Sunday Afternoon, June 22, 2025

Tutorial
Room Halla Hall AB - Session TS-SuA

Tutorial Session

Moderators: Heeyeop Chae, Sungkyunkwan University (SKKU), **Han-Bo-Ram Lee**, Incheon National University

1:00pm **TS-SuA-1 ALD for Hydrogen Technology*, Jihwan An,*** POSTECH, Republic of Korea **INVITED**

The production and utilization of hydrogen energy have become essential components in the global energy transition to meet the energy demands of future generations. Fuel cells (FCs), which generate electricity from hydrogen, and electrolysis cells (ECs), which decompose steam into storable hydrogen fuel, offer effective solutions for the conversion and storage of renewable energy, with hydrogen serving as an energy carrier. Consequently, they hold great potential for applications in the future energy sector.

Recently, atomic layer deposition (ALD) has presented exciting research opportunities for FCs and ECs due to its unique features, such as conformality and precise thickness and doping controllability. Individual components of FCs/ECs—the electrolyte, electrolyte–electrode interface, and electrode—can be effectively engineered using ALD nanostructures to address the issues raised during operation.

In this tutorial, we will first provide an overview of the operating principles of FCs and ECs, followed by a discussion of the engineering challenges generally associated with electrochemical performance and stability. Recent examples of the application of ALD-processed nanostructures to FCs and ECs are reviewed, and the quantitative relationship between the ALD process, ALD nanostructures, and the performance and stability of FCs and ECs is elucidated.

1:45pm **TS-SuA-4 ALD Process Optimization Using Machine Learning: A Practical Tutorial for Domain Experts*, Pil Sung Jo,*** Gauss Labs Inc, Republic of Korea **INVITED**

As the demand for precise process control in Atomic Layer Deposition (ALD) continues to grow, machine learning (ML) has emerged as a powerful tool to optimize processes, improve efficiency, and enhance quality. However, for many professionals in the ALD field, the journey to incorporating ML into their workflows can seem daunting. This tutorial aims to bridge that gap by providing a practical and approachable introduction to ML, tailored specifically for domain experts in ALD.

The session starts with a quick introduction about me, sharing my journey from being a materials scientist and engineer with hands-on experience in semiconductor fabrication to leading a team of data scientists. I'll talk about why I made this career change and how it happened, showing how combining deep knowledge of a field with data science can create new opportunities and drive innovation.

Next, the basics of ML and introduce a ML system will be covered. I'll start by explaining key concepts like the difference between data-driven and physics-based models, regression vs. classification, and supervised vs. unsupervised learning. Then, we'll introduce a ML system (end-to-end ML pipeline) to help participants understand how machine learning works in real-world production settings—not just in experimental setups. This will include the entire process, from collecting and preparing data to training the model, deploying it, and monitoring its performance.

The core of the tutorial focuses on how domain experts can actively contribute to and benefit from ML. By leveraging their deep process knowledge, experts can play critical roles in feature engineering, validating explainabilty of models, and refining use cases. Particularly, the explainability of machine learning models is a crucial aspect since understanding how models make predictions not only helps in identifying potential biases but also ensures that the outputs align with established physical principles and process knowledge. Practical examples include virtual metrology (VM), such as VM-assisted APC, TTTM, and outlier detection. These use cases will demonstrate how ML can address real-world challenges.

Finally, I will introduce our company's ML solution, showcasing its capabilities through a live demonstration. This product is designed with domain experts in mind, making ML tools accessible and impactful for their research and development efforts.

Whether you are new to ML or looking to integrate it into your ALD workflows, this session will equip you with the knowledge and confidence to start your journey in combining domain expertise with machine learning.

2:30pm **TS-SuA-7 ALD-Enabled Synthesis of Metal-Organic Framework Thin Films: Fundamentals to Applications*, Junjie Zhao,*** Zhejiang University, China **INVITED**

With flexible reticular chemistry and well-defined pore structures, metal-organic frameworks (MOFs) have been widely explored as potential adsorbents, catalysts, sensors, drug delivery carriers, dielectrics and candidates for many other applications. Shaping MOFs into thin films provides avenues for innovative devices and composite structures. There are three major challenges for synthesizing MOF thin films: (i) common solvothermal conditions are harsh for delicate substrates; (ii) achieving long-range orders and high porosity is challenging for vapor-phase deposition; (iii) these films are brittle and difficult to transfer between substrates for facile integration. This tutorial briefly reviews the recent advances about ALD-enabled synthesis of MOF thin films, including the fundamental interfacial mechanism involved in the nucleation and growth of MOF thin films seeded/tuned by ALD surfaces, conversion routes from ALD oxides to MOFs, and confined reaction-diffusion systems involving a hydrolyzable ALD surface for wrinkled MOF thin films. We will use representative examples to show how MOF thin films are promising for diverse applications. Finally, we will provide an outlook for the remaining challenges in this field.

3:30pm **TS-SuA-11 The Importance of Interconnect Technology of Si Devices and The Extension of ALD Processes*, Hoonjoo Na,*** Samsung Electronics, Republic of Korea **INVITED**

As we scale down, the proportion and importance of interconnect have been increasing for performance improvement, power savings, area scaling, and cost reduction. To meet the demands of the product, an atomic layer deposition (ALD) process has been developed to achieve lower resistance and to fill narrow and deep structures, thanks to the improvement of equipment and materials. Because of the reaction mechanism involving reactants, oxides or nitrides have been widely used for stable ALD processes, but pure metal ALD processes have also begun to be used in products over the past decade by controlling byproducts originating from halides or organic precursors. In the first part of this tutorial, the contributions of ALD processes for advanced interconnects will be covered with several examples from the front-end of line (FEOL), middle of line (MOL), to the back-end of line (BEOL). Resistance alone is not the only consideration for FEOL applications; the effects on transistor performance must also be taken into account. For MOL and BEOL, resistance is the most critical parameter, and there are both common and distinct approaches to achieve breakthroughs. In the second part, the limitations and challenges of ALD processes will be discussed, particularly as we move forward into the era of 3D structures. To overcome future issues and risks, it is essential to understand and adopt a more extensive process concept than what was used for legacy products. To enable further scaling down of devices, interconnect ALD processes must evolve along with advances in processing, equipment, and materials.

4:15pm **TS-SuA-14 Atomic Layer Etching: Basics, Chemistries, and New Developments*, Jane P. Chang,*** UCLA **INVITED**

This tutorial discusses the basics of atomic layer etching, with an emphasis on the surface reaction chemistry, followed by new developments.It presents current advances in atomic layer etching of function accelerated nanomaterials and related challenges and opportunities.Examples in both thermal and plasma assisted processes are included, addressing etching selectivity and specificity that are needed to fully integrate novel materials in complex architectures in integrated circuits for commercial and defense applications.

5:00pm **TS-SuA-17 The Era of Atomic Scale Processing: When Area-Selective Deposition Meets Atomic Layer Etching*, Silvia Armini,*** IMEC, Belgium **INVITED**

For future sub-5 nm technology nodes, as well as for the integration of high aspect ratio 3D structures such as 3D NAND or 3D DRAM memory devices, IC manufacturing will likely involve the use of area-selective atomic layer deposition (AS-ALD), as other conventional approaches, such as deposition and etch back, might not be viable anymore. While AS-ALD processes have been reported for a variety of materials and processes, which will be summarized in this tutorial, most approaches yield a limited selectivity, for example, due to growth initiation at defects or impurities on the non-growth area. Atomic layer etching (ALE) can be combined with AS-ALD as one step or in supercycles of alternate deposition and etching steps, to remove these defects, extending the process selectivity window.

Thermal atomic layer etching (t-ALE) is based on sequential, self-limiting reactions that yield controlled etching at the atomic level. Thermal ALE utilizes gas phase precursors and accomplishes etching without the ion bombardment employed in plasma ALE. Plasma ALE (p-ALE) is an anisotropic etching process because it uses ion bombardment to form and remove the modified layer. Because there are no line-of-sight restrictions, t-ALE yields isotropic etching and it has many applications in atomic scale processing, such as etching three-dimensional structures, surface smoothing or interface preparation and cleaning. When there are nucleation delays in ALD, deposition-etch back methods will be able to prepare ultrathin and conformal films.

A characteristic of ALE which does not have its direct counterpart in the field of AS-ALD, is the use of simultaneous deposition on one material and etching of another material. If compatible with the specific fabrication step, a mirrored approach could be used to obtain high selectivity when the non-growth area is etched, while material is deposited on the growth area. In this respect, it is also believed that ALD and ALE can be combined in more complex schemes to achieve high deposition selectivity and, vice versa, high etch selectivity.

In this tutorial, a review of ASD and ALE applications will be provided with special focus on their mutual synergy.

Monday Morning, June 23, 2025

Plenary Session
Room Tamna Hall A - Session PS-MoM

Plenary Session

Moderators: Heeyeop Chae, Sungkyunkwan University (SKKU), **Han-Bo-Ram Lee**, Incheon National University

8:45am **PS-MoM-1 ALD Welcome and Introductory Remarks***,*

9:00am **PS-MoM-2 ALD Plenary Lecture: The Evolution of DRAM: Scaling Challenges, ALD Innovations, and Future Architectures***, **Seiyon Kim,*** SK Hynix, Republic of Korea **INVITED**

For decades, Dynamic Random Access Memory (DRAM) has been the cornerstone of main memory in computing, meeting the demands of an ever-expanding workload. The need for greater capacity, higher bandwidth, and lower power consumption has continually driven advancements in DRAM technology. The recent surge in artificial intelligence (AI) applications has further accelerated the demand for high-speed memory, catalyzing the rise of High Bandwidth Memory (HBM). While the success of HBM underscores the importance of packaging innovations, traditional scaling continues to play a critical role in improving DRAM core die performance, such as power efficiency, area, and cost, ensuring its competitiveness.

DRAM is primarily composed of three key components: the cell transistor, storage node (SN) capacitor, and peripheral transistor. Each component presents unique scaling challenges due to differences in structure and functionality, yet they share similar material requirements. These include the ability to accommodate nanometer-scale dimensions, achieve high aspect ratios, and meet specific electrical property demands. Atomic Layer Deposition (ALD) has been instrumental in enabling advanced DRAM technology by providing atomically precise control over thickness, composition, and conformality.

As 2D DRAM approaches its scaling limits at sub-10nm nodes, next-generation architectures such as $4F^2$ vertical gate DRAM (VG-DRAM) and lateral 3D DRAM are emerging as potential solutions. VG-DRAM offers significant benefits in scalability and performance, though its implementation has posed considerable challenges. However, recent advancements in process technologies have revitalized its potential as a strong contender for next-generation DRAM. Meanwhile, lateral 3D DRAM presents unique advantages for future extensions by circumventing the limitations of areal scaling.

Future opportunities for ALD materials are vast, particularly in addressing the demands of these new architectures. For example, lateral 3D DRAM relies heavily on lateral processes with exceptional conformality and uniformity across hundreds of layers, which is challenging even for ALD technique. Furthermore, new ALD materials may enable more disruptive capacitor-less DRAM based on 2T gain cells or ferroelectric FET.

This presentation will provide an overview of DRAM applications and key components, highlighting the primary challenges in scaling and the critical role of ALD in overcoming these obstacles. Finally, the discussion will explore the future evolution of DRAM architectures and the new opportunities that lie ahead.

9:45am **PS-MoM-5 ALD 2025 Innovator Awardee Talk: Atomic Layer Deposition of Metal Phosphates and Metal Borates through Thermal and Plasma Activated Approaches***, **Christophe Detavernier,*** Ghent University, Belgium **INVITED**

Metal (boro)phosphate coatings are of interest for a wide range of applications, in particular for lithium ion batteries, electrocatalytic water splitting, and as biocompatible and protective coatings. In view of the need for thickness control and conformality in these applications, there has been a growing interest in developing ALD-based approaches for the deposition of such coatings.

Identifying a suitable phosphate precursor has proven a major challenge. In theory, phosphoric acid would be an ideal candidate, but its use in vapor deposition is prohibited by its low vapor pressure at room temperature and its tendency to decompose rather than evaporate upon heating. Trimethyl phosphate (TMP) is an attractive alternative, offering a vapor pressure of 15 mbar at 70°C. Thermal ALD processes using TMP have been demonstrated for a variety of metal sources, but it has proven difficult to incorporate a sufficiently high atomic percentage of phosphorus in the growing film, requiring an unpractically large number of phosphate sub-cycles for each metal pulse.

Dobbelaere et al. (*Chem. Mater.* 26, 6863 (2014)) explored the use of a TMP plasma, where the TMP precursor vapor is introduced into an inductively coupled plasma (ICP) discharge. At low substrate temperatures, exposure to a TMP plasma results in CVD-type coating in a process akin to plasma polymerisation. However, at sufficiently high substrate temperatures (300°C), saturated growth could be achieved in a true ALD regime, resulting in ALD growth of Al phosphate. Similar TMP-plasma based approaches proved successful for ALD of Ti, V, Zn, Sn, Fe, Ni, Co phosphates, as summarised in the review by Henderick et al. (*J. Appl. Phys. Rev. 9*, 011310 (2022)).

Inspired by the TMP-plasma based approach, Dhara et al. explored plasma activation of trimethyl borate (TMB) towards ALD of Al borate. Using TMB alone in the plasma form does not yield self-limiting ALD growth, as polymerized species continuously accumulate on the substrate. By co-dosing H_2O in the TMB plasma, saturated growth of Al borate films could be achieved at and above 250°C, with a high growth per cycle (~3.5 Å).

10:45am **PS-MoM-9 ALE Welcome and Introductory Remarks***,*

11:00am **PS-MoM-10 ALE Plenary Lecture: Challenges and Future of ALE Technology in Semiconductor Manufacturing***, **Chanmin Lee,*** Samsung Electronics, Republic of Korea **INVITED**

ALD Applications
Room Tamna Hall A - Session AA-MoA

Memory Applications I

Moderators: Hanmei Choi, Samsung Electronics, **Robert Clark**, TEL Technology Center, America, LLC

4:00pm **AA-MoA-11 Atomic Layer Technology for Ferroelectrics and Resistive Switching Devices: Advances in Epitaxial Growth, Doping, and Defect Control***, **Miin-Jang Chen**, Yu-Sen Jiang, Ting-Yun Wang, Chen-Hsiang Ling,* Department of Materials Science and Engineering, National Taiwan University, Taiwan **INVITED**

Atomic layer deposition (ALD), atomic layer epitaxy (ALE), and atomic layer annealing (ALA) have emerged as critical techniques for precise material engineering in advanced electronic devices, particularly for ultrathin ferroelectric and resistive switching materials in memory and energy storage applications. This presentation addresses two key areas: (1) ferroelectric/antiferroelectric materials, and (2) resistive random access memory (RRAM) devices. In the first area, novel ALD/ALE methods enable precise control of doping, crystallographic orientation, and domain dynamics in sub-10 nm ferroelectric films. The alternating multi-pulse ALD technique achieves homogeneous Zr doping in HfO_2, thereby enhancing ferroelectricity even at high Zr/Hf ratios. Monolayer engineering via atomic layer substitution in $Hf_{0.5}Zr_{0.5}O_2$ (HZO) significantly enhances the ferroelectricity at a thickness of only ~4 nm with nearly wake-up-free behavior. Epitaxial HZO films grown by ALE demonstrate record high ferroelectric polarization ($2P_r$ = 78.9 μC/cm^2) and ferroelastic domain switching correlated with time-resolved negative capacitance. Furthermore, antiferroelectric ZrO_2/TiN heterostructures achieve exceptional energy storage density (~118.6 J/cm^3) through orientation-controlled epitaxy. In addition, hydrogen-mediated ALE allows for low-temperature (300^{o}C) epitaxial growth of twin-structured TiN electrodes. For RRAM devices, ALA dramatically improves resistive switching properties by tailoring nitrogen vacancies with monolayer precision in sub-4 nm AlN and SiNx layers. ALA reduces operating voltages, improves switching uniformity, and enhances endurance and retention. Spatial vacancy control via ALA stabilizes conductive filament formation, which reduces cycle-to-cycle variation. These results demonstrate ALD, ALE, and ALA as transformative techniques for next-generation nanoscale electronics, offering pathways toward high-performance memory and energy storage solutions.

4:30pm **AA-MoA-13 Study of Resistivity in TiN Films with SiH_4 Doping in the Thermal ALD Process***, **Siun Song**, Chaewon Kwak, Yooseong Kim, Kyubeom Lee, Dongwon Seo,* Hanwha Semitech, Republic of Korea

As semiconductor devices continue to scale down, precise control over deposition rate (D/R) and uniformity has become increasingly critical, making atomic layer deposition (ALD) a preferred technique. Titanium nitride (TiN) is widely employed in semiconductor applications, serving as a contact material for storage nodes and electrode materials due to its low resistivity (~155 μΩ•cm) and compatibility with ALD. However, as the demand for high-performance TiN films grows, further process optimization is needed to enhance TiN film properties, particularly in terms of resistivity.

In this study, we investigate the impact of SiH_4 introduction in the thermal ALD process of TiN films using the I2FIT facility model manufactured by Hanwha, with a focus on its effects on resistivity. The introduction of SiH_4 in TiN ALD sequence—($TiCl_4$-Purge-SiH_4-Purge-$TiCl_4$-Purge)-(NH_3-Purge)—was expected to induce a substitution reaction with $TiCl_4$, forming volatile $SiCl_4$ and thereby reducing the Cl impurity concentration in the deposited TiN film. TiN films were deposited at 550℃ with SiH_4 flow rates ranging from 25 to 850 sccm, followed by an evaluation of SiH_4 effects on resistivity across a broader temperature range of 450 to 660℃.

The resistivity of TiN films exhibited a U-shaped trend as a function of SiH_4 flow rate, decreasing to 149 μΩ•cm at 250 sccm before increasing to 186 μΩ•cm at 850 sccm, compared to a reference sample value of 154 μΩ•cm. Similar trends were observed at other deposition temperatures, with the lowest resistivity recorded at 250 sccm for 450℃ and 20 sccm for both 570℃ and 600℃. X-ray Photoelectron Spectroscopy (XPS) analysis exhibited an increase in Si incorporation with higher SiH_4 flow, which may contribute to the degradation of TiN resistivity. Additionally, the behavior of Cl impurities—initially decreasing with SiH_4 flow but subsequently increasing—supports the characteristics of SiH_4-doped TiN films. Furthermore, a denser film density was observed with increasing SiH_4 flow rate compared to the reference sample at 450℃ (Reference 4.873 g/cm^3; with SiH_4 at 650sccm: 4.979g/cm^3). However, at 600℃, film density decreased with increasing SiH_4 flow, with a reference density of 5.121 g/cm^3. These results highlight the complex influence of SiH_4 on the properties of TiN films, particularly resistivity, emphasizing the critical need for careful optimization of deposition temperature and gas flow in the ALD process. Additional experimental details and results will be presented at the conference.

4:45pm **AA-MoA-14 ALD of ferroelectric TiN/$Hf_{0.5}Zr_{0.5}O_2$/TiN stacks; growth and interfacial oxidation studied by *in situ* spectroscopic ellipsometry***, **Stijn van der Heijden**,* Eindhoven University of Technology, Netherlands*; Florian Wunderwald, Uwe Schroeder,* Namlab, Germany*; Marcel Verheijen, Erwin Kessels, Bart Macco,* Eindhoven University of Technology, Netherlands

Ferroelectric devices, particularly those based on $Hf_{0.5}Zr_{0.5}O_2$ (HZO), are a promising upcoming technology to enable high-speed, low-power computation.[1,2] However, for the successful implementation of these ferroelectric devices, several obstacles must be overcome. One such obstacle is the internal bias field, which – similarly to imprint – causes a shift in the coercive field making it more difficult to switch to the opposing polarization. The cause of this internal bias field is still subject to investigation, yet it is suspected to come from a defective interface between the metallic electrode and the ferroelectric material within the metal-ferroelectric-metal (MFM) stack. To form functional ferroelectric devices, the ability to accurately analyze the growth and interfacial formation of these MFM stacks is thus essential.

