrates to attract plasma electrons to the surface. The copper precursors and the plasma electrons were supplied in pulses separated by argon purge steps. The deposition was monitored *in situ* by a QCM sensor specially developed for e-CVD². Self-limiting deposition was found from the mass gain per deposition cycle for the time of precursor pulse, plasma exposure and purge. X-ray photoelectron spectroscopy show the formation of fluorinated copper species, suggesting some level of redeposition of ligand fluorine to the copper surface. We found that the residual fluorine could be removed by further plasma exposure. A plausible explanation supported by optical emission spectroscopy and mass spectroscopy is offered on the formation of volatile compounds as byproducts from the longer plasma exposure. Based on these results, a possible surface chemical mechanism will be discussed.

References:

1. H. Nadhom et al. J. Vac. Sci. Technol. A 2020, 38, 033402.
2. P. Niiranen et al. Rev. Sci. Instrum. 2023, 94 023902.

3:00pm **AF1-WeA-7 Exploration of Nucleation Phenomena in Ultra-Thin ALD Films on NMC 811 Substrates: An in Situ Quartz Crystal Microbalance Study**, *Léo Lapeyre, L. Pethö, J. Michler*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *P. Raynaud*, LAPLACE, France; *I. Utke*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Ultra-thin films deposited by ALD have emerged as essential components in improving the performance and stability of Li-ion battery systems. Particularly, the utilisation of ultra-thin films as artificial solid electrolyte interfaces (SEIs) holds significant promise for enhancing battery efficiency and lifespan. However, the accurate characterisation of these films by ex situ methods presents significant challenges, primarily due to their low thicknesses which provides low signal-to-noise ratios and potential contamination from air exposure. Additionally, the substrate's influence on film properties remains a critical but often overlooked factor. Many studies rely on silicon substrates for process development and film characterization, yet the disparities between silicon and actual battery substrates, such as NMC 811, can significantly impact film growth and characteristics. Among others aspects, unsaturated surface coverage, non-linear growth per cycle (GPC), or compositional variations during early stage growth may result from an ALD process not specifically optimized for the particular substrate in use. Consequently, these variations can adversely affect battery performances.

To address these challenges, we use in situ Quartz Crystal Microbalance (QCM) techniques with NMC 811-coated QCM crystals to achieve closer-to-application conditions and overcome limitations associated with ex situ methods. This approach enables us to investigate nucleation phenomena and growth kinetics of ultra-thin films with fine precision [2], providing a better understanding of the substrate's influence on film properties and facilitating the development of tailored deposition strategies for enhanced battery performance.

Our study encompasses the deposition of various materials, including SnO₂ and LiNbO₃, using both ALD and PE-ALD techniques. We aim to compare the influence of deposition methods (thermal and plasma ALD) on the early-stage growth dynamics of films and explore the effects of deposition parameters (such as temperature, precursor's exposure time and number of cycles) on growth behaviours. Ultimately, we seek to optimize the deposition process to minimize non-linear growth and enhance film quality.

Finally, we will assess the electrochemical performance of NMC 811 electrodes coated with SnO₂ and LiNbO₃ films, investigating their capacity retention, cycling stability, and rate capability. Through this comprehensive analysis, we strive to advance our understanding of ultra-thin film deposition processes and their impact on battery performance, ultimately contributing to the development of high-performance energy storage solutions.

3:15pm AF1-WeA-8 The Role of the Oxidizing Co-Reactant in Pt Growth by Atomic Layer Deposition Using MeCpPtMe₃ and O₂/O₃/O₂-Plasma, Jin Li, Ghent University, Belgium, China; S. Klejna, AGH University of Krakow, Poland; M. Minjauw, J. Dendooven, C. Detavernier, Ghent University, Belgium