In this work, full TiN/HZO/TiN stacks were grown by ALD without breaking vacuum. For TiN, the used precursor was $Ti(NMe_2)_4$ and the co-reactant was a plasma containing a mixture of Ar and NH_3. For HZO, the used precursors were $CpHf(NMe_2)_3$ and $CpZr(NMe_2)_3$, and the co-reactant was either O_3 or an O_2 plasma. The growth of TiN and HZO in both nucleation and steady-state phases was measured using *in situ* spectroscopic ellipsometry. The film thicknesses for TiN and HZO were approximately 14 and 10 nm, respectively. Crucially, the oxidation of the bottom TiN electrode caused by plasma and ozone exposure when growing HZO – which is suspected to be a significant source of the internal bias field – could be investigated using ellipsometry. The TiN/HZO/TiN stacks were subsequently annealed and ferroelectric measurements were performed, confirming the suspected trend: increased interfacial oxidation leads to an increased internal bias field. Our studies thus show the capability of *in situ* ellipsometry to measure the growth and interfacial oxidation of TiN/HZO/TiN, aiding the optimization of the growth process of ferroelectric devices.

[1] J.P.B. Silva et al. APL Mater. 11, 089201 (2023)

[2] U. Schroeder, M.H. Park, T. Mikolajick, C.S. Hwang. *Nat Rev Mater* **7**, 653–669 (2022)

5:00pm **AA-MoA-15 Stable Synaptic Function and Orientation Selectivity Recognition Under Strain in Bilayer Stretchable Memristors via Atomic Layer Deposition***, **Ying-Jie Ma**, Ai-Dong Li,* Nanjing University, China

Memristors trigger enormous potentials in neuromorphic computing and advanced artificial intelligence due to their advantages in information storage and cognitive computation. However, the integration of memristors into flexible and stretchable devices, such as wearable health monitors, non-biological prosthetics, and soft robotics, suffers a tough challenge. Great efforts have been made on flexible memristors to meet the increasing demands, however report on stretchable memristors remains scarce. It is critical for ensuring the performance stability of stretchable devices under strain.

In this work, stretchable memristor of PDMS/Au/HfO_2/Al_2O_3/Ag was developed based on a discrete structural design. The discrete structure was achieved through sacrificial layer transfer and photolithography, with 10 nm Al_2O_3 and 10 nm HfO_2 functional layers deposited via atomic layer deposition (ALD), providing stable retention(up to 10^4 s) and reproducibility (100 cycles). Compared to conventional continuous designwithout photolithography, it exhibits a higher flexibility up to 30%. Under dynamic stretching and releasing, the device maintains stable resistive switching behavior and accurate replication of synaptic functionality. Even at 30% strain, the memristor's switching ratio remains at 10^3 and simulates a series of synaptic functions, including paired-pulse facilitation (PPF), long-term potentiation/depression (LT_P/LT_D), post-tetanic potentiation (PTP), short-term potentiation to long-term potentiation transition (STP-LTP), spike amplitude-dependent plasticity (SADP), spike width-dependent plasticity (SWDP), spike frequency-dependent plasticity (SRDP), and spike-timing dependent plasticity (STDP).

Furthermore, the threshold sliding effects, enhanced depressive effects (EDE), and orientation selectivity recognitionin Bienenstock-Cooper-Munro

(BCM) learning rule have been realized in our stretchable memristors by leveraging the memristor's history-dependent plasticity. This work provides a new structural and material framework for stretchable memristors, ensuring reliable performance in dynamic environments, which is vital for the next generation of flexible electronics.

5:15pm **AA-MoA-16 P-Type Tellurium Thin Film Transistor with Sacrificial Atomic Layer Deposition***, **Wonho Choi**, Byongwoo Park, Seungjae Yoon, Jeong Woo Jeon, Gwangsik Jeon, Sangmin Jeon, Sungjin Kim,* Seoul National University, South Korea*; Chanyoung Yoo,* Hongik University, Republic of Korea*; Cheol Seong Hwang,* Seoul National University, South Korea

A complementary thin film transistor (CTFT) has long been a desired device structure for monolithic three-dimensional integration architecture with the complementary metal oxide semiconductor (CMOS) field-effect transistors fabricated on a Si wafer surface[1]. They must also be compatible with the back-end-of-line conditions with limited thermal budgets (< 400 ^{o}C)[2]. The n-type TFTs with reasonable performances are available using amorphous oxide semiconductors. Still, the lack of p-type TFT (p-TFT) with comparable performance hinders the advancement of CTFT technology[3]. P-type two-dimensional transition metal dichalcogenides, such as WSe_2, have drawn attention for this application, but their flake-based process is incompatible with the standard CMOS processes[4]. Elemental tellurium (Te) is another candidate for p-type channel material due to its unique high hole mobility[5]. However, the reported fabrication processes are incompatible with the CMOS processes[6]. Another crucial issue is ensuring the channel material's intimate contact with the source and drain electrodes[7]. While the contact properties are fundamentally determined by the electron affinity of the channel material and contact metal work function, the metal-induced gap state adversely affects the Schottky barrier formation, pinning the Fermi level at an undesired position within the band gap[8]. Therefore, no CMOS-BEOL-compatible p-TFT devices have been reported regarding the fabrication process (low growth temperature and non-flake type) and electrical performance (comparable or even higher drive current density than the n-type counterpart).

This study introduces an innovative sacrificial atomic layer deposition (s-ALD) for crystalline Te film for p-TFT fabrication, which is required for monolithic three-dimensional device integration. It selectively grows p-type Te channel film on the gate insulator with its high hole mobility axis (c-axis) aligned with the electric current flowing direction (substrate surface direction) while forming a semimetal $NiTe_2$ interlayer on the Ni metal contacts for low contact resistance. The p-TFT device outperforms the previous works with 1.3×10^{-5} $A\mu m^{-1}$ on-current density, 40 $cm^2V^{-1}s^{-1}$ hole mobility, and 0.9 kΩμm contact resistance, which remained unaffected by atmospheric exposure over 250 days. Furthermore, the low deposition temperature of 80 ^{o}C and wafer-scale uniformity enhance its compatibility with CMOS technology.

5:30pm **AA-MoA-17 Atomic-Scale Processing of Ruthenium Thin Films via ALD and ALE for Advanced Interconnects***, ChangHwan Choi, **YoungSeo Na**, HyunJin Lim, SangKuk Han, HyoJin Ahn, YehBeen Im, WonJae Choi,* Hanyang University, Korea

Ruthenium has been recognized as a next-generation interconnect material capable of overcoming the scaling limitations of copper interconnects. To effectively integrate ruthenium into complex three-dimensional semiconductor structures, precise control of atomic layer deposition (ALD) and atomic layer etching (ALE) processes is essential. In this study, we investigated the electrical and chemical properties of ruthenium thin films deposited at various temperatures via ALD to achieve low-resistivity ruthenium films. The optimized ALD-grown films were subsequently processed via ALE for precise thickness regulation.

The ALD-Ru process was performed in the temperature range of 225-375°C using (ethylbenzene)(1-ethyl-1,4-cyclohexadiene)ruthenium(0) (EX03Ru) as the Ru precursor, with O_2 as the reactant. At the ALD window (375°C), a high-quality ruthenium thin film with a very low resistivity (~20.3 μΩ·cm) and a growth per cycle (GPC) of 0.61 Å/cycle was achieved (Fig. S1). X-ray photoelectron spectroscopy (XPS) analysis confirmed that the content of non-conductive RuO_x decreased from 12.9% at 225°C to 2.8% at 375°C, leading to reduced resistivity (Fig. S2). In contrast, X-ray diffraction (XRD) results revealed that the film exhibited the highest crystallinity at 275°C (Fig. S3). Additionally, post-deposition forming gas annealing was performed on the film deposited at 275°C at the back-end-of-line (BEOL) thermal budget of 400°C for 1 hour, resulting in a 72% improvement in resistivity, grain growth, and a reduction in surface roughness from an RMS value of 1.54 nm to 1.18 nm. Furthermore, a plasma-enhanced ALE process was developed to achieve uniform etching of the optimized Ru film. The ALE process consisted of two primary sequential steps: (1) surface modification via oxidation with O_2 plasma or fluorination with CF_4 plasma, forming a self-limiting modified layer on the surface, and (2) selective removal of the modified layer using low-energy Ar plasma. Through process optimization, the self-limiting nature of ALE was maintained even in high-aspect-ratio (12:1) structures, minimizing surface contamination and ensuring stable and uniform etching. These results confirm that ALD and ALE support the fabrication of high-performance thin films while enabling precise sub-nanometer thickness control and achieving reliable material processing, underscoring the potential of an integrated atomic-scale approach for next-generation interconnect technology.

ALD Fundamentals
Room Halla Hall AB - Session AF1-MoA

ALD on 3D Structures

Moderators: Hao Van Bui, Phenikaa University, **Arrelaine Dameron**, Forge Nano

4:00pm **AF1-MoA-11 Continuous Production of Nanocoated Powders***, **Sébastien Moitzheim**,* Powall, Netherlands **INVITED**

Powder-based processes are critical to a wide range of industries, from battery materials to pharmaceuticals. Achieving the desired performance often depends on precise surface modifications.Over the past decade, Powall has been developing a scalable nanocoating technology that combines the atomic-level precision of Atomic Layer Deposition (ALD) with the speed and throughput of Chemical Vapor Deposition (CVD), enabling continuous and cost-effective production.

In this presentation, Dr. Moitzheim (CTO) will share Powall's key learnings on transitioning gas-phase coating methods from lab to pilot-scale and beyond. Specific attention will be paid to how the technology can be adapted to accommodate powders of varying sizes, shapes, and porosities, while still ensuring uniform and high-quality coatings. The talk will also provide an update on the upcoming commercial pilot-scale equipment and outline the path toward large-scale manufacturing. By illustrating the core challenges and advancements in scaling powder nanocoatings, this talk will offer a balanced perspective for researchandindustry.

4:30pm **AF1-MoA-13 Plasma-Enhanced Spatial ALD on 2D and 3D Surface Topologies: The Case of Amorphous and Crystalline TiO_2***, **Mike van de Poll**,* Eindhoven University of Technology, Netherlands*; Jie Shen,* Holst Centre / TNO, Netherlands*; James Hilfiker,* J.A. Woollam Co., Inc.*; Marcel Verheijen, Paul Poodt,* Eindhoven University of Technology, Netherlands*; Fieke van den Bruele,* Holst Centre / TNO, Netherlands*; Erwin Kessels, Bart Macco,* Eindhoven University of Technology, Netherlands

As of late there were two key research questions regarding the conformality of plasma-enhanced spatial ALD (PE-s-ALD): can the technique be used to deposit highly conformal films, and how do the material properties – like crystallinity and composition – of such films change throughout the coated 3D structures? We have recently answered the first question by showing that exceptionally conformal films can be grown by PE-s-ALD with subsecond plasma exposures, thanks to the high radical density in the atmospheric plasma [1]. However, various crystallization and growth effects can influence the film profile and crystallinity, and understanding these effects and their interplay is key.

In this work, we demonstrate the complex growth mechanism of TiO_2 using PE-s-ALD, and study conformality not just in terms of films thickness, but also in terms of film properties. TiO_2 films are deposited both on planar substrates and inside lateral high-aspect-ratio (LHAR) test chips (PillarHall^{TM} by Chipmetrics Ltd). These LHAR structures uniquely allow for spatial material property mapping in trenches using spectroscopic ellipsometry, Raman spectroscopy and X-ray photoelectron spectroscopy. Conditions that result in the anatase phase on a planar surface only partially form this phase inside LHAR structures, with the deepest part of the film being amorphous. This partial crystallization is ascribed to the film thickness inside the LHAR structure gradually dropping below the critical thickness for crystallization. In turn, the partial crystallization is shown to have a significant effect on the resulting thickness profile, due to an enhanced growth per cycle on crystalline surfaces. A framework of the interplay between effects is proposed, offering insights that enable better control of the crystallinity and thickness throughout the entirety of coated surfaces of 3D structures by PE-s-ALD.

Additionally, the recombination probability of O-radicals during this atmospheric-pressure PE-s-ALD process at 200 °C is determined to be $3\times10^{-}$

[5], which is similar to low-pressure PE-ALD [2]. This result indicates that differences in conformality between the two types of ALD are not the result of differences in recombination probability, but rather of differences in initial radical density and diffusion behavior.

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4:45pm **AF1-MoA-14 Rapid Test for ALD in High Aspect Ratio Spaces Utilizing Thermally Bonded Chips and Hydrazine with Titanium Tetrachloride for TiN Deposition***, Amy Ross, Dipayan Pal, Dohyun Go, Diego Contreras Mora, Ping-Che Lee,* UC San Diego*; Danish Baig,* Georgia Institute of Technology*;* ***Adrian Alvarez****,* RASIRC, USA*; Dan Le, Jeffery Spiegelman,* RASIRC*; Muhannad Bakir,* Georgia Institute of Technology*; Andrew Kummel,* UC San Diego

The increasing demand for high-bandwidth memory necessitates the development of devices with 3D structures, such as DRAM. These devices rely on the deposition of conformal, particle-free films with complete coverage in high-aspect-ratio (HAR) spaces. Transmission electron microscopy (TEM) is the standard technique for verifying these parameters, but it is costly, time-intensive, and only inspects a very small area of the surface of interest. This study demonstrates a rapid and non-destructive alternative involving thermally bonded chips that provide HAR spaces for deposition. The chips can be debonded and analyzed using scanning electron microscopy (SEM) and atomic force microscopy (AFM).ALD titanium nitride (TiN), typically utilized as a 2 nm diffusion barrier between tungsten (or copper) and SiO_2 (or SiCOH) in HAR spaces, was employed using $TiCl_4$ and N_2H_4 precursors, to deposit a 20 nm layer in a thermally bonded chip with a 2000:1 aspect ratio (fig. 1). This is 10x the normal thickness of diffusion barriers to increase sensitivity to particle formation.

A control test was conducted on a clean, thermally bonded sample with no TiN deposition (fig 2). The debonded dies were analyzed as planar samples using AFM, SEM, and energy-dispersive spectroscopy (EDS), confirming no detectable titanium (0% atomic percent) in any region (edge, middle, center). The AFM RMS was measured at 2.06 nm. For TiN deposition, increasing precursor doses 1×, 2×, and 3× normal exposure (1x = 500 ms $TiCl_4$, 2750 ms N_2H_4, 30 sec purge, substrate temperature 475°C) were employed to evaluate penetration depth and particle formation. The RMS roughness values for the top die remained low at 1.92 nm, 1.77 nm, and 1.64 nm, respectively. This indicates no particle formation. Atomic Ti percentages from EDS decreased as the effective aspect ratio increased from 475:1 to 2000:1 aligning with predictions from the Gordon Model [1]. Additionally, the 3x smaller %Ti decreases at the center between the 3× and 2× dose sample further support the model's estimation of precursor penetration. Temperature variations across the sample may have prevented complete surface saturation. The low RMS roughness and absence of large features suggest that CVD particle formation did not occur in the HAR space, consistent with the $TiCl_4$ + N_2H_4 chemistry avoiding $NH_4Cl(s)$ formation [2].

AFM was used to analyze an area of over 111 μm^2, revealing no defects or CVD particles. In comparison, a typical TEM survey covers only 0.004 μm^2. This means SEM/AFM in debonded chiplets examined a region ~30,000x larger than TEM allowing large area determination of particles formation in HAR.

5:00pm **AF1-MoA-15 Enhancing Step Coverage in High-Temperature Ald for Advanced Semiconductor Scaling***, Seung Hyun Lee, Deok Hyun Lee,* Soulbrain Co., Ltd., Republic of Korea*; Kok Chew Tan,* Soulbrain Co., Ltd., Malaysia*; Sung Gi Kim,* ***Gyun Sang Lee****, Jung Hun Lim, Jae Sun Jung,* Soulbrain Co., Ltd., Republic of Korea

As semiconductor technology advances, improvements in performance, power efficiency, and area optimization continue to drive innovation. However, increasing device complexity and higher integration levels have exacerbated step coverage challenges during the deposition of high-k thin films in DRAM capacitors, metal gate insulators, and block oxides in 3D NAND. In particular, achieving uniform thin-film deposition on high-aspect-ratio patterns has become increasingly difficult. Additionally, the application of high-temperature processes to enhance film quality can lead to precursor decomposition, further deteriorating step coverage. To address this issue, this study proposes the use of inhibitor technology as an effective approach to improving step coverage in high-temperature atomic layer deposition (ALD) processes. Our experimental results demonstrate that the inhibitor remains stably adsorbed on the substrate surface under various ALD conditions, effectively mitigating step coverage issues. Notably, this inhibition effect persists even at temperatures above 600°C during the growth of Al_2O_3 thin films. Furthermore, a newly developed hydrocarbon-based inhibitor has been identified as optimal, as it fully decomposes into water and carbon dioxide upon reacting with ALD precursors, leaving no residual impurities in the film.

5:15pm **AF1-MoA-16 ALD as the Solution for Uniform Cu Electroplating in High Aspect Ratio Vias***,* ***Matthew Weimer****, Sara Harris,* Forge Nano*; Irina Stateikina,* Centre de Collaboration MiQro Innovation (C2MI), Canada*; Dane Lindblad,* Forge Nano*; Marc Guilmain, Xavier Gaudreau-Miron,* Centre de Collaboration MiQro Innovation (C2MI), Canada*; Arrelaine Dameron,* Forge Nano

Scaling interconnects to increase device density is a critical bottleneck for a range of applications in the 3D and advanced packaging field. Currently, interconnect density is limited by, amongst other things, the ability to produce reliable, low resistivity, Cu vias at high aspect ratios (AR). Some microelectromechanical system (MEMS) applications, where the interconnect in the device layer is defined by the size of the active component, called the proof mass, are restricted in height due to fabrication limitations of high AR interconnects. As a result, some device architectures are inaccessible, limiting the utility of devices, such as high-sensitivity inertial sensors. While some progress has been made, single-side deposition used in blind vias is limited to 8:1 or less. The source of that limitation is the physical vapor deposition (PVD) processes used to apply adhesion and/or nucleation layers required for successful Cu electrochemical deposition (ECD). PVD provides high-quality layers, but those layers are applied in a non-conformal fashion, leading to device failure in non-line-of-site or high AR features, as shown in Figure 1. We have been working on a complete thermal ALD solution at <300 °C consisting of a high-quality SiO_2 dielectric barrier, breakdown voltage >12 MV/cm, a dense TiN Cu diffusion barrier, density ~5.0 g/cm^3, which also functions as a Ru nucleation layer, and low resistivity Ru metal Cu seed layer, resistivity <20 $\mu\Omega\cdot$cm at 20 nm. In this work, we demonstrate successful Cu seed application by depositing this ALD dielectric/diffusion barrier/Cu seed layer stack on Si trenches, where the state-of-the-art PVD solution has multiple failure modes. Successful conformal ECD has been demonstrated with 15-20 nm of Ru in vias with AR from 4:1 to 25:1 and in through glass vias (TGV) with AR from 6:1 to 30:1. Further tests are ongoing with collaborators at the National Institute of Standards and Technology (NIST) to refine Cu ECD conditions and measure via resistivity of Cu ECD in the vias.

5:30pm **AF1-MoA-17 Multi-Scale Model for Optimization of Low-Temperature Al_2O_3 ALD Process Conformality Within High Aspect Ratio Trench***,* ***Ivan Petraš****, Yury Shustrov, Andrey Smirnov,* Semiconductor Technology Research d.o.o. Beograd, Serbia

ALD is typically characterized by two main steps with self-limiting reactions on the surface and purging. Each step requires a certain time to ensure complete coverage of the surface by precursor and complete removal of the precursor from the reactor volume during the purging steps. ALD process optimization requires achieving the minimal ALD cycle duration while preserving good conformality within the trench structures over the wafer surface. Optimal process conditions are changed with respect of the trenches pattern, trench surface density and aspect ratio. Therefore, the process adjustment on the blanket wafers becomes inefficient, while the adjustment cost with the patterned wafers is typically high. In this sense, multi-scale models with the coupled reactor-scale and feature-scale simulations can be applied for reducing of process development costs. Focus of this work is aimed at the improvement of low-temperature Al2O3 ALD performance with consideration of patterned wafers through adjustment steps duration and operating conditions. An integrated modeling approach was developed with self-consistent coupling of modeling tasks on different scales. The reactor-scale model of TMA delivery, oxidation by H2O and purging includes unsteady mass transport with surface chemical reactions. The trench-scale model includes tracing TMA and H2O species as well as products of surface chemical reactions.It is demonstrated that increasing of trench aspect ratio leads to remarkably longer time for achieving of ALD conformality on patterned wafer during both TMA delivery and oxidation steps. The increase of precursor impulse duration results in the reducing of time required for full coverage, but simultaneously it increases the needed time for purge step before introduction of the next precursor. As the result the increasing the precursor pulse duration for better conformality within the trench may lead to requirements of longer time for ALD cycle and thus decrease the throughput of the process. Pressure effect on the trench coverage time demonstrates different trends with the aspect ratio change during TMA and

H_2O steps. At lower aspect ratio of 20 the pressure decrease leads to faster trench coverage, while for high aspect ratio of about 100 there is the non-monotonic behaviour of coverage speed with pressure change. It is demonstrated that a detailed consideration of low temperature oxidation mechanism is important to correctly describe the oxygen incorporation into the film and resulting ALD conformality. Effect of temperature and H_2O purge step duration on the resulting film stoichiometry are discussed.