Atomic layer deposition (ALD) of Pt using MeCpPtMe₃ and O₂/O₃/O₂-plasma (O₂*) at 300°C is investigated with *in vacuo* X-ray photoelectron spectroscopy (XPS) and density functional theory (DFT) to gain a better understanding of the Pt growth mechanism.¹ Most notably, the chemical state of the surface Pt atoms and the role of surface O species in Pt growth are revealed. In the MeCpPtMe₃/O₂ process, the surface Pt atoms remain in a metallic Pt⁰ state throughout the ALD cycle, and the surface O species generated by the O₂ exposure only exist as unstable adatoms, desorbing in vacuum. As for the O₃/O₂* processes, the surface Pt layer is oxidized to a mixture of Pt⁰, Pt²⁺O and Pt⁴⁺O upon O₃/O₂* exposure and then fully reduced to Pt⁰ during the precursor exposure. Surface Pt oxides are stable in vacuum but can be reduced by hydrocarbon vapors. DFT reveals differences in the combustion mechanism for Me vs. Cp species, during the metal precursor and co-reactant pulses. Quantification analysis shows that the O₃/O₂* processes have a much higher surface O species content than the O₂ process after the co-reactant exposure, favoring precursor ligand combustion over dehydrogenation in the next precursor exposure and leading to lower surface C density after the precursor pulse. Regarding the surface C species, apart from common -C_xH_y/-Cp groups, -C_x is recorded as a highly dehydrogenated product only in the MeCpPtMe₃/O₂ process. For all processes, no C-O/C=O or -OH group is identified by *in vacuo* XPS, in line with DFT energetics. Importantly, the differences in the surface O content do not significantly affect the growth per cycle. Moreover, the MeCpPtMe₃/O₂ process with surface O species and a tailored MeCpPtMe₃/O₂ process without surface O species, both at 300°C, yield nearly identical growth rates and as-deposited Pt with the same chemical state. This indicates that surface O species present before the precursor exposure have limited impact on the overall Pt growth, in contrast to previous assumption.

KEYWORDS: *In vacuo* XPS; DFT; ab initio thermodynamics; surface reaction mechanism; Atomic layer deposition; Pt; growth mechanism; combustion of hydrocarbons mechanism

J. Li, S. Klejna, M. M. Minjauw, J. Dendooven and C. Detavernier, *J. Phys. Chem. C*, DOI:10.1021/acs.jpcc.3c07568.

ALD Fundamentals

Room Hall 3A - Session AF2-WeA

Growth and Characterization: *In-situ* and *in-vacuo* Analysis, Surface Science of ALD II

Moderators: Prof. Markku Leskelä, University of Helsinki, Finland, Prof. Mikko Ritala, University of Helsinki

4:00pm AF2-WeA-11 In vacuo XPS Growth Studies During ALD of ErNiO₃, Matthias Minjauw, Ghent University, Belgium; A. Illiberi, M. Givens, ASM, Belgium; A. Leonhardt, I. Issah, L. Bottiglieri, ASM, Finland; J. Dendooven, C. Detavernier, Ghent University, Belgium

Rare-earth nickelates (RNiO₃, with R = rare earth element) have a broad range of unique and tunable physical properties, making them relevant for future applications in electronics, electrocatalysis, solid oxide fuel cells, electrochromic windows and microelectromechanical systems. As a result, several RNiO₃ ALD processes (R = La, Nd) have been reported, and the general approach is to combine two binary ALD processes for R_xO_y and NiO

in supercycles.¹⁻³ As two distinct ALD processes are combined into one ALD process, several non-idealities may occur, such as a larger impurity content than for the binary processes, nucleation effects leading to irreproducibility issues, and unexpected high/low growth leading to deviating compositions.⁴

In this work, we combined the ALD NiCp₂/O₃ and Er(MeCp)₃/O₃ processes at 300°C using the supercycle approach, leading to Er_xNi_yO_z films with low impurity content. Figure 1a shows the growth per cycle (GPC) of the ALD process as a function of the NiO cycle ratio. Ideally, a linear curve should be obtained between the GPC values for the binary processes, but this is clearly not the case. In Figure 1b, it is seen that the Ni atomic concentration as found by *in vacuo* XPS is also much lower than expected based on the rule of mixtures.⁴

To investigate the origin of these non-idealities, *in vacuo* ALD-XPS nucleation studies were conducted, and a selection of XPS data is shown in Figure 2. Although an Er signal is visible from the first Er(MeCp)₃ pulse on an ALD NiO substrate, it takes ~ 4 cycles of the NiO process to get a clear Ni signal on an ALD Er₂O₃ surface. In Figure 3, a plot is shown of the Ni and Er atomic percentage as a function of ALD cycles, obtained by quantifying the XPS data. The fact that there is a nucleation delay for NiO growth on Er₂O₃, but not for Er₂O₃ on NiO, explains the non-idealities described above. The present XPS data hint that incomplete surface reactions of the NiCp₂/O₃ process on the carbon-rich ALD Er₂O₃-surface are at the basis of this nucleation delay, with more research currently ongoing to elucidate this.