ALD Fundamentals
Room Tamna Hall B - Session AF2-MoA
Precursor Chemistry I

Moderators: Seán Barry, Carleton University, **Haripin Chandra**, EMD Electronics, USA

4:00pm **AF2-MoA-11 The Emergence of New Ligands for ALD Precursor Development***, Anjana Devi,* Leibniz Institute for Solid State and Materials Research, Germany **INVITED**

Advances in atomic layer processing of functional materials crucially depend on the progress made in precursor development. Without persistent research on precursors, atomic layer deposition (ALD) technology would not be the fastest growing thin-film technology in microelectronics industry or could not expand towards new emerging applications in nanotechnology and energy sector. The beneficial properties of ALD namely low temperature processing, conformal coverage, composition control can be exploited if the precursors and the co-reactants are fine-tuned to achieve the desired film properties. The understanding of precursor chemistry and their design and synthesis concepts needs specific attention. In this presentation, the recent research in ligand design and ALD precursor chemistry that governs layer formation and thin film characteristics for different material systems will be discussed. One representative example is using dimethylamino-propyl (DMP) ligand for various metals (Al, Zn, Ru, Mg). It not only serves as effective ligands for metalorganic precursor synthesis, but DMP-based compounds can be used as intermediates as well as reducing agents for metal deposition implying the broad applicability of the DMP ligand. The chelating nature of the DMP ligand furthermore yields sterically and electronically saturated metal centers, enabling the formation of monomeric complexes with enhanced volatility. The emergence of the DMP ligand system has also resulted in developing non-pyrophoric metal precursors that are suitable for temporal ALD, plasma ALD and spatial ALD applications. These findings reveal the promising potential of ligand engineering towards precursor development to meet the demands of materials for advanced technological applications.

4:30pm **AF2-MoA-13 Perspective on Beryllium Compounds as Precursors for ALD Applications***, **Dominik Naglav-Hansen,*** Ruhr University Bochum, Germany*; Magnus Buchner,* University of Marburg, Germany*; Martin Wilken,* Ruhr University Bochum, Germany*; Deniz F. Bekiş,* University of Marburg, Germany

Until this day there has been almost no development of beryllium precursors with tailor-made properties for their application in ALD processes, be it the deposition of Be-metal, BeO or Be_2N_3-layers on any kind of substrate. Since these three beryllium based materials are of high importance in the microelectronics industry and for high performance ceramic materials, it is somehow confusing that not much research been done in this field so far. [1-6] One reason might be the „infamous“ toxicity of beryllium and its compounds, which hindered progress in the field of beryllium chemistry for ages. The authors of this work contributed a lot to this debate in the past. [7-13] However, the development of volatile beryllium compounds is still scarce and to the best of our knowledge no systematic studies and experiments were performed until today. In this perspective work the concepts and preliminary results of several beryllium compounds, which differ in their chemical compositions, bonding modes and physico-chemical properties, are presented and discussed. First insights into the relationship between the chemical and electronic structure of those compounds and their influence on their volatility are highlighted. Proof of concept depositions for different classes of beryllium based thin films are planned to be presented opening the gate to a new way of making these materials.

4:45pm **AF2-MoA-14 Anhydrous Hydrogen Iodide Source for ALD of CsI and Other Metal Halides***, **Georgi Popov,** Alexander Weiß, Anton Vihervaara, Kenichiro Mizohata, Mikko Ritala, Marianna Kemell,* University of Helsinki, Finland

Metal halides are an emerging group of compounds with a steadily increasing number of ALD processes published each year.[1] Most metal halide ALD processes employ volatile metal halides, such as TiX_4 or SnX_4, as halide (X = F, Cl, Br, I) precursors. ALD processes were first developed for metal fluorides using HF, with a later transition towards volatile metal fluorides (for example, TiF_4 and TaF_5) as safer and less corrosive alternatives to HF. The main applications of metal fluoride films are in optics and batteries.

Among metal halides other than fluorides, the main interest is in iodides, motivated by the desire to deposit halide perovskites with ALD. Halide perovskites are primarily iodides that exhibit outstanding performance in solar cells and several other applications. Existing ALD processes for iodides use volatile metal iodides as iodine precursors. For instance, SnI_4 acts as an iodine source in the ALD process for $CsPbI_3$ perovskite.[2] SnI_4 as an iodine source contaminates the film with Sn, which is detrimental for halide perovskite applications. Furthermore, Sn compounds are not relevant for photovoltaic industry due to their high costs and supply chain risks.[3]

Anhydrous hydrogen iodide (HI) gas is the least expensive, simplest, and most straightforward iodine precursor to deliver and use. HI does not suffer from issues related to metal halides, such as SnI_4. However, HI is not commercially available, likely due to a lack of industrial demand. We contacted many gas and chemical suppliers during 2015 – 2019, but none were willing to supply HI.

In this work we demonstrate a source design that produces anhydrous HI gas on-site. The source is constructed from catalogue vacuum parts with a total cost of less than 1000 USD and uses inexpensive common bulk chemicals (ca. 20 USD to fully fill the source). To demonstrate the feasibility of this source, we developed a new ALD process for CsI using Cs(btsa) (cesium(I)bis(trimethylsilyl)amide) and HI. Using this chemistry, CsI can be deposited over a wide temperature range of 150 – 325 °C. GPC is independent of the deposition temperature within 150 – 200 °C and 250 – 300 °C. The deposited CsI films are uniform, crystalline, and pure. Furthermore, cost analysis showed a 40% decrease in the CsI ALD process cost with our HI source compared to SnI_4.

1. Leskelä et al., AVS 70th International Symposium, Nov. **2024**, Tampa, FL.

2. Weiß et al., Chem. Mater. **2022**, 34, 13, 6087.

3. Schileo and Grancini, *J. Mater. Chem. C,* **2021**, *9* (1), 67–76.

5:00pm **AF2-MoA-15 Evaluating Trisilylamine and Diiodosilane as Silicon Precursors for PEALD of Silicon Nitride in Front-End-of-Line Applications***, **Keerthi Dorai Swamy Reddy,** Marco Lisker,* IHP - Leibniz Institut fuer innovative Mikroelektronik, Germany

The ubiquitous use of Silicon Nitride (SiN) in front-end-of-line (FEOL) applications such as spacers, etch stop layers, optical waveguide materials, and trench liners has made it essential to develop deposition methods meeting its stringent requirements. Well-established techniques like low-pressure chemical vapor deposition (LPCVD) and plasma-enhanced chemical vapor deposition (PECVD) have successfully addressed many of the film property constraints for specific applications. However, the rapid miniaturization of devices has shifted the focus towards achieving conformality and uniformity at lower deposition temperatures, making Plasma-enhanced atomic layer deposition (PEALD) the most suitable method.

Following the choice of deposition method, the selection of precursors plays a critical role in determining key film properties, such as the impurity content, stoichiometry, density, and etch rate. These layer properties, in turn, significantly influence the electrical characteristics of devices. In addition to meeting the requirements for film properties, the chosen precursors must also enable an economical process to ensure the feasibility of high-volume manufacturing. For PEALD, halides, aminosilanes, or silylamines are typically used as Si precursor sources. In this study, we compare two Si precursors, namely, Trisilylamine (TSA) and Diiodosilane (DIS), in terms of PEALD process development parameters and their corresponding film properties, aiming to achieve an economical process suitable for FEOL applications.

In this work, a direct plasma ALD tool was used to compare the deposition process of SiN at 250 °C. For TSA, a combination of Nitrogen and Hydrogen plasma was used as a co-reactant, whereas for DIS, nitrogen plasma alone served as the co-reactant. In both cases, Argon was used as the carrier gas. The SiN process development was initially studied for both precursors by varying the respective PEALD process parameters. A comparison of ALD cycle time, precursor pulse time, growth rate per cycle, precursor consumption, and economic value of the precursors for the layer growth is presented in Table 1 (in PDF). The etch rates of as-deposited and annealed films in two different etchants are compared in Table 2 (in PDF). Additionally, the average refractive index, uniformity, conformality, and stoichiometry are compared. For device applications, key electrical characteristics such as breakdown voltage and leakage current are also compared. Although both TSA and DIS-based films result in uniform and conformal films, TSA appears to be a better suitable candidate for SiN deposition due to its lower precursor consumption and better economic value.

5:15pm **AF2-MoA-16 Precursor Design for Thermal ALD of Silver Metal***,* ***David Emslie****, Nick Hoffman,* McMaster University, Canada

Thin films of metallic silver are of interest as transparent electrodes for solar cells and LEDs,[1] and in photonics/plasmonics.[2] ALD is a uniquely capable method for the deposition of highly uniform and conformal thin films, and a handful of methods for silver thermal ALD have previously been reported. For example, several publications describe the use of [(hfac)Ag(COD)] (hfac = hexafluoroacetylacetonate; COD = 1,5-cyclooctadiene) as a precursor for Ag ALD, in combination with ^{n}PrOH[3-5] or ^{t}BuNHNH$_2$[4] as the co-reactant. However, the [(hfac)Ag(COD)] precursor is thermally unstable and requires direct liquid injection, and the reported processes exhibit a narrow (5–23 °C) temperature window. ALD methods have also been reported using [(hfac)Ag(PMe$_3$)] (Me = methyl) in combination with formalin ($H_2C{=}O/H_2O$),[6] or in a multi-step process involving reactions with AlMe$_3$ and then H_2O.[6] However, these methods afforded nanoparticles rather than continuous films. Finally, thermal ALD of Ag has been achieved using [(fod)Ag(PEt$_3$)] (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) with BH$_3$(NHMe$_2$), affording films with a matte finish due to a rough microstructure.[7]

This presentation will describe the synthesis of a family of new silver alkoxide complexes, [{L$_x$Ag(OR)}$_n$] (L = PR'$_3$, CNR', NHC; R = C(CF$_3$)$_3$ or C(CH$_3$)$_3$; R' = Alkyl; NHC = N-heterocyclic carbene), comparison of their solid-state structures, volatility, melting points, and thermal stability, their solution reactivity with potential ALD co-reactants, and thermal ALD of silver metal using one of the precursors.

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5:30pm **AF2-MoA-17 A Novel Liquid Cocktail Precursor for Atomic Layer Deposition of Hafnium-Zirconium-Oxide Films for Ferroelectric Devices***,* ***Akihiro Nishida****, Tsukasa Katayama, Takashi Endo, Yasutaka Matsuo,* Hokkaido University, Japan

$Hf_xZr_{1-x}O_2$ (HZO) thin film is a promising material for next-generation ferroelectric memory devices. Ferroelectric HZO films are industrially produced using atomic layer deposition (ALD) technique. However, conventional ALD precursors for ZrO_2 exhibit lower thermal stability than those for HfO_2; thus, the deposition temperature is limited by the Zr precursor processing temperature (320 °C), limiting the quality of HZO.[1] In this study, we developed a novel ALD precursor for HZO: a liquid homoleptic cocktail precursor referred to as FER-1, which is composed of tetrakis(1-(*N*,*N*-dimethylamino)-2-propoxy)hafnium [Hf(dmap)$_4$] and tetrakis(1-(*N*,*N*-dimethylamino)-2-propoxy)zirconium [Zr(dmap)$_4$] in a 1:1 mol% mixture.(Fig. 1) Both Hf(dmap)$_4$ and Zr(dmap)$_4$ are stable at temperatures as high as 371 °C. In addition, these compounds have a similar vapor pressure (Fig. 2), similar ALD window, and excellent mixture stability. Furthermore, FER-1 is a volatile compound that shows a very clean thermogravimetry curve without decomposition or residue formation at 10 Torr. (Fig. 3) The ALD window was estimated to range from 300 to 360 °C. (Fig. 4) This is the first report of ALD of HZO film using cocktail precursor greater than 320 °C. Interestingly, the Hf/Zr concentration ratio of the HZO film prepared using FER-1 was the same as the Hf/Zr concentration ratio in the precursor mixture, demonstrating that the Hf/Zr composition can be easily controlled.MIM TiN/HZO/TiN devices were fabricated to evaluate the ferroelectric properties of the HZO films. The remanent polarization $2P_r$ reached 36.9 µC/cm^2.(Fig. 5) The *C*–*V* curve of the HZO film exhibits butterfly-shaped hysteresis loop, indicating the ferroelectric nature of the film. The dielectric constant of HZO film was varied in the range of 35.5–40.8 by voltage sweep. (Fig. 6) Our findings show that FER-1 is a highly useful ALD precursor for industrial HZO production.

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ALD & ALE
Room Tamna Hall A - Session ALDALE-MoA
Student Award Session

Moderators: Jihwan An, Pohang University of Science and Technology (POSTECH), **Parag Banerjee**, University of Central Fllorida

1:30pm **ALDALE-MoA-1 ALD Student Award Finalist Talk: Integrating Machine Learning into Atomic Layer Deposition: A Case Study on Hafnium Oxide Process Optimization***,* ***Minjong Lee****, Doo San Kim, Thi Thu Huong Chu, Dushyant Narayan, Dan Le, Soubhik De,* University of Texas at Dallas*; Si Joon Kim,* Kangwon National University, Republic of Korea*; Jiyoung Kim,* University of Texas at Dallas

Industry 4.0 integrates intelligent information technologies into manufacturing, with machine learning (ML) offering significant potential to enhance flexibility, improve efficiency, and minimize process errors.[1] ML integration is particularly valuable in semiconductor fabrication, where deposition processes such as ALD require a comprehensive understanding of numerous parameters—especially with the rise of three-dimensional (3D) structures. Leveraging ML is expected to accelerate process optimization and expand ALD applications in cutting-edge semiconductor manufacturing. While real-time monitoring with self-feedback capabilities is the most effective strategy for ML-driven ALD, the increased processing time and maintenance demands of *in-situ* monitoring systems present challenges. This study introduces a “pipeline research” approach, outlining strategies for integrating ML into ALD processes as a foundation for digital twin technologies.

Case studies focus on ALD HfO$_x$ film deposition, extending beyond conventional ML applications that have primarily been restricted to film thickness prediction.[2] While thickness remains a key metric within ALD windows, it provides only a partial understanding of film quality. To address this, film density was incorporated as an additional critical factor to ensure optimal film characteristics. A deep neural network (DNN) model was employed instead of traditional regression-based ML algorithms to improve predictive accuracy by capturing the complex, non-linear features of ALD processes. Such a model not only enhances film property predictions but also generates prediction maps of film properties, which were further analyzed to explore broader parameter spaces across an extended range. Additionally, investigations were conducted to determine the optimal dataset size required for effectively training a DNN system, providing key guidelines for integrating ML into ALD processes. The advantages of using DNNs for ALD process optimization will be comprehensively highlighted, particularly in their ability to efficiently handle high-dimensional process parameters.

This analysis demonstrates how ML-driven innovations simplify experimental design and reshape ALD process optimization strategies. The presentation will cover technical methodologies, integration strategies, and the workflow of prototype implementations for ML-driven ALD studies, offering insights into the future of autonomous ALD process control systems.

This work was supported by KEIT granted by MOTIE (Nos. 20010806 and 1415187770) and NRF (RS-2024-00450836).

[1] K. J. Kanarik et al., Nature 616, 707 (2023).[2] A. Arunachalam et al., JVST A 40, 012405 (2022).

1:45pm **ALDALE-MoA-2 ALD Student Award Finalist Talk: The AtomicLimits ALD/E Database: Unlocking the Future of ALD/E with Large Language Models**, ***Eleni Poupaki,*** Eindhoven University of Technology, Netherlands; *Sameer Sadruddin, Jennifer D'Souza,* TIB Leibniz Information Centre for Science and Technology, Germany; *Alex Watkins, Bora Karasulu,* University of Warwick, UK; *Sören Auer,* TIB Leibniz Information Centre for Science and Technology, Germany; *Adrie Mackus, Erwin Kessels,* Eindhoven University of Technology, Netherlands

Launched by TU/e in 2019, the *AtomicLimits* ALD/E database [1,2] has become a pivotal crowd-sourcing, open-domain platform for the atomic scale processing community by providing a comprehensive overview of processes reported in the scientific literature. In its current form it compiles basic information, such as deposited materials, reactants used, and relevant references. For ALE processes, it also reports whether the process is isotropic or anisotropic. Despite its extensive repository, vast amounts of (unstructured) data remain unexploited limiting the database's potential for advancing material science discovery in ALD and ALE processes.

Artificial Intelligence (AI), and particularly Large Language Models (LLMs), present transformative opportunities to bridge this gap. LLMs can solve tasks beyond their initial training scope, excelling at understanding, generating and processing text. These capabilities make them highly suitable for recognizing patterns, synthesizing knowledge and producing human-like outputs. Thus, they provide a powerful and scalable alternative for structured data extraction from the vast literature on ALD/E. [3]

In this work, we present the current state of the *AtomicLimits* ALD/E database and demonstrate how LLMs can be employed to enhance it with additional structured data. We highlight a case study where LLMs extract valuable ALD-related information from unstructured literature text using a structured framework. This framework is iteratively generated by LLMs and refined through ALD-expert feedback. The final structure, combined with ALD literature, enables knowledge extraction using LLMs. The extracted data is then represented as a knowledge graph, specifically using the Open Research Knowledge Graph (ORKG). [4] This approach not only enables the creation of extensive datasets for ALD and ALE research but also lays the foundation for a new era of data-driven material science discovery in the atomic-scale processing domain.

[1] DOI: 10.6100/alddatabase

[2] DOI: 10.6100/aledatabase

[3] Schilling-Wilhelmi, M. *et al.* From text to insight: large language models for chemical data extraction. *Chem. Soc. Rev.* 10.1039.D4CS00913D (2025) doi:10.1039/D4CS00913D

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2:00pm **ALDALE-MoA-3 ALD Student Award Finalist Talk: Influence of Hydrocarbon Chain Length in Phenyl(Alkyl)trimethoxysilane Inhibitors on AS-ALD Selectivity: Comparison of Adsorption Mechanisms in Gas-phase and Liquid-phase**, ***Hae Lin Yang,*** *Minchan Kim,* Hanyang University, Korea; *Eun Chong Cho,* Sungkyunkwan University, Korea; *Seunghwan Lee, Beomseok Kim, Changhwa Jung, Hanjin Lim,* Samsung Electronics Co., Inc., Republic of Korea; *Jung-Hoon Lee, Youngkwon Kim,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea; *Jin-Seong Park,* Hanyang University, Korea

Area-selective atomic layer deposition (AS-ALD) has become a critical technique for precise material fabrication, particularly in complex nanoarchitectures. Achieving high selectivity in AS-ALD requires the strategic use of effective small molecular inhibitors (SMIs) to prevent undesired growth on non-target surfaces[1,2]. In this study, we investigated how variations in the hydrocarbon chain length (n = 1–6) of Phenyl(Alkyl)trimethoxysilane inhibitors influence their adsorption and precursor-blocking performance during the AS-ALD of vanadium dioxide (VO_2). To analyze the adsorption characteristics, we employed two different adsorption methods: (1) liquid-phase adsorption via spin-coating and (2) gas-phase adsorption by supplying vaporized SMIs into the chamber. The SMI-coated SiO_2 surfaces formed through liquid-phase adsorption exhibited highly similar characteristics, with water contact angle (WCA) variations within 5° among different SMIs. Furthermore, after 100 ALD cycles of VO_2 deposition, all samples demonstrated high selectivity above 90%, regardless of the SMI used. However, in the gas-phase adsorption process, significant differences were observed depending on the chain length. The WCA varied by more than 20°, indicating substantial surface property differences. Additionally, after 100 cycles, selectivity ranged from a maximum of 89.9% (n = 2) to a minimum of 4.5% (n = 6), revealing a significant disparity in selectivity. To elucidate these differences, we employed density functional theory calculations and random sequential adsorption simulations[3]. Experimental validation was conducted using WCA, X-ray photoelectron spectroscopy, X-ray fluorescence, and scanning electron microscopy. These findings highlight the importance of appropriate molecular characteristics and structures depending on the adsorption method and underscore the necessity of tailored molecular design to achieve optimal AS-ALD performance.

2:15pm **ALDALE-MoA-4 ALD Student Award Finalist Talk: Molecular Layer Deposition (MLD): A New Platform for Precision Engineering of Water Filtration Membranes**, ***Ruoke Cai,*** *Brian Welch, Tamar Segal-Peretz,* Technion Israel Institute of Technology, Israel

Molecular Layer Deposition (MLD) offers atomic-scale precision for fabricating organic and hybrid materials, yet its applications in membrane technology remains relatively underexplored. Nanofiltration (NF) and reverse osmosis (RO) are critical techniques in desalination and water purification, addressing the growing challenges of water scarcity. Here, we explore MLD as a new platform for fabricating polyamide-based filtration membranes, utilizing MLD precision for creating high-performance filtration membranes.

We developed MLD polyamide thin layer growth on top of porous ultrafiltration support through the integration of sacrificial layers. The resulting asymmetric structure is essential for the membranes' functionality. Trifunctional acid chlorides (i.e., trimesoyl chloride) and difunctional amines (i.e., m-phenylene diamine and piperazine) were employed as MLD precursors to form aromatic and semi-aromatic polyamides, yielding ultrathin, ultrasmooth RO and NF membranes, respectively. In-situ quartz crystal microbalance and ex-situ ellipsometry showed a sub-2 Å growth per cycle. This precise control over thickness and composition yielded high-performance membranes, with water permeability and salt rejection comparable to state-of-the-art commercial RO and NF membranes.

Our results demonstrate that MLD achieves sub-2 Å precision in polyamide growth, enabling controlled thickness and composition and comparable performance to commercial membranes. This highlights MLD's unique capability for molecular-level design, offering new avenues for advancing the science of thin-film fabrication.

2:30pm **ALDALE-MoA-5 ALD Student Award Finalist Talk: Diffusion Behavior Study for Vapor Phase Infiltration Using Quartz Crystal Microgravimetry and its Application in Energy Storage Materials**, ***Rongliang Shang,*** *Jin Xie,* ShanghaiTech University, China

Vapor phase infiltration (VPI), derived from atomic layer deposition (ALD), facilitates the growth of inorganic components into organic polymers, emerging as an effective technique for fabricating organic-inorganic hybrid materials. VPI involves prolonged exposure of gas-phase precursors (typically several minutes to hours), allowing their diffusion into porous substrates. However, the complexity of diffusion behavior during the VPI process presents challenges in studying diffusion kinetics, particularly for highly reactive precursor-polymer systems such as trimethylaluminum (TMA) and poly(ethylene oxide) (PEO). This limitation hinders the study of VPI kinetics in PEO systems.

In this work, we investigate the VPI process of TMA in PEO using in-situ quartz crystal microgravimetry (QCM), which enables measurement of diffusion behavior and kinetics with high temporal resolution (0.1 s). PEO film was spin-coated on the QCM crystal, and then sent to VPI. In a typical mono-pulse VPI process, TMA was pulsed into a reaction chamber, followed by prolonged exposure and then nitrogen purging. The mass of the film was recorded during the whole process.

QCM measurements indicated that the VPI process consists of two main regions: a rapid diffusion process, corresponding to the initial penetration of the precursor into the film, followed by a slower relaxation process, attributed to the ongoing chemical reaction. The equivalent diffusion coefficient (D_e) was estimated to be on the order of 10^{-9} cm^2/s at 100 °C. In multi-pulse VPI, the mass gain per cycle decreased with successive pulses, attributed to the reduction in available reactive sites and the reduction of diffusion coefficient. When water was introduced as a co-reactant in multi-cycle VPI processes, the formation of Al–O clusters further inhibited diffusion, shifting the process from reaction-limited to diffusion-limited behavior. Finally, VPI-modified PEO was used as solid polymer electrolytes (SPEs) for lithium metal batteries as a proof-of-concept, demonstrating enhanced mechanical properties, suppressed dendrite growth, and higher Coulombic efficiency (89.5% after 50 cycles vs. 60% for unmodified PEO).

This study provides a novel understanding of the VPI process for TMA in PEO, highlights the critical role of diffusion and reaction kinetics in determining material properties, and ultimately contributes to the development of next-generation materials for energy storage and beyond.

2:45pm **ALDALE-MoA-6 ALE Student Award Finalist Talk: Lateral Etching of 2D MoS_2 Crystalline Layers Using Sequential Ozone and Thionyl Chloride Exposures***, **Janine Sempel,*** University of Colorado at Boulder*; Taewook Nam,* Sejong University, Korea (Democratic People's Republic of)*; Tianyi Zhang, Jing Kong,* Massachusetts Institute of Technology*; Steven George,* University of Colorado at Boulder

Atomic layer controlled etching of 2D MoS_2 crystalline layers is important for the fabrication of MoS_2 channel transistors. Individual 2D MoS_2 layers must be removed to reduce MoS_2 multilayers to MoS_2 bilayers and monolayers. The removal of individual MoS_2 layers requires lateral etching in the 2D plane of each MoS_2 layer. In this study, the lateral etching of 2D MoS_2 crystalline layers was demonstrated using two sequential reactions for surface modification and volatile release of the modified layer. O_3 (ozone) was used for MoS_2 oxidation to MoO_3 and $SOCl_2$ (thionyl chloride) was used for the volatilization of MoO_3 as MoO_2Cl_2.

The studies were performed using high quality MoS_2 bilayers on silicon coupons. The etching of the 2D MoS_2 was examined by optical microscopy and atomic force microscopy (AFM) at 175°C. A decrease in the optical contrast of the MoS_2 bilayer during MoS_2 etching was visualized by optical microscopy. Etching was observed by AFM as triangular etch pits inside the 2D MoS_2 crystalline domains and removal of MoS_2 from the edge of 2D MoS_2 crystalline domains. The triangular etch pits and the gap between crystalline domains grew progressively versus number of etching cycles (Figure 1). The depth of the triangular etch pits was equal to one MoS_2 bilayer.

The AFM images were consistent with lateral etching at step edges of the 2D MoS_2 crystalline layer. The lateral etching could be quantified by going back to the same location after various numbers of etching cycles. The enlargement of the triangular etch pits versus number of etching cycles was "inside-out" lateral etching (Figure 2A). The loss of MoS_2 from the edge of 2D MoS_2 crystalline domains versus number of etching cycles was "outside-in" etching (Figure 2B). These AFM collocation experiments determined that "inside-out" and "outside-in" 2D lateral etching rates were equivalent at ~5 Å per etching cycle at 175°C (Figure 3). This lateral etch rate represents ~2 MoS_2 units removed at the step edge of the 2D MoS_2 layer.

3:00pm **ALDALE-MoA-7 ALE Student Award Finalist Talk: A Sustainable and Precise Solution to IGZO Etch Residual Challenges Using Transient-Assisted Processing (TAP)**, ***Atefeh Fathzadeh,*** KU Leuven and Imec, Belgium*; Philippe Bezard, Thierry Conard, Frank Holsteyns,* IMEC Belgium*; Stefan De Gendt,* KU Leuven and Imec, Belgium

The increasing demand for memory-intensive applications, such as AI, necessitates significant advancements in DRAM performance and power efficiency. A promising approach to address these challenges is the 2T0C (2 Transistors, 0 Capacitor) cell architecture, where the write transistor relies on a semiconductive oxide channel to minimize leakage, ensuring long retention times and low power consumption. Among candidate materials, $InGaZnO_4$ (IGZO) stands out due to its superior electrical properties. However, the etching process used for IGZO patterning can generate residues contributing to leakage. Superior device performance has been demonstrated using conventional plasma etching over ion-beam etching due to its ability to reduce these unwanted residues[1]. Among possible etchants, CH_4–based plasma allows the formation of volatile by-products such as $(CH_3)_3In$, $(CH_3)_3Ga$, and $(CH_3)_2Zn$. However, Ga_xO_y is slower to be etched than In_xO_y and ZnO. As a result the plasma-exposed surfaces become Ga-rich, leading to residue formations. Even Atomic Layer Etching (ALE), despite its excellent control capabilities, still exhibits Ga residues for CH_4/Ar mixture. Introducing Cl_2 to the process enables the formation of volatile $GaCl_3$, which enhances Ga removal. However, non-volatile $InCl_3$ and $ZnCl_2$ are also produced, requiring precise chlorine dosing to minimize residues. This presents a challenge even for ALE unless the different gases are separated into dedicated cycles- an approach that dramatically increases processing time, cost, and environmental impact.

Transient-Assisted Plasma Processing (TAP) provides a breakthrough solution to these challenges. TAP operates in controlled cycles, where reactive species are briefly injected into a carrier gas, creating a transient decrease in their concentration[2]. The plasma is ignited at the most convenient timing to ensure optimal ion over neutral ratio (similar to ALE) but also to control the nature of the formed species. This control over the dosage and timing of reactive gases enables balanced etching of different elements, ensuring uniform material removal, preserving surface composition and minimizing residues. Notably, TAP's benefits extend beyond IGZO, making it applicable to a wide range of materials and semiconductor applications[3–6].

This paper presents a scalable and sustainable IGZO patterning process that minimizes residues and gas consumption while achieving near-vertical profiles at 28 nm pitch—the tightest pitch enabled by 0.33 NA EUV lithography to ensure scalability, as illustrated in Figure 1. The demonstrated approach enables production-compatible processing times, with a linear control of the etched depth through the number of cycles,supporting the advancement of energy-efficient memory technologies.

Atomic Layer Etching
Room Samda Hall AB - Session ALE-MoA

ALD+ALE - Emerging ALE

Moderators: Silvia Armini, IMEC Belgium, **Huichan Seo**, SK Hynix

4:00pm **ALE-MoA-11 Revolutionizing Semiconductor Scaling with Atomic Layer Etch Pitch Splitting***, **Jonas Sundqvist**, Reza Jam, Robin Athle, Yoana Ilarionova, Asif Hassan, Intu Sharma, Amin Karimi,* AlixLabs, Sweden*; Fred Roozeboom,* AlixLabs, Netherlands*; Dmitry Suyatin,* AlixLabs, Sweden **INVITED**

We introduce Atomic Layer Etching Pitch Splitting (APS™), a new cost-effective patterning alternative to Self-Aligned Multi Patterning (SAMP) for realizing sub-20-nm features. APS combines atomic-level processes like Atomic Layer Etching (ALE) with existing production techniques, enabling selective etching without the need for the multiple deposition and etch steps required in SAMP. This results in exceptional precision and patterning accuracy, which is crucial for defining critical device features.

The feasibility of APS on silicon and gallium phosphide (GaP) nanowires was previously reported.[1,2] In this study, we apply APS to electron beam lithography (EBL) patterned lines on 300-mm silicon wafers. We achieve a half-pitch of 20 nm and critical dimensions (CDs) below 15 nm on both single-crystalline and amorphous silicon (a-Si) wafers, see Fig. 1. Additionally, when applied to GaP wafers, APS achieves CDs as small as 3 nm (Fig. 2). The layers created by APS can serve as universal split masks for further etching into various materials, including dielectrics, metals, and high-k dielectrics. Alternatively, these structures can be directly used to define critical features such as fins for FinFETs. In addition to the pitch, it is possible to control the CD and height of the fins. The APS process is selective towards different materials, making it a suitable for multi-stack device processing. The gentle nature of APS process minimizes damage to underlying materials, as shown by high-resolution transmission electron microscopy images, Fig. 2.

Unlike its counterparts, APS is free from pattern shrinkage, "bird's beak," tilting, and kinking,[3] and etch damage.[4] This makes APS a highly repeatable process with the potential for high yield and exceptional resolution, which is vital for future semiconductor technology. We estimate that APS may reduce wafer manufacturing costs and increasing throughput. This positions APS as a competitive and complementary alternative to established techniques like SAMP and multiple lithography-etch processes. Furthermore, using less process gases and eliminating several fabrication steps, APS meets industry goals for reduced resource consumption and CO_2 emissions.

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2. US Patent 11,424,130, Aug. 23, 2022.

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4. J. Sundqvist et al., SPIE 2025, paper 13429-28.

4:30pm **ALE-MoA-13 Exploring Atomic Layer Etching Behavior Differences in ZnO Crystallographic Planes and Surface Energy Analysis via DFT***, Jin Seong Park, **Ji Hyun Gwoen**, Hae Lin Yang, Min Chan Kim, Gyeong Min Jeong,* Hanyang University, Korea*; Cas Visser, Erwin Kessels,* Eindhoven University of Technology, The Netherlands

Oxide semiconductor thin films are widely studied for their high electron mobility, uniformity over large areas, and potential for low-temperature processing. These films can be deposited using various methods, including pulsed laser deposition (PLD), molecular beam epitaxy (MBE), chemical vapor deposition (CVD), and sputtering. However, as semiconductor scaling becomes more demanding, precise thickness control and high film quality are increasingly required. To address this, atomic layer processes (ALP), including atomic layer deposition (ALD) and atomic layer etching (ALE), have gained significant attention for their atomic-level precision.

While ALD research on oxide semiconductors has been active since the early 2000s, ALE studies have only gained momentum in the late 2010s and remain relatively limited. Most ALE research has focused on process development and reaction mechanisms, with less emphasis on the characteristics of ALE-processed films, an important aspect for advancing semiconductor technology. Further exploration of ALP, particularly ALE, is crucial for achieving ultra-high integration in semiconductor devices.

In this study, we analyzed the physical properties of ZnO thin films grown by ALD and those processed with both ALD and ALE (ALD+ALE), focusing on crystallinity. The etching behavior of ZnO during ALE was examined experimentally and further analyzed using density functional theory (DFT) simulations. X-ray diffraction (XRD) analysis revealed that the metastable (103) plane appears at a lower thickness in ALD+ALE ZnO films compared to ALD-only films. A significant reduction in the intensity of the (002) plane in ALD+ALE films indicated its preferential etching during ALE. DFT simulations supported this finding by calculating surface energy and adsorption energies of etching reactants. The etch per cycle (EPC) was determined as 0.68 Å/cycle for the (002) plane and 0.53 Å/cycle for the (103) plane, further confirming the preferential etching of the (002) plane.

By integrating DFT simulations with experimental results, we provide a predictive approach to understanding etching behavior. This methodology can be extended beyond ZnO to analyze ALE behavior in other oxide semiconductors, offering valuable insights for future semiconductor processing advancements.

4:45pm **ALE-MoA-14 Investigation of Plasma ALD and ALE of Al_2O_3 in Nanoscale Structures: Towards Corner Lithography at the sub-20 nm Scale***, **Nicholas J. Chittock**,* Oxford Instruments Plasma Technology, UK*; Erwin Berenschot, Niels Tas, Melissa J. Goodwin,* University of Twente, Netherlands*; Marcel A. Verheijen,* Eurofins Materials Science, Netherlands*; Meghali Chopra, Yang Ban,* Sandbox Semiconductor*; Erwin Kessels, Adriaan J.M. Mackus,* Eindhoven University of Technology, Netherlands

Alternative techniques to photolithography are required to facilitate fabrication of 3D nanoscale structures. Corner lithography (CL) is a technique for patterning 3D structures at the wafer scale, that avoids the use of multiple photolithography steps but is limited to features > 20 nm.[1,2] CL is achieved by performing deposition followed by etching, which selectively deposits material only in concave corners. ALD and ALE are perhaps ideal candidates for sub-20 nm CL due to their precise thickness control combined with conformal and uniform deposition and etching, respectively.

In this work, plasma ALD and plasma isotropic ALE of Al_2O_3 are employed on a 3D structure to demonstrate CL at the sub-20 nm scale. Studying the conformal deposition and etching around corners in nanoscale 3D structures provides insight into growth and etch behaviour in these geometries, which can be useful for many different applications (e.g. GaaFET, DRAM, nanoparticle coating). To confirm the isotropic nature of the plasma processes, a 2 nm Al_2O_3 film is deposited on the 3D structure by combining 5 nm of ALD and 3 nm of ALE. Analysis of TEM images post ALD and ALE show that the planar regions of the structure are coated in 2 nm of Al_2O_3. In contrast, a thicker film is observed in the corners compared to the planar regions. By exploiting the enhanced deposition in the corner from ALD, CL is demonstrated by performing 5 nm of ALD and 5 nm of ALE. Post ALD and ALE TEM analysis shows that a ~5 nm thick film is deposited only in the concave corners. The successful demonstration of CL by combining ALD and ALE highlights their utility for fabricating 3D structures at the nm-scale without the use of multiple photolithography steps. In future work, the Al_2O_3 in the corner could then be used as a structural part of a device, or as a mask for further CL processing.[1,2]

1. Jonker, D., *et al,*. (2024). *Electrochemical Sensing with Spatially Patterned Pt Octahedra Electrodes*. Advanced Materials Technologies, 9(5).
2. Ni, S., *et al,*. (2020). Wafer-scale 3D shaping of high aspect ratio structures by multistep plasma etching and corner lithography. Microsystems & Nanoengineering, 6(1), 25.

5:00pm **ALE-MoA-15 Optimizing EUV Etching with In-Situ Atomic Processing: Where and Why?***, **Philippe Bezard**,* IMEC Belgium*; Atefeh Fathzadeh,* KU Leuven and Imec, Belgium

As pattern dimensions shrink with each new manufacturing node, the thickness of many sacrificial patterning stack layers also decreases. This reduction benefits atomic processing by shortening processing time, a key concern in Atomic Layer Etching (ALE). However, a critical question arises: which process steps should adopt atomic processing first, and which should avoid it?

Additionally, the latest etch chambers now offer in-situ PEALD capabilities, enabling fully in-situ spacer-assisted patterning.

This paper explores how atomic processing techniques—such as PE-ALE, PE-ALD, and Transient Assisted Processing (TAP)—can extend the capabilities of conventional etching (RIE) in EUV lithography era. Using a 14 nm pitch Self-Aligned Double Patterning flow as a case study, we demonstrate how TAP and in-situ PEALD enable simplifications. We then compare ALE, TAP, and RIE across key steps (descum, core etching, spacer deposition, core pull) in terms of roughness, processing time, sustainability (gas and energy consumption), and fundamental limitations. While ALE and TAP significantly outperformed RIE in descum and core etching, evaluating their impact on sustainability and throughput revealed complex and interesting trade-offs due to unique process flow simplifications enabled by these techniques.

Monday Evening, June 23, 2025

ALD Fundamentals
Room Event Hall - Session AF-MoP

ALD Fundamentals Poster Session

AF-MoP-1 Atomic Layer Deposition of P-type Oxide Semiconductor Thin Films Using a Novel Precursor for Transistor Applications

__Sol-Hee Jo__, Jung-Hoon Lee, Jimin Seo, Bo Keun Park, Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

P-type oxide semiconductors are challenging to fabricate with high performance due to their low carrier mobility and concentration, unlike n-type oxide semiconductors. Despite these limitations, the development of p-type oxide semiconductors with reliable electrical performance is essential in the fields of Complementary Metal-Oxide-Semiconductor (CMOS) circuits, high-resolution displays, and monolithic three-dimensional (3D) integration technologies. We successfully deposited tin monoxide (SnO) by atomic layer deposition (ALD) using a novel precursor, and H_2O as a reactant. The SnO films exhibited an optical bandgap of ~ 2.5 eV and a refractive index of 2.4 or higher, which are typical optical properties of SnO. We confirmed that there were almost no impurities through X-ray photoelectron spectroscopy (XPS) measurement and the O/Sn ratio was ~ 1.0. Consequently, our experimental results showed that the novel Sn precursor is suitable for the ALD process. In addition, a p-type oxide semiconductor was applied as the channel layer in a thin-film transistor (TFT), resulting in the fabrication of a p-type oxide semiconductor TFT. These experimental results indicate that stable p-type devices can be fabricated and applied to future applications.

AF-MoP-2 Silicon Nitride Ald Process Using Diiodosilane and Hydrazine for Low Temperature Deposition

__Hayato Murata__, Takuya Yoshikawa, Yoshifumi Wada, Hideharu Shimizu, Taiyo Nippon Sanso Corporation, Japan

High quality ALD silicon nitride (SiN) is required for advanced device structure complexity. Especially, there is the demand for SiN films that are resistant to wet HF at deposition temperature below 500℃. Therefore, researchers around the world are studied silicon precursors and nitriding agents recently. For example, nitriding agent as high purity hydrazine (N_2H_4) is a promising nitrogen source for low temperature ALD nitride process due to its high reactivity [1-2].