References:

- [1] H. Seim et al. *J. Mater. Chem.* **7**, 449–454 (1997).
- [2] H. H. Sønsteby et al. *Nat. Commun.* **11**, 2872 (2020).
- [3] Y. Sun et al. *ACS Appl. Electron. Mater.* **3**, 1719–1731 (2021).
- [4] A. J. M. Mackus et al. *Chem. Mater.* **31**, 1142–1183 (2019).

4:15pm AF2-WeA-12 Surface Chemistry of Aluminum Nitride ALD, Pamburayi Mpofo, H. Hafdi, H. Pedersen, Linköping University, Sweden

The properties of aluminum nitride (AlN), including a wide bandgap (6.2 eV), high dielectric constant ($k \sim 9$), high electrical resistivity ($\rho \sim 10^{11}$ – 10^{13} Ω cm), and high thermal conductivity (2.85 W/K cm)¹ make it one of the commonly used materials in microelectronics and optoelectronics. AlN is also used in microelectromechanical systems (MEMS devices) due to its piezoelectric properties. It also presents good miscibility with other nitrides and can be used in ternary materials when combined with Ga, In, Ti and Hf, which increases the range of its potential applications.

Although ALD of AlN from AlMe₃ (TMA) has been widely reported to date, the surface chemistry of AlN ALD from other precursors, particularly Al(NMe₂)₃ (TDMAA) have not yet been reported. We compared AlN ALD with TMA and TDMAA as Al precursors and NH₃ with and without plasma activation as the N precursor in the temperature range from 100 to 400 °C. Using mass spectrometry, we find that the surface chemistry of the TMA-process involves reductive elimination and ligand exchange from the gaseous CH₄ detected both during the TMA- and NH₃ pulses. The TDMAA-process also involves transamination mechanisms from the N(Me)₂ and HN(Me)₂, and CH₄ detected during the NH₃ pulses.

By comparing our experimental results to modeling results² drawn from density functional theory methods, we can deduce a detailed, atomistic surface chemical mechanism of TMA on an NH₂-terminated AlN surface. No literature is available for theoretical studies of AlN ALD from TDMAA, making our surface chemical mechanism for the TDMAA-process less detailed.

Refs.:

1. Kot, M. et al. Comparison of plasma-enhanced atomic layer deposition AlN films prepared with different plasma sources. *J. Vac. Sci. Technol.* **A37**, 020913 (2019).
2. Rönnyby, K. et al. Surface chemical mechanisms of trimethyl aluminum in atomic layer deposition of AlN. *J. Mater. Chem. C*, **11**, 13935–13945 (2023).

4:30pm AF2-WeA-13 Investigating Hf Oxide Growth with Ambient Pressure XPS and Ozone as Co-Reactant, Esko Kokkonen, Max IV Laboratory, Sweden; R. Jones, Lund University, Sweden; V. Miikkulainen, Aalto University, Finland; C. Eads, A. Klyushin, Max IV Laboratory, Sweden; J. Schnadt, Lund University, Sweden

Hafnium oxide is a promising material to be used in many applications such as high-k dielectrics or in advanced metal-oxide-semiconductor devices. The accurate knowledge of the deposition is crucial for creating pure,

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defect free, interfaces as well as optimising the reaction process timing and decreasing material consumption. In the past few years, ambient pressure X-ray photoelectron spectroscopy (APXPS) [1] has been used to study the ALD of HfO_x on various surfaces [2,3]. These studies have focused on revealing intricate details within the first few half-cycles and have discovered new surface species, inter- and intramolecular reactions, and bimolecular reaction pathways.

The previous APXPS studies have used water as the co-reactant, but in this work, we turn our focus to ozone. We show how the experimental APXPS setup was modified to incorporate an ozone generator, and the results from the XPS analysis. The measurements were conducted in such a way that we were able to separate the contributions from oxygen and ozone to the growth in the co-reactant half-cycle.

The data indicates that oxygen alone creates very strong changes on the surface and contributes to the growth of the layers removing some ligands from the Hf precursor. Each co-reactant pulse was initiated in pure oxygen and the ozone was only started after a short delay. Deposition temperature was varied in a large range which shows strong effects on the reaction mechanism of the first few half-cycles. The study shows the importance of in situ experiments and separating the process into its constituent components in order to understand them better.