Although we demonstrated SiN ALD using Si_2Cl_6 (hexachlorodisilane, HCDS) and N_2H_4 at 450℃, wet etching rate (WER) in dilute hydrofluoric acid (100:1 HF) was 150 Å/min. In this study, employing SiH_2I_2 (diiodosilane, DIS) instead of HCDS, we succeeded forming lower-WER SiN film at 450℃.

SiN ALD process was experimentally evaluated by delivering DCS/N_2H_4 or DCS/NH_3 to a hot-wall tubular reactor. SiN ALD using DIS/N_2H_4 or DIS/NH_3 were formed at 450-600℃.

In these results, SiN ALD using DIS/N_2H_4 were demonstrated even at 450℃ although SiN ALD using DIS/NH_3 were unable to form thin films below 550℃.GPCs (growth per cycle) in DIS/N_2H_4 ALD were found to be 0.11-0.42 Å/cycle while those in DIS/NH_3 ALD were 0.26 Å/cycle at 600℃. These results indicate that N_2H_4, as higher reactive nitriding source than NH_3, has an effect on formation of SiN film at lower temperature.

In addition, WER in 100:1 HF of DIS/N_2H_4 film at 450-550℃ was 92-12 Å/min. The WER of DIS/N_2H_4 film was lower than that of HCDS/N_2H_4 film. These indicates that the iodine atoms included in the DIS adsorbed on the substrate are readily removed during the nitriding process, since Si-I bond dissociation energy (E_d) is lower than that of Si-Cl (E_d of Si-I: 274 kJ/mol, E_d of Si-Cl: 392 kJ/mol). Thought phenomenon of N_2H_4 removing halogen through stronger nitridation than NH_3 is overserved [3], it is expected that the chlorine atoms in the absorbed HCDS remains as impurities in the SiN film. Therefore, the SiN film quality of DIS/N_2H_4 was superior to that of HCDS/N_2H_4.

Thus, we concluded that DIS/N_2H_4 is very promising precursor and nitriding agent for ALD with high reactivity at low temperature and that DIS/N_2H_4 is practical option for ALD process development to be satisfied with both throughput and SiN film quality.

[1] D. Alvarez et al., PRiME2020, G02-1668 (2020).

[2] H. Murata et al., ALD/ALE2023, AF-MoP-6 (2023).

[3] H. Murata et al., TAIYO NIPPON SANSO Technical Report, No.39 (2020).

AF-MoP-3 Characterization of Novel Precursors for Improved ALD Performance in HfO_2 Films

__Dahyun Lee__, Hohoon Kim, Sejin Jang, Seonah Kim, Dong-geun Lee, Merck KGaA, Darmstadt, Republic of Korea*; Khang Ngo, Randall Higuchi,* Merck KGaA, Darmstadt

In atomic layer deposition (ALD), the selection of precursors is crucial, as they significantly influence film quality and the formation of thin films. It has been reported that the electrical characteristics of HfO_2 films improve when deposited at higher temperatures, creating a strong demand for Hf precursors that exhibit high thermal stability to facilitate high-temperature ALD of HfO_2. Currently, widely used precursors such as $CpZr(NMe_2)_3$ and $CpHf(NMe_2)_3$ (where Me = methyl and Cp = cyclopentadienyl) have limitations that have become evident as equipment and processes have evolved. Notably, $CpHf(NMe_2)_3$ exhibits a clear sign of thermal decomposition at 350℃. To address these challenges, we have designed a new series of precursors, termed the Helia series, which incorporates a Cp-based ligand. Experimental results demonstrate that the Helia series precursors possess superior thermal stability and reactivity, offering enhanced step coverage compared to conventional $CpHf(NMe_2)_3$ precursors, along with a wider ALD window. Specifically, the Helia series precursors have a wider ALD window than $CpHf(NMe_2)_3$, and unlike $CpHf(NMe_2)_3$, Helia-02 maintains an ALD window above 350℃. These findings indicate that the Helia series precursors not only outperform traditional materials but also hold great potential for advancing high-k dielectric applications. This poster discusses the development and performance evaluation of the Helia series precursors.

AF-MoP-4 Effect of Impurities in Trimethylaluminum on Conformality of Al_2O_3 Thin Film on Patterned Substrate Grown by ALD

__Shuya Ikemura__, Kohei Iwanaga, TOSOH Corporation, Japan

Aluminum oxide (Al_2O_3) is an important dielectric material for various applications including surface passivation, dynamic random-access memory (DRAM) and gate dielectric in complementary metal-oxide-semiconductors (CMOS) [1-3]. The trimethylaluminum (TMA) is one of the most studied precursor for producing Al_2O_3 films. Impurities in TMA with semiconductor grade seem to have been managed by mainly trace metal analysis. We focused on the impurities which are not precisely detected by the trace metal analysis and found that controlling their concentration to a certain level surprisingly affects the conformality of deposited Al_2O_3 films.

Two types of TMA precursors, [**TMA-1**] and [**TMA-2**], were prepared with different concentration of impurities. **TMA-1** contains the lower concentration of the impurities than **TMA-2**. Al_2O_3 thin films were deposited using each TMA precursor on line-and-space (L/S) patterned SiO_2 substrates with the aspect ratio of 20 using atomic layer deposition (ALD) apparatus. TMA was delivered by a self-evaporation method to an ALD reactor chamber with the assistance of Ar carrier gas. O_3 gas was also introduced as the oxygen source. In addition, diluent Ar gas was added. The atomic composition of the films was analyzed by means of X-ray photoelectron spectroscopy (XPS) after Ar^+ sputtering. Transmission electron microscope (TEM) was used to characterize film conformality.

Cross-sectional TEM images at the L/S pattern area demonstrated excellent step coverage of 96.5% for the film deposited utilizing **TMA-1** but smaller step coverage of 91.7% for that deposited utilizing **TMA-2** although the atomic composition of two samples were estimated to be no difference from the XPS measurements of the films deposited on planar substrates.

We have achieved to improve the Al_2O_3 film conformality by decreasing the impurities in TMA.

References

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AF-MoP-5 Thermolysis of Silicon Precursors for High-Temperature Atomic Layer Deposition Processes

__Tanzia Chowdhury__, Okhyeon Kim, Hye-Lee Kim, Sejong University, Republic of Korea*; Jung Woo Park,* Hansol Chemical Co., Ltd., Republic of Korea*; Won-Jun Lee,* Sejong University, Republic of Korea

The success of the atomic layer deposition (ALD) process is highly dependent on precursor selection, as only certain precursors are suitable for a given ALD process. While low process temperature is critical for temperature-sensitive devices, high-temperature ALD processes are often preferred for memory devices, such as 3D NAND flash. Elevated ALD process temperatures can improve thin film properties in such devices, including leakage current and wet etch rate [1]. High-temperature processes are typically performed in hot-wall reactors, where precursors are exposed to high temperatures for extended periods. Therefore, the thermal stability of the precursor is akey factor in enabling such processes. In this work, we investigate the thermolysis reactions of various silicon precursors using density functional theory (DFT) calculations for ALD of silicon oxide (SiO_2) and nitride.DFTserves as an effective tool for screening precursors. The selected silicon precursors include aminosilanes, chlorosilanes with Si–Si bonds, and heteroleptic compounds. Silicon tetrachloride ($SiCl_4$) was also studied as a reference due to it being the most basic silicon precursor that had an activation energy of 4.92 eV for thermolysis. The thermal stability of these precursors, predicted by DFT, was validated by the maximum ALD temperature determined experimentally. $Si(NMe_2)_3H$ was the most stable among the aminosilane precursors studied, with an activation energy of 2.49 eV. DFT also predicted that CH_3SiCl_3had sufficient thermal stability with an activation energy of 3.40 eV. Experimental results showed that the maximum temperatures for SiO_2 ALD were 750 °C for CH_3SiCl_3 and 600 °C for $Si(NMe_2)_3H$, which were consistent with their respective thermolysis predictions from DFT. This work demonstrates that DFT can effectively predict the thermal stability of ALD precursors, which will accelerate the selection of suitable precursors, especially athigh process temperatures.

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AF-MoP-6 On an Initial Incubation Process of Thermal ALD Pt on ALD Al_2O_3 Measured by Temperature Stabilized In-line QCM

Masafumi Kumano, Micro System Integration Center, Tohoku University, Japan; *Makoto Shimizu,* Graduate School of Engineering, Department of Mechanical Systems Engineering, Tohoku University, Japan; *Takuma Yamamoto,* Graduate School of Engineering, Department of Mechanical Engineering, Tohoku University, Japan; *Shuji Tanaka,* Graduate School of Engineering, Department of Robotics, Japan

The initial process of a thermal ALD of Pt, with precursor $MeCpPtMe_3$ (abbr. as CpPt) and reactant O_2, on an ALD Al_2O_3 surface was monitored by an in-line QCM. A crystal with Tturnover of 285ᴼC or 240 ᴼC was used, and temperature profile around the crystal was optimized for use in a wide temperature range of 200-285ᴼC. A Quartz glass tube reactor of 300mm (L) × 40mm (D) was used. Reactant gases O_2 and H_2O were supplied by a measuring bottle of $10cm^3$ capacity, which limits the number of injected molecules to $2×10^{13}$.

Fig. 1 shows QCM profiles derived from 40 cycles of CpPt /O_2 at 265ᴼC, employing the crystal with Tturnoverof 285ᴼC (Inficon 1060). Prior to this, AlOH surface is prepared by 40 cycles of TMA/H_2O.

At the 1st CpPt injection, a rapid frequency increase, a = 1.83Hz, appears as found in Fig. 2. Utilizing the step frequency change in TMA/H_2O cycle, k = 3.8Hz, and an atomic mass of -Al-OH unit on the surface[1)], q = 44, a corresponding atomic mass reduction Δm (CpPt n = 1) is estimated as $(a/k)q$ = 21. Before the 1st CpPt injection, ideally no atomic Pt bond exists on the initial surface of the Al_2O_3 layer. Thus, a suggests the removal of a surface bound OH by CpPt, resulting in the retention of the same number of vacancies as the original AlOH sites. A frequency decrease, b = 0.48Hz, emerges subsequent to the peak of a, which is possibly related to a refill process of the vacancy with OH molecules and/or contaminated O_2 from the upper stream region of the reactor.

At the 1st O_2 injection, a quick frequency drop, c = 1.42Hz, is observed. The atomic mass increase Δm (O_2 n = 1) is $(c/k)q$ = 16.4, which suggests the adsorption of O and OH. Subsequent CpPt injection induced both PtO_x nucleation and OH removal on the AlOH surface. The net frequency difference during the first cycle, d (n = 1), is 0.06Hz. Refer to frequency decrease in the stabilized 40th cycle of CpPt (= 15.8Hz/cycle), the mass gain in the 1st cycle, i.e. Pt nucleation, is estimated as 0.38% of full coverage Pt surface. In the 2nd CpPt cycle, d (n = 2) is 0.43Hz, and the mass gain increases by 0.43/15.8 = 2.72% .

As the cycle repeats, a decreases and becomes almost zero at the 12th CpPt injection, indicating that no AlOH unit remains on the surface. The accumulated value of d from the 1st to 12th cycles is 14.62Hz, close to 15.8Hz of the frequency gain in the 40th CpPt cycle. In conclusion, the cycle step where no AlOH remains on the surface and the frequency increase a becomes zero can be defined as the end point of island growth.

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AF-MoP-7 Oxide Film ALD Using Oh Radicals Generated by Mixing Pure Ozone Gas with Hydrogen-Included Molecular Gas Over 200ᴼC

Naoto Kameda, MEIDENSHA Corp., Japan; *Kenichi Uehara, Shigeo Yasuhara,* Japan Advanced Chemicals Corp., Japan; *Soichiro Motoda, Tetsuya Nishiguchi,* MEIDEN NANOPROCESS INNOVATIIONS Inc., Japan

For the deposition of oxide films using ALD, various oxidizing gases such as water, oxygen plasma, and ozone are used. These oxidizing gases are selected according to the required film qualities, which are coverage of trenches with high aspect ratios, electrical properties, and high productivity by batch processing.

We have reported the quality of oxide films such as Al_2O_3 by ALD using high-concentration pure ozone gas (≥80 vol%) as the oxidizing source [1].Pure ozone gas has a longer half-life in the gas phase than conventional ozone gas (<10 vol%), so we have confirmed that Al_2O_3 can be formed in trenches with high aspect ratio(> 1500) [2]. Furthermore, pure ozone can produce OH radicals, which have higher oxidation reactivity than ozone, by mixing with ethylene gas (OER method). It has been confirmed that ALD using OER (OER-ALD) has improved film quality such as GPC and insulation of Al_2O_3 films at 150°C or less compared to ALD using pure ozone and is equivalent to oxygen plasma [1]. However, the range of applicable temperature of OER-ALD is lower than the ALD window temperature range (≥200°C) of many precursor species. In the case of OER-ALD, ozone and ethylene are highly reactive even at low temperatures, so gas mixing is required near the substrate using a shower head[3]. Increasing the substrate temperature requires more precise mm range subtle gap control between the shower head and the substrate due to increased reactivity of the gases involved and the short lifetime of radicals in-situ generated. Therefore, it becomes difficult to adjust the dimensions of the OER-ALD equipment configuration.

In this presentation, we will discuss the method of the OH radical generation using pure ozone gas and ethylene alternative gas above 200°C. This gas has lower reactivity with ozone than ethylene and must contain hydrogen atom in the molecular structure. Among the several gas species candidates to replace ethylene, water vapor (H_2O) is expected to be effective in reducing carbon residues in the film because it does not contain carbon. We will demonstrate the HfO_2 film qualities using this OH radical ALD.

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AF-MoP-8 Novel Indium Precursor with Improved Physical Properties and ALD Window for Atomic Layer Deposition of Indium Oxide

Randall Higuchi, *Khang Ngo,* Merck KGaA, Darmstadt; *Lukas Mai, Paul Mehlmann,* Merck KGaA, Darmstadt, Germany; *Daniel Moser, Bhushan Zope,* Merck KGaA, Darmstadt; *Holger Heil,* Merck KGaA, Darmstadt, Germany

Indium gallium zinc oxide (IGZO) is an important film for thin-film transistors (TFT) due to its excellent electrical and optical properties. (1) Precursor selection is crucial for ALD of the separate indium, gallium and zinc precursors as they all need to be deposited at the same temperature. Currently trimethylindium (TMI) is commonly used due to having a similar ALD window as other common precursors for gallium and zinc oxide. (2) TMI has limitations as a precursor because it is a solid at room temperature as well as being pyrophoric.

A new precursor has been developed for indium oxide deposition that is non-pyrophoric and a liquid at room temperature. Through thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) we confirmed liquid phase at room temp, vapor pressure (1 Torr at 40C) and decomposition temperature showing good performance for an ALD precursor. Deposition testing was completed using this new In precursor and ozone showing an ALD window for In_2O_3 from 275C-325C. Linear growth was observed and a dep rate of 0.7A/cycle was found in the ALD window. The findings show a promising Indium precursor for IGZO deposition.

AF-MoP-9 Atomistic Modeling Methodologies for Atomic Layer Deposition*, **Yong-Ju Kang**,* Synopsys Korea Inc., Republic of Korea*; Suresh Kondati Natarajan,* Synopsys Inc., Denmark*; Rafshan Ul Atik,* Synopsys India Pvt. Ltd., India*; Jess Wellendorf, Søren Smidstrup,* Synopsys Denmark ApS, Denmark

Atomic layer deposition (ALD) is a thin-film deposition method, which grows one atomic layer sequentially with precise control of thickness and precursor chemistry. It means that understanding atomistic nature of precursors and their surface reactions became more important than other conventional chemical vapor deposition method. Atomistic simulation methodologies are powerful tools for analyzing surface reactions and elucidating complex dynamical processes of ALD at atomic scale, given process conditions. In this work, we will present various atomistic modeling approaches for atomic layer deposition (ALD) by using QuantumATK software [1,2] developed by Synopsys. In thermochemical analysis, Gibbs free energy of surface reactions calculated using the density functional theory (DFT) and the energy of reactants and products compared according to process temperature and partial pressure to find favorable surface reactions. Using the kinetic approach, deposition rate was obtained by calculating activation barrier of surface reaction and solving equation of time dependent surface coverage. In dynamical approach of reactions, molecular dynamic simulations impacting precursor molecule onto the film surface performed to understand dynamical process of surface reaction. In this approach, with generation of explicit atomic structure of the surface and reaction products, reaction properties such as probabilities of events and sticking coefficient were extracted by using classical or machine learned force fields [3,4].

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AF-MoP-10 Unraveling the Influence of Substrate Surface and Temperature on Microstructural Evolution of Crystalline MoS_2 in Atomic Layer Deposition*, **Seung Ho Ryu**, Seong Keun Kim,* Korea University, Republic of Korea

In this study, we examine the atomic layer deposition (ALD) growth behavior of crystalline MoS_2 films on various substrates, including SiO_2, mica, and Al_2O_3, at deposition temperatures of ≥ 650 °C. The results show that the substrate surface energy and temperature significantly influences the MoS_2 growth dynamics, affecting the layer nucleation, surface morphology, and growth rate. High temperatures generally favor a stepwise growth pattern with a step size of one monolayer; however, the substrate surface energy distinctly affects the grain size and crystallinity. MoS_2 growth on mica, which has the lowest surface energy, results in larger, highly crystalline triangular grains and enables multilayer growth, whereas Al_2O_3, which has the highest surface energy, produces smaller, less crystalline grains. Temperature elevation further enhances the lateral grain expansion and crystallinity, especially on Al_2O_3 substrates with higher surface energies. By tailoring the substrate surface and deposition temperature, the key pathways for optimizing MoS_2 ALD growth are highlighted with the aim of enhancing the film uniformity and quality for nanoelectronic applications. This study provides critical insights into the ALD parameters that govern the growth of crystalline MoS2 with implications for advancing scalable, high-performance 2D materials.

AF-MoP-11 Novel Alkoxy-Bridged Silicon Precursor for Plasma Enhanced Chemical Vapor Deposition of Low-k SiCOH Spacer Thin Film*, **Jongryul Park**, Sooyong Jung, Seokhee Shin, Yongjoo Park,* SK Trichem, Republic of Korea

Low dielectric constant(low-k) materials are essential for various applications due to their unique material properties and play a broad role in semiconductor devices. Dynamic random access memory(DRAM) has continued to shrink to gain higher data storage capabilities. At the same time, its manufacturing will face many challenges at advanced technology node, such as the decreased retention time and the insufficient sensing margin. Reducingthe parasitic capacitance between the bit line(BL) and the storage contact is one method to block the leakage of the cell is the solution to make up the decreasing of retention time and solve the insufficient sensing margin.[1] To prevent the increase of parasitic capacitance as the cell sizes decrease, a low-k material be used between the BL and the storage contact. In addition, it should have high density and good resistance properties to etching for subsequent processes.

Previous studies have investigated the properties of the silicon oxycarbonitride(SiOCN, k=5.2). However, they are not suitable for low-k materials due to their relatively high dielectric constant.[2]

In this study, a new alkoxy-bridged silicone precursor with low viscosity and good volatility was developed to form a SiCOH-based low-k spacer materials. The SiCOH thin film was formed through a PECVD process using O_2 plasma at 400℃ on the new silicon precursor. The characteristics of the formed thin film were confirmed through the evaluation of k-value, reflective index(R.I.), density and wet etch rate. It has the characteristics of a low-k spacer material suitable for application to next-generation semiconductor devices.

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AF-MoP-12 High Temperature Atomic Layer Deposition of Hafnium Oxide Film using Novel Liquid Hf Precursor Deposition*, **Kim Daeyeong**,* SK Trichem, Republic of Korea*; Oh Jieun, Lee Seo-Hyun, Kim Woo Hee Kim,* Hanyang University, Korea*; Park Yongjoo,* SK Trichem, Republic of Korea

Hafnium oxide (HfO_2) is a high-k dielectric material that has contributed to the scaling of memory and logic devices, and is also explored for storage class memories. As memory devices become more complex, conformal deposition of HfO_2 films on nano-sized 3D structures is increasingly important. Deposition temperature plays a key role in achieving high-quality films, as low-temperature processes may hinder property preservation due to thermal budget constraints in 3D integration. Although low-temperature deposition is desirable, high-temperature processing is crucial for optimizing the HfO_2 film’s high-k properties. Therefore, a process capable of depositing HfO_2 films at elevated temperatures is necessary.[1]

In ALD of HfO_2, various precursors have been explored, with thermal stability being crucial to achieving high-quality films. Metal halides like $HfCl_4$ offer excellent stability but produce corrosive by-products and introduce chlorine impurities. Alkylamides like $Hf(NEtMe)_4$ provide high growth rates but suffer from limited thermal stability and impurity incorporation. In particular, $(CpR)Hf(NMe)_3$ (R = H, Me) provides an ALD window of 250–350 °C for HfO_2 growth, offering good crystallinity and stability at this temperature range. However, the relatively low ALD window temperature makes it unsuitable for high-temperature processes. [2]

Herein, we developed a novel liquid hafnium precursor with low viscosity, good volatility, and thermal stability. Using this precursor, we were able to achieve a high-temperature ALD window for HfO_2, ranging from 300 to 400 °C. The growth per cycle (GPC) during this process was 0.7 Å/cycle. X-ray reflectivity (XRR) was used to measure film density, and grazing incidence X-ray diffraction (GIXRD) was employed to investigate the crystalline structure of the films. Electrical characterization of the films was performed through leakage current density-electric field (J-E), interface trap density (D_{it}), and capacitance-voltage (C-V) measurements.