[1.] E. Kokkonen, M. Kaipio, H.-E. Nieminen, F. Rehman, V. Miiikulainen, M. Putkonen, M. Ritala, S. Huotari, J. Schnadt, and S. Urpelainen, *Ambient Pressure X-Ray Photoelectron Spectroscopy Setup for Synchrotron-Based in Situ and Operando Atomic Layer Deposition Research*, Review of Scientific Instruments **93**, 013905 (2022).

[2.] G. D'Acunto et al., *Bimolecular Reaction Mechanism in the Amido Complex-Based Atomic Layer Deposition of HfO₂*, Chem. Mater. **35**, 529 (2023).

[3.] R. Timm et al., *Self-Cleaning and Surface Chemical Reactions during Hafnium Dioxide Atomic Layer Deposition on Indium Arsenide*, Nat Commun **9**, 1412 (2018).

4:45pm **AF2-WeA-14 ALD/ALE 2024 Closing Remarks**, *Mikko Ritala, M. Leskelä*, University of Helsinki, Finland; *F. Roozeboom*, University of Twente and Carbyon B.V., The Netherlands; *D. Suyatin*, AlixLabs A.B., Sweden

ALD Fundamentals

Room Hall 3F - Session AF3-WeA

Growth and Characterization: Plasma Enhanced ALD II

Moderators: Prof. Matti Putkonen, University of Helsinki, Dr. Mikko Söderlund,, Beneq Oy

4:00pm **AF3-WeA-11 UHP PEALD Growth and High Field Dielectric Testing of κ -Ga₂O₃ Films**, *Bangzhi Liu*, The Pennsylvania State University

¹Bangzhi Liu, ¹Yeseul Choi, ¹Smitha Shetty, ²Gilbert B. Rayner, ¹Fan He, ³Kunyao Jiang, ¹Benjamin L. Aronson, ³Jingyu Tang, ⁴Yongtao Liu, ⁴Kyle P. Kelley, ^{3,5}Jr.; Robert F. Davis, ³Lisa M. Porter, ^{1,6}Susan Trolier-McKinstry

1. Materials Research Institute, Penn State University; 2. The Kurt J. Lesker Company; 3. Materials Science and Engineering, Carnegie Mellon University; 4. Oak Ridge National Laboratory; 5. Electrical and Computer Engineering, Carnegie Mellon University; 6. Materials Science and Engineering, Penn State University

Ga₂O₃ has multiple different polymorphs: α -, β -, γ -, and $\epsilon(\kappa)$ -phases. β -Ga₂O₃ has drawn significant attention in the power electronics community since it is an ultra-wide bandgap semiconductor and, fortunately, the only thermodynamically stable phase. The ϵ (also called κ)-phase is the next most stable polymorph. This metastable phase has been predicted to be ferroelectric^{1,2} and can be a suitable candidate for non-volatile memory applications if its ferroelectricity is confirmed. Technically, using ALD to grow this film is ideal for memory device fabrication, given its precise thickness control and excellent conformality.

To this end, we invested significant effort in developing a Plasma-Enhanced ALD (PEALD) process to grow κ -phase with c -orientation on a conductive substrate for electrical testing. The deposition system used was a KJ Lesker ALD150LX operating under ultrahigh purity (UHP) conditions. A major challenge was to find conditions that favor the formation of metastable κ -phase while suppressing the growth of stable β -phase. By controlling O₂ flow, vacuum level, plasma power, growth temperature and substrate type, we successfully grew c -oriented κ -phase (50 nm thick) on platinumized

sapphire substrates. The films were characterized by ellipsometry, FESEM, XRD, and ToF SIMS for material properties and by high field dielectric testing and Piezoresponse force microscopy for the possible ferroelectric properties. A comparison was made to Metal-Organic Chemical Vapor Deposition (MOCVD) grown thick films (700 nm) with predominantly the κ -phase prepared by our collaborators in parallel to better evaluate the ferroelectricity of κ -Ga₂O₃³.