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AF-MoP-13 Analysis of Plasma Characteristics and Substrate Damage Using a Dual-Frequency PE-ALD Process with 13.56 MHz and 100 MHz*, **Da-Eun Bae**, Hyung Min Kim, Jae Yeon Han, Jae Ho Choi, Jae Hack Jeong,* CN1 Co., Ltd., Republic of Korea

Compared to other deposition methods, ALD processes are widely applied in mass production due to their high step coverage, atomic-level thickness control, and uniform film deposition. However, thermal ALD requires high temperature (>400℃) to achieve high-quality properties when depositing nitride films such as SiN_x, AlN, TiN, and TaN. This has led to the application of plasma-enhanced ALD (PE-ALD). It offers enhanced reactivity and higher deposition rates, even at low temperatures. However, it also presents several technical challenges, including plasma-induced substrate damage and limited step coverage in increasingly thinner and deeper structures. To address these issues, the use of very high frequency (VHF) plasma is required.

We have studied plasma characteristics and substrate damage during the deposition of silicon nitride (SiN_x) films using a PE-ALD process at low temperatures (≤200°C) with very high-frequency plasma. In this process, the use of 100 MHz alone resulted in insufficient discharge and poor uniformity due to standing wave effects, and thus a dual-frequency approach was applied by combining 13.56 MHz with 100 MHz to improve plasma stability. Plasma characteristics, such as electron temperature (T_e), ion flux, and ion density, were characterized using a Langmuir probe. Plasma-induced substrate damage was examined using TEM, and film thickness and refractive index (RI) were measured using ellipsometry.

Acknowledgments

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AF-MoP-14 High-Temperature, High-Growth Rate Atomic Layer Deposition of Silicon Oxide Thin Films Using a Novel Precursor

Changgyu Kim, *Mi-Soo Kim, Okhyeon Kim, Jihwan Lee,* Sejong University, Republic of Korea*; Seunggyun Hong, Byung-Kwan Kim, Jin Sik Kim, Wonyong Koh,* UP Chemical Co., Ltd., Republic of Korea*; Hye-Lee Kim, Won-Jun Lee,* Sejong University, Republic of Korea

As the number of layers in three-dimensional (3D) vertical NAND devices continues to increase, so does the aspect ratio of the channel holes. Atomic layer deposition (ALD) is essential to form dielectric thin films with excellent step coverage in these high-aspect-ratio structures. Since higher process temperature improves the physical and electrical properties of ALD dielectric films, there is a growing demand for high-temperature thermal ALD processes in 3D NAND fabrication. In a previous study, we demonstrated the feasibility of a novel silicon precursor, HTS-1, for high-temperature ALD applications [1]. We achieved high growth rates exceeding 2.5 Å/cycle at 600–800°C, more than two times higher than $SiH(NMe_2)_3$. We also observed excellent step coverage at 750°C. However, the maximum temperature for SiO_2 ALD using HTS-1 was not determined, and the detailed investigation of film properties over different process temperatures was lacking. In this work, we systematically investigated the SiO_2 film deposited by alternating exposure to HTS-1 and ozone at different temperatures. First, we determined the saturation doses of precursor and ozone. Then, we analyzed the growth rate as a function of deposition temperature to determine the maximum ALD temperature, which was confirmed by evaluating the step coverage at different deposition temperatures. Finally, we analyzed the physical and electrical properties of the deposited film at different temperatures, including composition, impurities, shrinkage, and leakage current. The properties of SiO_2 films prepared with HTS-1 were also compared with those prepared with $SiH(NMe_2)_3$, providing insight into the advantages of the novel precursor for high-temperature ALD.

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AF-MoP-15 Development of New Group 3 Metal and Lanthanide Precursors with Volatility and Thermal Stability for ALD

Yongmin Go, *Bo Keun Park,* 141, Gajeong-ro, Yuseong-gu, Republic of Korea

Group 3 metals and lanthanide metal oxides are known for their high permittivity and wide band gaps, making them ideal materials for MOSFETs and DRAMs. Various thin film deposition techniques are employed in the production of metal oxide films, among which atomic layer deposition (ALD) stands out due to its ability to produce high-quality films, self-limiting growth, and precise control over film thickness.

To carry out the ALD process, the use of ALD precursors is essential. These precursors must possess volatility, thermal stability, and high reactivity with the reactants, making the development of new ALD precursors with these characteristics of great importance. However, the size of Group 3 metals varies depending on the specific metal, and an appropriate ligand must be used.

In this work, we have developed a new Group 3 metal novel ALD precursor and analyzed its suitability for use as an ALD precursor. The characteristics of the newly synthesized Group 3 metal precursors were confirmed through various analysis methods, such as NMR, EA, TGA, and vapor pressure. Among them, the new lanthanum precursor was confirmed to form a thin film through the ALD deposition process.

Additionally, we proposed an ALD process for La_2O_3 using the new lanthanum precursor and compared it to the commonly used $La(^iPrCp)_3$ precursor. By processing at high temperatures with the new lanthanum precursor, we successfully obtained La_2O_3 thin films with excellent crystallinity, higher density, and improved leakage current characteristics. These results suggest that the new precursors we developed are promising candidates for the formation of metal oxide thin films through ALD and deposition processes.

AF-MoP-16 Exploring Ultrathin SnO_2 Films via Atomic Layer Deposition for Facilitating the Formation of the Rutile TiO_2 Phase

*InHwan Baek, **YooHyeon Jung**, InHong Hwang,* Inha University, Republic of Korea

Tin dioxide (SnO_2) is a chemically stable and conductive oxide material that is currently being investigated for potential application in DRAM electrodes, driven by the increasing demand for semiconductor scaling. The practical limitations of increasing capacitance by continuously reducing the thickness of the dielectric film have led to a growing need for new dielectric materials. Among these materials, rutile-TiO_2 ($k > 100$) is particularly noteworthy. However, synthesizing a high-k rutile phase requires high-temperature processes exceeding 700 ˚C, which are incompatible with the CMOS process. To overcome this challenge, the rutile structure of SnO_2 can be employed as a seed layer, enabling the low-temperature synthesis of rutile TiO_2 via local epitaxy. In this study, we developed a method for synthesizing rutile SnO_2 by atomic layer deposition (ALD) using H_2O_2 as co-reactant, which facilitates more effective ligand removal from Sn precursor by enhanced byproduct exchange. The resulting films exhibit superior physical, chemical, and electrical properties, ensuring their suitability for advanced dielectric integration. This approach eliminated the need for ozone, which has the potential to oxidize the DRAM bottom electrodes. We believe that the SnO_2 seeds layer can be utilized to fabricate the next generation of dielectric films, rutile TiO_2, regardless of bottom electrode type.Acknowledgment: This work was supported by Korea Institute for Advancement of Technology(KIAT) grant funded by the Korea Government(MOTIE) (RS-2024-00409639, HRD Program for Industrial Innovation)

AF-MoP-17 Novel ALD Indium Precursor for In_2O_3 Thin Film Fabrication

***Dong Hyeon Bang**, Bo Keun Park, Yongmin Go, Sunyoung Shin, Ji Yeon Ryu,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Indium oxide thin films are utilized in various applications, including catalysis, displays, gas sensors, and transistors. To fabricate these metal oxide thin films, vapor-phase deposition techniques such as Metal-Organic Chemical Vapor Deposition (MOCVD), Physical Vapor Deposition (PVD), and Atomic Layer Deposition (ALD) are commonly employed. Among these techniques, ALD offers the advantage of precise control over film thickness by adjusting the number of deposition cycles. It also enables the formation of high-quality thin films with low contamination compared to other deposition methods. To leverage these advantages of ALD, precursors with high volatility and thermal stability are required. In this study, we synthesized novel heteroleptic indium precursors by introducing thermally stable enaminolate ligands to $InMe_2Cl$. The molecular structures of compounds **1**–**3** were confirmed using X-ray crystallography (XRD), which revealed that all three compounds possess dimeric structures and adopt distorted trigonal bipyramidal geometries. Thermogravimetric analysis (TGA) indicated that compounds **1**–**3** exhibited single-step weight loss behavior, with non-volatile residues at 500 °C measured as 24% for **1**, 30% for **2**, and 20% for **3**. Additionally, it was observed that the sublimation temperatures of compounds **1**-**3** ranged from 30 to 35 °C at a pressure of 0.65Torr. The thermal properties and vapor pressures of compounds **1**-**3** indicate their potential suitability as precursors for atomic layer deposition process.

AF-MoP-18 Optimization of ALD Processes and High-Quality Thin Film Formation Using the Liquid Aluminum Precursor 1,5-Dimethyl-1-Alumina 5-Azacyclooctane, *Sangick Lee, **Sanghun Lee**, Yunsik Park, Sejin Jang, JoongJin Park, Sangyong Jeon, JunHee Cho,* DNF, Korea (Democratic People's Republic of)

This study introduces an atomic layer deposition (ALD) process utilizing the liquid aluminum precursor 1,5-Dimethyl-1-Alumina 5-Azacyclooctane (hereafter referred to as DMACO), designed to meet the demands of advanced integration and miniaturization in semiconductor devices. To achieve higher DRAM capacitance, precise control over the amount of Al_2O_3 in the dielectric layer is crucial; however, the TMA precursor's high deposition rate limits this control. A new ALD precursor with a significantly lower deposition rate, while maintaining film quality and cost efficiency, is needed. DMACO exhibits a stable ALD window in the temperature range of 350–550℃, with superior thermal stability and lower impurity levels compared to TMA.DSC analysis revealed that TMA thermally decomposes at approximately 237℃, while DMACO decomposes at around 405℃ using the same method.The deposition rate of TMA was approximately 0.87–2.27 Å/cycle at 350–550℃, whereas DMACO showed a lower deposition rate of about 0.77–1.08 Å/cycle under the same conditions. Despite this lower deposition rate, Al_2O_3 films deposited on Si substrates via the ALD process using DMACO exhibited high uniformity and excellent step coverage, showing performance comparable to high-k dielectric materials deposited with TMA. Furthermore, XPS and TEM analyses confirmed the formation of high-quality thin films with minimal carbon (C) and other impurities. This presentation will delve into the thermal properties of DMACO (TGA/DSC), deposition rate trends, optimization of ALD process conditions, and the physical and chemical characteristics of the deposited films.

AF-MoP-19 Low-Resistivity Molybdenum Thin Films Deposited by ALD Using Molybdenum(0) Organometallic Compounds and Iodine-Containing Reactant, *Sang Ick Lee, **Ji Hyeon Youn**, Yo Han Jo, Won Mook Chae, Sang Yong Jeon, Joong Jin Park, Se Jin Jang,* DNF Co., Ltd., Republic of Korea

Selecting suitable candidates for interconnects and metal contacts has become increasingly challenging due to the exponential rise in metal resistivity at reduced pitches. Molybdenum (Mo) has emerged as a promising alternative to traditional metals like copper and tungsten, thanks to its low electrical resistivity and long electron mean free path. However, the deposition of Mo metal films typically requires high temperatures (600℃) and inorganic solid precursors, which can restrict its applicability. To address this limitation, a low-temperature deposition process is needed, which can be achieved by introducing an iodine-containing reactant.

Studies have shown that iodine acts as a catalyst, enhancing the growth rate and promoting denser, more uniform nucleation. Additionally, when iodine-containing species were briefly introduced during deposition, nucleation improved significantly, resulting in the formation of smoother films. [1,2] These iodine sources are also believed to help improve electrode leakage characteristics by reducing surface roughness.

In this study, the reactivity of specific reactants containing molybdenum(0) organometallic compound and iodine-containing reactant was investigated based on literature findings, and ALD deposition was carried out accordingly. The ALD process was analyzed to confirm key behaviors such as saturation, process window, and linearity. The deposited film was identified as an Mo film through characterization techniques, including XRD, XPS, and SIMS. Furthermore, evaluations on a patterned wafer verified its step-coverage and bottom-up characteristics.

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AF-MoP-20 Valence-state Controlled Growth of P-type Tin(II) Monoxide Films by Atomic Layer Deposition using a Novel Sn Precursor, *Jeong Hwan Han, **Jeong Eun Shin**,* Seoul National University of Science and Technology, Republic of Korea; *Heesun Kim, Bo Keun Park,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Tin monoxide (SnO), in its divalent oxidation state, exhibits excellent p-type conductivity due to the valence band maximum structure formed by the hybridization of Sn 5s and O 2p orbitals, making it a promising candidate for p-channel thin-film transistors (TFTs) [1]. However, physical vapor deposition methods such as evaporation and sputtering often struggle to achieve single-phase SnO films with precisely controlled Sn/O composition while minimizing the formation of undesired Sn or SnO_2 phases [2]. To address this issue, atomic layer deposition (ALD) has been explored to produce high-quality crystalline SnO films at low temperatures. Previous ALD SnO processes utilizing various divalent Sn precursors have been limited by poor crystallization within a narrow temperature rangedue to low precursor reactivity and thermal stability.

In this work, we developed an ALD process for SnO thin films using a novel divalent Sn amide precursor with a low sublimation temperature and high thermal stability. Thermogravimetric analysis revealed a single-step sublimation curve, confirming the excellent volatility and stability. The self-limiting ALD characteristics were verified by varying the Sn precursor and H_2O pulse times. The deposited SnO films were characterized using SEM, XRD, XPS, and UV-Vis, confirming the formation of pure andcrystalline SnO film. ALD SnO based TFT demonstrated excellent switching performance, exhibiting a field-effect mobility of 3.68 cm^2/V·s, a sub-threshold swing of 4.94 V/dec, and an on/off current ratio of 2.74×10^3.

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AF-MoP-21 Synthesis and Characterization of Ge and Sn ALD Precursors with Aminoketone Ligands, ***Chang Min Lee**, Bo Keun Park, Heesun Kim, Ji Min Seo, Yongmin Go,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea; *Seung Uk Son,* Sungkyunkwan University, Korea; *Ji Yeon Ryu, Taek Mo Chung,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Thin films, with thicknesses ranging from nanometers to micrometers, can be produced through various physical or chemical methods. Atomic Layer Deposition (ALD) is particularly valued for its ability to deposit uniform thin films, where precursor selection plays a critical role in determining process success. For ALD, precursors must exhibit thermal stability, chemical reactivity, and produce volatile by-products. Among group 14 elements, germanium (Ge) and tin (Sn) have garnered attention due to their superior electrical and optical properties. Their oxides, GeO_2 and SnO_2 , have been extensively studied in thin film applications. In this study, we synthesized novel Ge and Sn precursors suitable for ALD and characterized their properties. $GeCl_2$ -dioxane and $Sn(btsa)_2$ were reacted with ligands dmadma (2-(dimethylamino)-N,N-dimethylacetamide) and dmadmb (1-(dimethylamino)-3,3- dimethylbutan-2-one). The resulting complexes formed stable five-membered rings, which effectively filled vacant coordination sites and prevented oligomerization. The synthesized compounds were thoroughly characterized using NMR, FT-IR, elemental analysis (EA), TGA, and XRC. All compounds exhibited high volatility and thermal stability, indicating their potential as promising precursors for ALD applications.

AF-MoP-22 M(II) (M = Ni, Cu, Ge, Sn) ALD Precursors Using N-tert-butylformamide Ligand, ***Mi Jeong Kim,*** Korea Research Institute of Chemical Technology (KRICT), Republic of Korea; *Ji Min Seo,* korea research Institute of Chemical Technology (KRICT), Republic of Korea; *Heesun Kim,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea; *Yongmin Go,* korea research Institute of Chemical Technology (KRICT), Republic of Korea; *Seung Uk Son,* Sungkyunkwan University, Korea; *Ji Yeon Ryu, Taek-Mo Chung, Bo Keun Park,* korea research Institute of Chemical Technology (KRICT), Republic of Korea

Atomic layer deposition (ALD) has become an essential technology in advanced applications that require uniform and precise thin film deposition. The success of the ALD process depends on the selection of appropriate precursors. Accordingly, we conducted research to develop various M(II) precursors. We synthesized $[Ni(tbfa)_2]_2$ (**1**), $[Cu(tbfa)_2]_2$ (**2**), $Ge(tbfa)_2$ (**3**), and $Sn(tbfa)_2$ (**4**) complexes using N-tert-butylformamide (tbfa) ligands, and characterized them by various analytical techniques, including NMR, FT-IR, elemental analysis, and thermogravimetric analysis. In particular, complex 4 showed the highest volatility and stable thermal properties in the TGA results, and thus could be expected to be used as a good ALD precursor.

AF-MoP-23 Reaction Pathway of Copper Atomic Layer Deposition via Time-of-Flight Mass Spectrometry*, Camilla Minzoni, Caroline Hain, Krzysztof Mackosz,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; Andreas Werbrouck,* Thin Film Coatings and Materials Electrochemistry Lab, University of Missouri-Columbia, Missouri, USA*; Carla Frege,* ***Bensaoula Abdel,*** Tofwerk AG, Thun, Switzerland*; Patrik Hoffmann, Ivo Utke,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Time-of-Flight Mass Spectrometry (ToFMS) has emerged as a powerful analytical technique for unraveling the complex reaction mechanisms occuring during Atomic Layer Deposition (ALD), particularly in the challenging field of copper thin film fabrication. Thanks to its unique advantages in terms of high sensitivity, high resolving power, rapid data acquisition, and ability to simultaneously detect species across a wide mass range, ToFMS enables real-time tracking of surface reactions volatile byproducts.

In this study, in-situ ToFMS monitoring was employed to investigate the ALD process of copper, using dehydrated $Cu(hfac)_2$ as the Cu source and diethylzinc (DEZ) as the reducing agent. Until now, no experimental proof of the occurring surface reaction mechanism was attempted according to published literature.

Lee et al. [1] previously proposed a transmetalation reaction 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 $Zn(hfac)_2$, along with the generation of copper alkyl surface species. These copper alkyl species rapidly undergo reductive elimination, producing copper metal and butane (C_4H_{10}) [2].

Alternately, Elliott et al. [3] proposed another possible mechanism, involving a half ligand exchange reaction. This second pathway results in the formation of EtZn(hfac) and copper alkyl species, which subsequently react to yield copper metal and butane

In situ ToFMS monitoring enabled real-time detection of the expected volatile surface reaction products from both the transmetalation and half-ligand exchange mechanism with varying proportion in the ALD half-cycles of the copper precursor $Cu(hfac)_2$ and the reducing DEZ agent. By identifying the parent peaks of $Zn(hfac)_2$ and EtZn(hfac), along with their specific fragmentation pathways, ToFMS provided the first experimental validation of both reaction mechanisms under vacuum ALD conditions.

The combination of ALD and ToFMS is therefore proving to be a powerful method for a depth understanding of complex ALD reaction mechanisms, an insight that would be challenging to obtain through other means.

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AF-MoP-24 Bimetal Thin Film Deposition Using Novel Organometallic Dinuclear RuCo Complex*,* ***Kazuaru Suzuki****, Tomohiro Tsugawa, Subhabrata Das, Yohei Uchiyama, Ryosuke Harada, Hirofumi Nakagawa,* Tanaka Precious Metal Technologies Co. Ltd.,, Japan

K. Suzuki, T. Tsugawa, S. Das, Y. Uchiyama, R. Harada, and H. Nakagawa, Tanaka Precious Metal Technologies Co. Ltd., 22, Wadai, Tsukuba, Ibaraki 300-4247, Japan

Thin films composed of multiple metal elements are attracting attention. In addition to those exhibiting catalytic activity or electro-magnetic properties, in the field of advanced semiconductors, multiple types of metal thin films are being studied for barrier / liner films for Cu wiring [1, 2]. In the production of such film, it is a common method to perform repetition of film formation operations according to the kinds of metal element, but it is complicated to perform film formation under different conditions for each metal. Further, it is difficult to deposit a smooth continuous film while having an extremely thin film thickness. In this study, we report the results of bimetal thin film deposition in a single process using novel organometallic dinuclear RuCo complex as a precursor.

Novel RuCo complexes containing several organic ligands were synthesized. Based on the results of TG measurement, the complex with high volatility and thermal stability was selected and used as a raw material for film formation. As the intial evaluation, CVD deposition test was performed on Si and SiO_2 substrates. The film formation was controlled at substrate temperatures ranging from 300 to 400 ºC. When the films were formed in nitrogen atmosphere, high-resistance films containing impurities were obtained, but in the hydrogen atmosphere, the low-resistance metal films were obtained. From the results of SEM, it was confirmed that the flat and continuous films with no agglomeration or particles were obtained. In addition, the EDS measurement results showed that Ru and Co elements in the film were uniformly distributed without aggregation.

We have developed the novel precursor that can produce a uniform bimetal film containing Ru and Co elements by the deposition process with single precursor. Since an extremely thin and continuous film is required for use in the barrier/liner film of Cu wiring, the development of an ALD process is more necessary in the future.

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AF-MoP-25 Atomic Layer Deposition of Composition Engineered Nitrogen-Doped SnOX Films for Enhanced Performance of Thin-Film Transistor*, Han Jeong Hwan,* ***Lee Hyun Hak****, Shin Jeong Eun, Lee Na Yeon,* Seoul National University of Science and Technology, Republic of Korea

Tin oxide (SnO_x, x = 1,2) has been widely used in various applications, including thin-film transistor (TFT) channel layers, solar cells, and transparent electronic devices, due to its excellent electrical and optical properties. By controlling stoichiometry, tin oxide can achieve n-type SnO_2 and p-type SnO semiconductors. However, the formation of unintended intrinsic defects such as oxygen vacancy and tin vacancy can degrade device stability and complicate carrier concentration control. To address this issue, studies on anion doping, such as nitrogen, have been explored. However, Nitrogen-doped oxide semiconductors produced by sputtering processes face challenges in controlling doping concentrations. In contrast, atomic layer deposition (ALD), which enables atomic-scale deposition through self-limiting reactions, allows for precise doping concentration control via a super-cycle approach.

In this study, nitrogen (N)-doped SnO_x films were grown using thermal ALD, incorporating alternating ALD SnO_x and SnN_x sub-cycles. By varying the sub-cycle ratio of SnO_x:SnN_x, the nitrogen concentration in N-doped SnO_x film was precisely adjusted. The influences of nitrogen doping concentration on crystallinity, surface morphology, chemical states, and optical and electrical properties were systematically analyzed using XRD, SEM, AFM, XPS, and UV-vis spectroscopy. Finally, the electrical performance of ALD N-doped SnO_x TFTs were evaluated depending on the nitrogen doping levels.

Acknowledgments

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AF-MoP-26 Atomic Layer Deposition of Molybdenum Using a Dual-Purpose Molybdenum Precursor for Advanced Metallization*,* ***David Mandia****, Matthew Griffiths, Youness Alvandi, Arya Shafiefarhood,* Lam Research Corporation

The resistivity increase with decreasing width of interconnect lines is a major challenge for the continued downscaling of integrated circuits. As middle-of-line (MOL) metal interconnects in advanced logic devices scale down to the sub-2 nm node with an associated reduction in the overall current-carrying cross-sections, the effects of specular electron scattering at grain boundaries[1] or impurities like carbon/oxygen become tremendously amplified. As we inflect to a Molybdenum (Mo)-based metallization solutions in our customer integration schemes (and away from Cobalt (Co), Ruthenium (Ru), and tungsten (W)), the previously mentioned challenges remain the same. Our typical integration schemes for S/D or contact metallization are based on recessed features with ALD/CVD Mo gap-fill within (i) inherently selective structures with a barrierless W via bottom or (ii) structures with a conformal diffusion barrier on, for example, a metal silicide/Si. To improve upon previous approaches to gap-fill of structure (i), which were based on an oxygen-containing Mo precursor, we employed an oxygen-free, halide-containing Mo precursor ($MoX_a(L)_b$). This allowed for a cleaner, bottom-up (selective) growth profiles with an oxygen-free Mo-W interface. As will be shown in various analyses (e.g., PED), we obtain single-grain Mo in most (>90%) vias of ourLam-internal test vehicle structures due to the lack of grain boundary formation,which tends to form if there are significant Mo precursor and feature sidewall interactions. Due to its oxophilicity (i.e., its high affinity to oxidize to MoOx), Mo is a challenging metal from both a processing and precursor design point of view. Herein we leverage the various deposition and etching properties of a $MoX_a(L)_b$ precursor and its applications in various metallization schemes.

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Keywords: Metallization, $MoX_a(L)_b$, selective deposition, ALD, semiconductor manufacturing

AF-MoP-27 Demonstration of ALD $Hf_xZr_{1-x}O_2$ Using Various Oxidant Sources Over Ultra-High Aspect-Ratio Structure for Memory Applications

Dan Le, RASIRC*; Jin-Hyun Kim, Thi Thu Huong Chu, Soubhik De, Dushyant Narayan, Minjong Lee,* University of Texas at Dallas*; Walter Hernandez, Josh Garretson, Adrian Alvarez, Jeffrey Spiegelman,* RASIRC*; Jiyoung Kim,* University of Texas at Dallas*; **Lorenzo Diaz,*** RASIRC

As memory devices continue to evolve toward higher density and enhanced performance, particularly in 3D architectures, the need for precise control over material properties at the nanoscale has become critical. $Hf_xZr_{1-x}O_2$ (HZO) is a promising material for next-generation memory applications, such as ferroelectric random-access memory (FeRAM) and high-k dielectrics for DRAM. Due to its ferroelectric properties and high dielectric constant, HZO plays a key role in improving device performance, lowering power consumption, and enhancing scalability. However, the successful integration of HZO into memory devices requires a precise, conformal deposition technique capable of maintaining uniformity across complex 3D structures.

In this work, we focus on demonstrating the deposition of HZO on ultra-high aspect-ratio structures using various oxidant sources, including anhydrous hydrogen peroxide (H_2O_2) and ozone (O_3) at 250°C. We will explore ALD process developments, such as stop valve processing and multiple dosing techniques, to successfully deposit HZO on features with aspect ratios as high as 10,000:1. The ultra-high aspect-ratio substrates used in this study feature advanced membrane technology that enables easier evaluation of HZO conformality across the complex structures without requiring complex sample preparation. In addition to optimizing the deposition process, material characterizations on blanket samples will be conducted to monitor the properties of the HZO films achieved using the developed ALD processes. Techniques such as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and other advanced characterization methods will be employed to assess film crystallinity, chemical composition, and other critical material properties. These analyses will ensure that the final HZO films meet the stringent requirements for next-generation memory applications, including high performance, scalability, and reliability for integration into advanced memory devices.

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AF-MoP-28 Bottleneck-Effect on Thin-Film Conformality in High Aspect Ratio ALD

***Mikko Utriainen**, Jussi KInnunen, Jani Karttunen, Feng Gao,* Chipmetrics, Finland*; Anish Philip,* Aalto University, Finland

Atomic Layer Deposition (ALD) is an important method for conformal film deposition into high aspect ratio structures. It is widely used in advanced 3D semiconductor devices as well as batteries and MEMS devices. However, achieving an uniform film on thenarrow and complex shapes is challenging. Once 3D designs become more complex, or random shapes in porous structures increases, the small and variable opening dimensions will become more prevalent. These features will increase the difficulty of the deposition process development and optimization. The present understanding and research methodology to study the effects of narrow openings and bottlenecks is limited.

In this study, we demonstrate a novel experimental method to approach the problem. We used the PillarHall® lateral high-aspect ratio (LHAR) test structure to study the bottleneck effects on ALD thin film formation into the high aspect ratio cavities. The LHAR test structure setup enable to adjust the size of the entry into a cavity and study its effect on the film penetration profile. We performed thermal ALD to deposit Al_2O_3 on three LHAR structures and one vertical high aspect ratio (VHAR) structure. One LHAR sample, with a trench gap height of 500 nm, served as a reference with no bottleneck. In two other LHAR samples, we reduced the gap from 500 nm to 400 nm by adding a 50 nm layer at the trench opening, which created bottlenecks using non-conformal deposition of either Al_2O_3 or TiO_2. The VHAR structure had a bottleneck at the entry by design.

The measurements showed that without a bottleneck, the film could penetrate up to 152µm . When a bottleneck was present, the penetration depth decreased to 133–135µm, regardless of whether Al_2O_3 or TiO_2 was used. We employed line-scanning reflectometry to measure these structures, a method that could even differentiate between layers when TiO_2 formed the bottleneck. These results are in line with the diffusion-limited deposition model by Gordon et al. [1] and allowed us to compare the behavior of LHAR and VHAR structures. Based on our findings, carefully designed bottleneck structures could lead to improved models for predicting film growth in complex geometries, and this approach could be extended to cases with multiple bottlenecks within a cavity.

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AF-MoP-29 Low Temperature Deposition of SiO_2 and SiOC Films

Chad Brick, Gelest, Inc*; Tomoyuki Ogata,* Mitsubishi Chemical Corporation, Japan

Atomic layer deposition (ALD) has emerged as a critical thin film deposition technique, particularly in the semiconductor, photonic, and energy storage industries, due to its ability to produce conformal, uniform films with atomic-scale precision. However, many ALD processes require elevated temperatures or harsh co-reactants to drive the reactions, which limits the applicability of ALD towards thermally or chemically sensitive substrates. This work presents the development and characterization of a novel low temperature ALD process for the deposition of silicon dioxide (SiO_2) thin films using a newly designed precursor and oxidant combination. The novel process enables the deposition of stoichiometric SiO_2 films at, near, or even below ambient temperatures and with acceptable cycle times, circumventing the need for high substrate temperatures and expanding the scope of SiO_2 ALD for temperature-sensitive applications. Furthermore, it will be shown that the highly specific and gentle oxidation conditions of the process afford ample opportunity opportunities for area-selective deposition, deposition of SiO_2 films on chemically sensitive organic substrates, or selective doping of the growing SiO_2 films with carbon-containing species for the formation of SiOC films. Plasma and thermal densification of the resulting films as well as characterization of the as-deposited and densified films will be discussed.

AF-MoP-30 Vanadium-Sulphide Layers with Atomic Layer Deposition

***Zsófia Baji**, Zsófia Bérces,* Centre for energy research, Hungary*; Zoltán Szabó, Zsolt Fogarassy, Péter Vancsó,* Centre for Energy Research, Hungary

Vanadium sulfides are a novel class of materials that have garnered significant interest due to their unique electronic, structural, and catalytic properties. Vanadium sulphide materials can exist in different compositions, among which VS_2 is the most researched as a 2D material. The other stoichiometries of vanadium sulfides have not received as much attention, and so far there is hardly any data on the structure and properties of VS. A comprehensive understanding of the full range of vanadium sulfides remains limited, prompting the need for advanced computational studies.

The present work compares the properties of atomic layer deposited VS layers from tetrakis(ethylmethylamino)vanadium (TEMAV) and H_2S, and computational models obtained with density functional theory (DFT) calculations. The ALD VS layers are amorphous, exhibiting a mixture of different stoichiometries with an internal composition of 63% V and 37% S. Upon removal from the ALD reactor, oxidation begins immediately. Annealing the samples in a sulfur-containing atmosphere promoted crystallization and resulted in a pure VS stoichiometry, with the top part of the layer polycrystalline and the lower portion remaining amorphous. The annealed VS layers were found to be semiconductors, with the sulfur treatment enhancing the stability and oxidation resistance of the material [1].

To further understand the grown material's properties, DFT calculations were performed. These simulations aimed to identify the different stable crystalline structures of VS that grown on the amorphous form of VS. Due to the very limited DFT data for VS, we employed different theoretical methods: standard DFT in the generalized-gradient approximation (GGA), GGA+U methods as a function of the U parameter, and hybrid functionals

(HSE) to reveal the electronic, magnetic and optical properties. Additionally, we investigated the effect of the defects to gain insights into its modified electronic behaviour and its potential applications.

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AF-MoP-31 Film and Surface Stress Measurements during Tungsten Atomic Layer Deposition*, Ryan B. Vanfleet*, *Steven M. George,* University of Colorado at Boulder

Film and surface stresses were measured during tungsten (W) atomic layer deposition (ALD) using *in situ* wafer curvature techniques. Tungsten was deposited at temperatures between 125 °C and 285 °C using tungsten hexafluoride (WF_6) and disilane (Si_2H_6) as the reactants on aluminum oxide (Al_2O_3) ALD surfaces. Tensile film stresses were observed at all deposition temperatures (Figure 1). The maximum film stress was ~2.2 GPa at 150 °C. The film stress decreased to ~1.0 GPa at 285 °C. For comparison, Al_2O_3 ALD films deposited at 125-285 °C have much smaller tensile film stresses of ~0.5-0.1 GPa. The large tensile stress in W ALD films may be generated at the grain boundaries. Atoms are too far apart at grain boundaries and experience an attractive force that wants to pull them together.

Surface stresses were also measured during the individual WF_6 and Si_2H_6 exposures during W ALD. For W ALD at 200 °C (Figure 2), the individual WF_6 exposures produced a tensile stress of ~+2 N/m. This tensile stress is correlated with the removal of sacrificial SiF_xH_y surface species and the deposition of W and WF_z surface species. The individual Si_2H_6 exposures then partially released the tensile stress with a compressive stress change of ~-1 N/m. There is a net tensile stress change per W ALD cycle of ~+1 N/m. The Si_2H_6 exposures redeposit sacrificial SiF_xH_y surface species.

Other *in situ* stress measurements on SiO_2 native oxide on Si wafers have shown that the large tensile stresses in W ALD films can lead to delamination. The large tensile stresses in W ALD films can be reduced by periodic trimethylaluminum (TMA) exposures. The addition of TMA modifies the film surface and forces the re-nucleation of the W ALD film. The reduced stresses during the nucleation phase of W ALD growth contribute to a reduced tensile stress in the overall W ALD film. W ALD film stress can be tuned by the frequency of the TMA exposures.

AF-MoP-32 Modifying Vanadium Oxide by Atomic Layer Plasma Treatment*, Ritwik Bhatia*, *Mohammad Saghayezhian,* Veeco Instruments*; Ganesh Sundaram,* Veeco

VO2 shows a insulator to metal phase transition when it undergoes a transition in crystal structure from monoclinic to rutile as it is heated through the transition temperature ~ 68ºC. ALD VO2 deposited via alkylamido precursors (TDMAV and TEMAV) ~ 150-200ºC is amorphous as deposited and requires high temperature annealing (400-670ºC) to obtain a material with adequate crystallinity to show the metal-insulator transition [1,2,3].

ALD is a cyclic process with discrete steps – precursor introduction, precursor purge, co-reactant introduction, co-reactant purge. This allows the introduction of other steps into the ALD cycle to tune the film properties. One such approach (atomic layer annealing or atomic layer bombardment) injects energy to the film-growth surface by introducing an inert gas plasma step into the ALD cycle. It has been shown to produce epitaxial AlN [4] and GaN [5] films at low temperatures and to improve density and electrical properties of HfO2 [6].

In this work, apply the principle of atomic layer annealing to VO2. We have characterized changes to the film properties as a function of plasma exposure. VO2 grown with water as a co-reactant responds very differently to plasma exposure compared to O3 as a co-reactant. ALA causes a large increase in film roughness (porosity?) and reduction in refractive index for the water based process. The ozone based process shows a slight increase roughness and the refractive index due to ALA. Grazing incidence x-ray diffraction and Raman spectroscopy do not show crystallization of the film due to ALA.

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AF-MoP-33 Prediction of Adsorption/Desorption Equilibrium Constants and Surface Reaction Rate Constants Using Neural Network Potentials for ALD Process Design*, Noboru Sato*, *Naoki Tamaoki, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

For systematic design of ALD processes, adsorption/desorption equilibrium constants of precursors and reactive gases as well as surface reaction rate constants are required. Density functional theory (DFT) calculations can be used to determine the structures and energies of the adsorption states of chemical species and the transition states of surface reactions. However, the calculation of the reference vibrational frequencies needed for entropy and partition function evaluations requires an enormous computational cost. Consequently, discussions have often been based solely on changes in energy while neglecting entropy and partition functions. As a result, even when the activation energy for the surface reaction rate constant is obtained, it has been necessary either to assume a frequency factor of 10^{13} s^{-1} for the rate constant or to adjust the frequency factor to match experimental results.

Recently, atomistic simulation using neural network potentials (NNP) have attracted attention. An NNP is an atomic potential constructed by machine-learning on DFT calculation data, and it can perform calculations in less than one second that would otherwise take several hours using DFT. Therefore, atomistic simulators employing an NNP now enable the computation of reference vibrational frequencies within a practical time frame. In this study, we investigated whether atomistic simulator (Matlantis™) using the Preferred Potential (PFP) can be applied to the design of ALD process by calculating surface adsorption/desorption equilibrium constants and surface reaction rate constants with sufficient accuracy.

Figure 1 shows the results of calculating the transition state for the reaction in which CO_2 from the gas phase directly collides with an H atom adsorbed on Cu(111) to form a formate group, along with the vibrational frequencies of each mode in the transition state. The activation energy from the physisorption state is 80 kJ/mol; however, since an Eley–Rideal (E–R) type reaction is assumed, ΔE_{TST} becomes 53 kJ/mol after subtracting 27 kJ/mol corresponding to the physisorption energy. The presence of exactly one imaginary vibrational mode confirms that the structure is indeed a transition state. Based on these results, the reaction probability was calculated, and the comparison with experimental values [1] is shown in Figure 2. The reaction probability could be reproduced with an error of less than a factor of two. This indicates that the use of an NNP enables optimal design of the ALD process based on surface reaction rate constants.

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AF-MoP-34 *In Situ* Synchrotron Hard X-Ray Scattering Studies of the Structural Evolution of InAlN During Growth by PEALD*, Jeffrey Woodward*, U.S. Naval Research Laboratory*; Kenneth Evans-Lutterodt,* Brookhaven National Laboratory*; David Boris, Michael Johnson,* U.S. Naval Research Laboratory*; Zachary Robinson,* University of Rochester Laboratory For Laser Energetics*; Ruipeng Li, Masafumi Fukuto,* Brookhaven National Laboratory*; Karl Ludwig,* Boston University*; Charles Eddy, Scott Walton,* U.S. Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) is a promising technique for the growth of indium aluminum nitride (InAlN) and other alloys due to its atomic-level control of layer thicknesses and non-equilibrium process conditions, which can enable compositions within miscibility gaps. However, unlike the conventional model of atomic layer deposition (ALD) which assumes ideal layer-by-layer growth, the PEALD growth of highly crystalline films is often far more complex, with dynamic evolution of the nanoscale morphology occurring rapidly during the early stages of growth and depending on factors such as the plasma properties[1] and the strain evolution within the film.[2] Furthermore, compared to the growth of binary compounds, the growth of ternary alloys using the standard supercycle approach poses additional challenges as the constituent layers may exhibit differences in growth mode (e.g., island versus layer-by-layer) which could lead to deviations from the intended alloy composition, reductions in material quality, or even promote kinetic phase separation. Understanding how the process parameters and related properties influence the growth kinetics and the resultant material properties is essential for the realization of the PEALD growth of high quality alloy films. Grazing incidence small-angle x-ray scattering (GISAXS) using synchrotron radiation is well suited to this task, as it is nominally nondestructive, capable of probing nanoscale structure in real time, and is compatible with arbitrary process environments.

In this work, we investigate the influence of supercycle period on the nanoscale structural evolution of InAlN during growth by PEALD on gallium nitride (GaN) using *in situ* GISAXS experiments conducted at the Integrated *In Situ* and Resonant Hard X-ray Studies (ISR) beamline of National Synchrotron Lightsource II (NSLS-II). As the supercycle period is varied, significant differences in the evolution of the film structure are observed which do not follow a simple monotonic trend. The InAlN films are characterized *ex situ* using grazing incidence wide-angle x-ray scattering (GIWAXS), x-ray diffraction (XRD), in-plane grazing incidence diffraction (IP-GID), x-ray reflectivity (XRR), and atomic force microscopy (AFM).