4:15pm **AF3-WeA-12 Crystalline Phase Control of Manganese Oxide Films by Plasma Enhanced Atomic Layer Deposition**, *Zhongwei Liu, J. Ren, H. Fang, L. Sang*, Beijing Institute of Graphic Communication, China

Over the past decades, manganese oxides have attracted increasing interests due to their various compositions, such as MnO, Mn₂O₃, MnO₂, Mn₃O₄, and Mn₅O₈, in which several oxidation states, +2, +3, and +4 exist. The multitude of structures and valence state offer a number of applications for manganese oxides in catalysis, microelectronic, biosensors, and Li ion battery. In this work, we developed a plasma enhanced pulsed chemical vapor deposition process for manganese oxide (MnOx) thin films using bis(1,4-di-tert-butyl-1,3-diazabutadienyl)manganese(II) (Mn(dad)₂) as the Mn precursor. Mn(dad)₂ is an active compound with high volatility, and suitable for CVD or ALD process. MnOx film was characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM) (FEI Talos F200S). The effects of the deposition temperature and the types gases, such as H₂, Ar, H₂ plasma and Ar plasma, on phase composition of manganese oxides were carefully investigated. When Ar or H₂ gas was employed as the discharge gas and the deposition temperature was 120 °C, amorphous or nanocrystalline MnOx was obtained. In contrast, the film grown in Ar plasma was a face-centered cubic (fcc) MnO structure. In the case of H₂ plasma, the diffraction peaks can also be indexed to fcc MnO, except that the preferred orientation of the film was different. As the deposition temperature was increased to 180 °C, the film deposited in Ar or H₂ gas showed Mn₃O₄ structure. Similar to that grown at 120 °C, the film deposited at 180 °C in Ar or H₂ plasma was identified to be MnO, indicating that the deposition temperature has negligible effect on the film crystallinity under plasma condition. If the deposition temperature was further raised to 240 °C, a mixture MnO and Mn₃O₄ was obtained for the films grown in Ar or H₂ gas, while in the case of Ar or H₂ plasma, the afforded film is still MnO. These results indicated that the plasma had a significant effect on MOx crystalline phase.

4:30pm **AF3-WeA-13 Superconducting Ultrathin Niobium Nitride Films for Quantum Application**, *Mario Ziegler, E. Knehr, E. Mutsenik, S. Linzen, G. Qeslner, E. Il'ichev, R. Stolz*, Leibniz Inst. of Photonic Technology, Germany

Superconducting thin films are the basis for a wide range of applications such as quantum cryptography, sensing, quantum metrology or quantum computing. On one hand, devices such as superconducting nanowire single photon detectors (SNSPDs) are in need for high-quality films with high critical temperatures (T_c) [1]. Especially in transition from single- to multi-pixel devices, the properties have to be uniform over a large surface area. On the other hand, novel concepts of second generation quantum devices such as charge quantum interference devices based on coherent quantum phase slip require disordered superconductors with high kinetic inductance [2,3]. NbN is a promising candidate as the T_c (bulk T_c = 16 K) in comparison to TiN, TaN, MoSi or WSi allows for higher operating temperatures, higher switching currents, and thus a better signal-to-noise ratio. Nevertheless, the variety of applications demands for a flexible and adaptable manufacturing process with very good control of the thin-film properties, ideally over a larger surface area.

In this context, plasma-enhanced atomic layer deposition (PE-ALD) exhibits very good thickness homogeneity over a broad surface area as well as a nearly perfect thickness control. But when it comes to quantum applications, homogeneity is not only determined by roughness and layer thickness. Also, electrical properties such as normal sheet resistance, critical temperature, or critical current density must be considered. Up to now, PE-ALD processed NbN achieved T_c of 14 K for a 21 nm thick film [4] and even films with 2.7 nm thickness are still superconductive [2]. NbN films made by PE-ALD revealed a complex chemical composition not only consisting of stoichiometric NbN but also of niobium carbide, niobium oxide, and niobium-oxynitride. We observed that the electrical properties changed drastically, whereas film thickness and roughness remained almost constant. The deviations might originate from the reactor geometry or fluctuations of precursor supply during the deposition process. We will

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present optimized fabrication recipes for SNSPDs with high T_c as well as for circuits of highly disordered superconducting materials [2,3,5].

References

1. Knehr et al., *JVST A: Vacuum, Surfaces, and Films* 39 (2021).
2. Shaikhaidarov et al., *Nature* 608, 45 (2022).
3. De Graaf et al., *Nature Phys* 14, 590 (2018).
4. Ziegler et al., *IEEE Trans. Appl. Supercond.* 27, 1 (2017).
5. Mutsenik et al., *Low Temperature Physics* 49, 92 (2023).

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