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AF-MoP-35 Thermal ALD Vanadium Nitride (VN) as Next-Generation Electrode, ***Antony Jan**, Hae Young Kim,* Eugenus, Inc.

As semiconductor devices continue to shrink in scale, there is an increasing demand for electrode materials with improved properties. A current electrode material in use for many applications is titanium nitride (TiN), valued for its low resistivity, thermal and chemical stability, and compatibility with semiconductor processes. However, next-generation electrode materials--such as for DRAM applications--require lower resistivity, higher work function, higher density, and capability of highly conformal deposition into high aspect ratio structures. Vanadium nitride (VN) is one material that may possess these superior properties.

In this work, we have developed a thermal ALD vanadium nitride process on our 300 mm wafer tool. VN could be deposited over the tested range of 300 to 550°C, with a with-in-wafer thickness non-uniformity as low as 1%. On blanket wafers, VN films exhibited lower resistivity than reference TiN at all tested temperatures and thicknesses, as low as 110 µΩ*cm at a thickness of 10 nm. Work functions of VN films were consistently higher than for reference TiN, as measured by ultraviolet photoelectron spectroscopy (UPS). VN composition was roughly 1:1, with less than 1% of C or Cl detected by XPS. Grazing incidence x-ray diffraction (GIXRD) showed the films have a cubic structure with lattice parameter 4.11Å. VN films were highly conformal and could be deposited with step coverage values of 90 to 100%, into vias with aspect ratio as high as 70:1.

AF-MoP-36 ALD Synthesis of Transition Metal Phosphides, ***Raul Zazpe**, Jaroslav Charvot, Jhonatan Rodriguez-Pereira, Milan Klikar, Filip Bures, Jan Macak,* University of Pardubice, Czechia

The ever-increasing global energy demand together with the environmental issue originated from the use of fossil fuel, has triggered an intense search for sustainable and clean energy alternatives, such us hydrogen energy, biomass and solar energy among others. In this context, a pivotal key to deliver sustainable and superior energy systems lies on the rational design and development of high-quality and cost-effective catalyst offering enhanced stability, activity and selectivity. Consequently, intense efforts have been devoted in the search and synthesis of new catalyst materials to replace the scarce and expensive traditional noble metals (e.g. Pt, Pd, Au and Ru) for energy conversion and energy storage applications.

Among the recently explored novel catalyst materials, metal phosphides (MPs) have emerged in recent years, attracting significant attention thanks to their intriguing properties [1]. In particular transition metal phosphides (TMPs) exhibit striking properties. The moderately strong M−P bonds lend outstanding mechanical properties, high thermal stability and outstanding chemical resistance to chemical attack and oxidation in acidic and alkaline solutions. Additionally, Co, Ni, Mo-based phosphides demonstrated excellent catalytic and bifunctional properties, in particular towards water splitting as both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [2,3].

Herein, we present the synthesis of TMPs by thermal Atomic Layer Deposition (ALD) based on the use of different transition metal precursors and tris(trimethylsilyl)phosphine. The physical and chemical properties of the resulting TMPs thin films were extensively characterized by different methods, including atomic force microscopy, X-ray photoelectron spectroscopy and X-Ray diffraction. The presentation will introduce and describe the synthesis of the TMPs and the corresponding physical and electrochemical characterization toward electrocatalytic application.

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AF-MoP-37 Atomic Layer Deposition of a Low Carbon Hafnium Oxide Using (2-methylindenyl)tris(dimethylamido)hafnium and Ozone, ***Drew Hood**, Rong Zhao,* Entegris

High-K metal oxide layers, such as hafnium oxide, find applications across various device architectures ranging from the well established to the cutting edge .[1,2] Emerging applications, such as ferroelectrics for ultralow-power logic, continue to drive the development of hafnium oxide deposition.[3] In established and emerging applications new hafnium oxide precursors that can provide better uniformity, higher film quality, or reduce tool time are desirable.

Here we report a new hafnium oxide ALD precursor, (2-methylindenyl)tris(dimethylamido)hafnium (2-MeIndHf(NMe2)3), focusing on deposition performance using ozone and water. The results are compared to benchmark compounds tetrakis(ethylmethylamino)hafnium (TEMAHf) and tris(dimethylamido)cyclopentadienylhafnium ($CpHf(NMe_2)_3$) with a focus on growth per cycle (GPC), saturation, and film quality. Using process conditions optimized for each precursor, 2-MeIndHf$(NMe_2)_3$ had the highest GPC at 0.86 Å/cycle, the lowest carbon incorporation, and better precursor/oxidizer saturation than benchmark compounds. Other advantages such as synthesis scalability are also discussed.

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AF-MoP-38 Rapid Low-Temperature Atomic Layer Deposition of HfO_2, *Xianhu Liang, Volkmar Hock, Hartmut Buhmann, **Johannes Kleinlein**, Laurens W. Molenkamp,* University of Wuerzburg, Germany

Hafnium oxide (HfO_2) thin films are extensively used as gate dielectrics. These films can be deposited by low-temperature atomic layer deposition using tetrakis-dimethylamido hafnium and water as precursor and oxidant, respectively, making them compatible with temperature-sensitive substrates. Recently, utilizing a homemade reactor, we successfully implemented such HfO_2 layers as gate dielectrics in various devices of thermally sensitive mercury telluride heterostructures [1-5]. However, in comparison to conventional (high-temperature) HfO_2 deposition protocols, at deposition temperatures of 30 °C, processes are time-consuming due to the long purge times involved [6]. In this talk, we present an innovative strategy to reduce the overall process time for a typical HfO_2 layer of 15 nm thickness by an order of magnitude, from 10 hours to 1 hour. This strategy involves reducing the purge time after each water pulse, accomplished by controlling the number of water molecules entering the reactor per pulse. This is achieved by significantly reducing the water vapor pressure in the source by cooling it below its freezing temperature, thereby forming water ice. The purge times are then adjusted to a minimum required for stable and reproducible deposition conditions. We present details of this process development and discuss the observed growth rate characteristics on thermally oxidized silicon wafers. For the optimized process parameters, the HfO_2 film thickness varies linearly with the number of cycles, and the deposition is homogeneous across the surface of the 2" sample stage. To demonstrate the applicability of this process, we apply the HfO_2 films as gate dielectric in lithographically patterned, high electron mobility quantum well devices. By performing electrical transport measurements, we investigate the gate performance at 1.4 K and find that the gate structures employing HfO_2 deposited using rapid low-temperature atomic layer deposition provide reliable and efficient gating, comparable to our previous technology. The relative permittivity of the HfO_2 extracted from the transport experiments is 11+-1 and the gate action is $1E12/Vcm^2$ for a 15 nm HfO_2 film. Consequently, we have established a rapid low-temperature atomic layer deposition process suitable for temperature-sensitive substrates that offers an order of magnitude reduction in deposition time.

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AF-MoP-39 Innovative Advanced Deposition Material (ADM) Technique for Low-Resistivity, High-Conformality Metal and Barrier Thin Films*, **Kok Chew Tan**, Changbong Yeon, Deok Hyun Cho, Jung Hun Lim, Jaesun Jung,* Soulbrain, Republic of Korea

As semiconductor device scaling approaches atomic dimensions, adopting next-generation metals for NAND, DRAM, and logic/foundry applications becomes crucial. Traditional metallization materials like copper and tungsten face increasing resistivity at reduced dimensions as well as challenges in barrier/liner scaling and deposition for complex patterns. Additionally, integrating high-performance metal gate electrodes with gate dielectrics layer requires addressing stringent electrical, thermal, and structural compatibility.

Molybdenum, with its low resistivity, short mean free path, and minimal diffusivity, offers a promising alternative for interconnects. For gate stacks integration, titanium nitride (TiN) serves as an effective barrier metal due to its high thermal stability, excellent diffusion resistance, and compatible work function. However, achieving uniform, ultra-thin, and defect-free TiN films with high conformality in high aspect ratio patterns is a significant challenge.

In this work, we present a novel Advanced Deposition Material (ADM) technique designed to deposit low-resistivity interconnect metals and barrier metal thin films including TiN at high temperatures with excellent step coverage. By leveraging inhibition and/or activation within each atomic layer deposition (ALD) cycle, the ADM method achieves precise control over film properties, resulting in low resistivity, enhanced conformality, and improved diffusion barrier performance. This ADM technique paves the way for advanced semiconductor device fabrication.

AF-MoP-40 Evaluation of a Hafnium Precursor with Higher Thermal Stability for the Atomic Layer Deposition of Hafnium Oxide Films*, Randall Higuchi, Khang Ngo, **Bhushan Zope**,* Merck KGaA, Darmstadt*; Joo-Yong Kim, Dong-Geun Lee,* Merck KGaA, Darmstadt, Republic of Korea

Hafnium oxide (HfO_2) is a critical material in the semiconductor industry used in DRAM, 3D-NAND and Logic Devices due to its excellent dielectric properties including a high dielectric constant and ferroelectric behavior (1). HfO2 films are used as high-k dielectric in capacitor for DRAM devices and in HKMG for Logic & DRAM devices. Additionally, these films are expected to find additional applications as blocking oxide in 3D-NAND and as BEOL capacitor dielectric in Logic devices. The key requirements of Hf precursors includes high thermal stability, enabling higher temp ALD window and HfO2 films with low film impurities and achieving excellent step coverage.

For this study we use the Chipmetrics Pillar Hall test vehicle to investigate the step coverage performance of this Hafnium precursor compared to other Hafnium precursors. By fixing the precursor flux during the dose and other process conditions, step coverage in the Pillar Hall trench can be compared at high aspect ratios.

In this study, we evaluate a Hf precursor that demonstrates superior thermal stability and improved step coverage up to 400°C compared to conventional precursors. This precursor has good vapor pressure for delivery for an ALD process and can be deposited up to 400°C without decomposition. The higher deposition temperature enabled HfO_2 growth with lower Carbon and Hydrogen content. Step coverage performance was evaluated and showed improved step coverage at 400°C compared to conventional precursors at their standard deposition temperature. The findings demonstrate the higher thermal stability and step coverage for this Hf precursor.

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AF-MoP-41 Modulation of $Hf_xZr_{1-x}O_2$ Thin Film Characteristics via ALD and ALE*, **Ming-Kuan Fan**,* National Tsing Hua University, Taiwan ; Taiwan Instrument Research Institute, Taiwan*; Yi-Cheng Chen,* National Tsing Hua University, Taiwan*; Chien-Wei Chen, Yang-Yu Jhang, Sheng-De Wong,* Taiwan Instrument Research Institute, Taiwan*; Hong-Luen Lin,* Tokyo Electron Taiwan Limited, Taiwan*; Ying-Hao Chu,* National Tsing Hua University, Taiwan

With the advance of the semiconductor industry, the pursuit of smaller transistor sizes presents a significant challenge in effectively controlling gate voltage. This challenge becomes particularly pronounced as transistors scale down, making it increasingly difficult to retain precise control over their on/off states. Herein, hafnium zirconium oxide ($Hf_xZr_{1-x}O_2$, HZO) has emerged as a significant material in the realm of higher-k. This solid-solution ceramic combines the advantageous characteristics of hafnium oxide (HfO_2) and zirconium oxide (ZrO_2), which is regarded as a promising candidate material for memory devices and related electronic devices. During the growth of nanolaminate HZO films, the TEMAHf and TEMAZr precursors were pulsed into the reaction chamber at different cycle ratios to form varied compositions. We used XPS survey spectra to quantify HZO stoichiometry precisely. This method can precisely control the atomic ratio of Hf and Zr to change the interface polarization state. With this modulation, the dielectric constant of HZO can be enhanced to 38, with equivalent oxide thickness below 0.6nm while maintaining a leakage current below $10^{-7}A/cm^2$.Besides, atomic layer etching (ALE) has been proposed for introduction into advanced semiconductor processes, especially in gate-all-around (GAA) or nano-sheet FET structures, due to its precise control and high etching selectivity. The crystallization temperature typically increases as the film thickness decreases due to the lower surface-to-volume ratio of thicker films favoring their crystalline phases. Consequently, when there are temperature constraints, amorphous HZO films may have to be grown thicker, annealed to crystallize, and then etched back to obtain the desired ultrathin crystalline thickness. In this study, we propose plasma ALE verification of $Hf_xZr_{1-x}O_2$ thin films using remote tetrafluoromethane (CF_4) plasma to achieve HZO surface fluorination and using dimethylaluminum chloride (DMAC) employed as the metal precursor for ligand exchange of fluoride removal layer. In the etching curve of HZO ALE, it can be estimated that the etching per cycle (EPC) of HZO at 400°C is approximately 0.55 Å/cycle.

AF-MoP-42 Atomic Layer Deposition of Lanthanum Oxide Using New La Precursors*, Junhyun Song, **Seungmin Han**, Jungwon Hwang,* Air Liquide, Republic of Korea

The continuous scaling of memory devices has led to challenges such as reliability issues due to leakage current and high power consumption. Lanthanum oxide (La_2O_3) is emerging as material for advanced memory devices because of its superior properties. For example, La_2O_3 is considered one of the promising materials for gate dielectrics due to its high dielectric constant (~27), wide bandgap (5.8~6.0eV), and thermodynamic stability in direct contact with Si. In addition, La_2O_3 is used as a dipole layer to adjust the effective work function of high-k metal gates, thereby reducing the threshold voltage. [1], [2]

Atomic layer deposition (ALD) is one of the most practical tools for advanced gate dielectric formation due to its precise thickness control, high uniformity and conformality. Air Liquide has developed three La precursors (La1, La2 and La3). Among them, La1 exhibits promising physical properties, including high vapor pressure and excellent thermal stability, making it a promising candidate for the ALD process. ALD evaluation was performed using La1 and ozone as the co-reactant. ALD window was observed up to approximately 350 °C, with a GPC >1A/cycle. Additionally, good step coverage (>90%) was achieved at 180 °C (S/C >90%, A/R=1:25). Carbon content within the films was dramatically reduced through a post-annealing process in the Ar atmosphere at 550 °C for 10 minutes.

Fig 1. Step coverage by using La1 with O_3 at 180°C

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AF-MoP-43 Ozone-Based Atomic Layer Deposition of Indium Oxide Thin Films: Impact on the Growth Rate and Its Uniformity of N_2 Supply in Ozone Generation

***Seung-Youl Kang**, Jaehyun Moon,* Electronics and Telecommunication Research Institute (ETRI), Republic of Korea*; Changbong Yeon, Jaesun Jung,* Soulbrain Co., Ltd., Republic of Korea*; Jong-Heon Yang, Chi-Sun Hwang, Seong-Mok Cho, Yong Hae Kim, Jae-Eun Pi, Seong-Deok Ahn,* Electronics and Telecommunication Research Institute (ETRI), Republic of Korea

Recently, thin indium oxide with a thickness of less than 5 nm has gained significant attention as an active material for thin film transistors due to its much higher electron mobility compared to other oxide semiconductors. When combined with the atomic layer deposition (ALD) method, it holds promise for use in back-end-of-line (BEOL) compatible transistors for monolithic 3D integration, as well as displays. The ALD method is particularly appealing for depositing ultrathin oxide semiconductors because it offers excellent thickness uniformity and controllability, with exceptional conformality that supports applications in monolithic 3D integration. To deposit oxide semiconductors using ALD, two key components are required: a metal precursor and a reactant. While various organometallic precursors for oxides have been developed and tested, the range of oxidants available is limited. Only a few molecules have been used as reactants, including water, hydrogen peroxide, ozone, oxygen plasma, and certain types of alcohols. However, not all oxidants are compatible with every precursor. For example, both water and ozone can be used with trimethylaluminum for Al_2O_3, whereas ozone is the only oxidant that can be used with trimethylgallium for Ga_2O_3, and DADI, InCp for In_2O_3. Ozone is often preferred for mass production because it is more reactive and easier to purge from the reaction chamber than water, though it does have drawbacks regarding deposition uniformity. In a previous report, we described the performance of TFTs using a new indium liquid precursor, DBADMI (N,N'-di-tert-butylacetimidamido)dimethylindium), renowned for its exceptional thermal stability across a wide temperature range (200°C to 350°C, which is the maximum temperature of our ALD equipment) . Like other indium precursors, DBADMI can be used to deposit In_2O_3 thin films with ozone, while water do not yield thin film formation. At an elevated temperature of 350°C, indium oxide films can be deposited with an acceptable growth per cycle (GPC) of approximately 1.1 Å per cycle, but the film thickness uniformity across the substrate was observed to be rather poor. In this article, we investigated the uniformity and growth rate of In_2O_3 thin films using DBADMI and ozone. Our findings revealed that the ratio of nitrogen (N_2) to oxygen (O_2) supply in the ozone generation process significantly affects the uniformity and growth rate of the In_2O_3 films. (Fig. 1.)

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AF-MoP-44 Promising ALD Precursor for Next-Generation Circuit Material: A Novel Ru-Based ALD Precursor with Lower Vaporization Temperature

***ziyu Yan**, Yong-Jay Lee,* Industrial Technology Research Institute, Taiwan

As the technology trend is focused on downscaling the size of transistors, the critical dimensions (CD) of integrated circuits (ICs) continue to shrink. Cu (copper) has the lowest bulk resistivity among other metals and therefore has become the primary material to use as a wire for electrical conductivity. However, as dimensions are scaled down, the resistivity of Cu increased by 2.5-fold under the size of 22 nm nodes, compared to bulk Cu. With the technology trend focused on downscaling the size of transistors, this phenomenon becomes fatal and will impact the overall performance of the circuit. According to past research, Ru (ruthenium) has a lower resistivity than Cu at thin metal lines starting from 10 nm in thickness. Therefore, it is expected to play an important role as a gate metal for next-generation circuit materials as an alternative to Cu.

Researchers can fabricate Ru metal thin films using various deposition techniques, such as electroplating, chemical vapor deposition, and atomic layer deposition (ALD). Among these methods, the ALD process has an extremely high application value because of its excellent film growth thickness controllability, step coverage, and large-area uniformity.

A high-quality ALD precursor needs to match several requirements, such as having a high vaporization rate, high reactivity, and high thermal stability. In this study, we successfully synthesized a novel ruthenium (Ru) ALD precursor, after TGA and DSC tests, it was found that the boiling point and vaporization temperature of this compound are lower than other commercial ruthenium precursors. Therefore, this precursor can be used at a lower processing temperature, which reduces energy costs and allows it to be applied to a wider range of ALD instruments with different specifications. At the same time, we are also developing other Ru precursors with different substituted groups to achieve different properties. We look forward to further developments of these precursors that can be used for next-generation circuit material.

AF-MoP-45 Low-Temperature ALD of Silicon Nitride Films Using Dis and Tis Precursors: A Strategy for Substrate Protection and High-Density Films

***Myeonghun Lee**, Taeheon Kim, Minchan Kim, Changkyun Park, Jinseong Park,* Hanyang University, Korea

Recently, various types of memory are being actively researched and developed to meet market demands for high performance and low power consumption. In emerging memory technologies, significant changes in cell materials and structures have made the gate spacer film increasingly important for protecting the cell material. Silicon nitride film has been used as gate spacer due to high density and reliable properties. ALD at high temperatures (>700°C) using DCS (Dichlorosilane, SiH_2Cl_2) has been the conventional method for deposition. However, this method can cause damage to the cell material, necessitating the development of alternative approaches to minimize such damage^1. We investigated ALD process with DIS(SiH2I2) and TIS(SiHI3) in lower temperature(<300°C) to prevent the damage by chlorine and high temperature. We first examined the ALD window of DIS, focusing on process temperature and plasma power. Our results show that higher temperatures lead to lower impurity levels, resulting in a Si/N ratio close to 75% at 300°C, which is ideal for SiNx films. Additionally, lower plasma power resulted in lower impurity levels, with a Si/N ratio stabilizing at 75% under 100W plasma power. When analyzing film roughness, lower plasma power also led to smoother films, which is beneficial for device performance. We then compared the activation energies of DIS and TIS, finding that TIS exhibited a lower activation energy than DIS. We also studied the effect of varying TIS ratios (0%, 1%, 4.4%) on film properties. The growth per cycle (GPC) and refractive index (R.I.) showed minimal changes with different TIS ratios, but the film density increased with higher TIS content, despite similar impurity levels. This increase in film density, coupled with the lower activation energy of TIS, suggests that TIS-added films may provide enhanced SiNx gate spacer films that can effectively prevent initial damage and better protect the cell material during post-processing steps.

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AF-MoP-46 Thermal Atomic Layer Deposition of Silicon Carbonitride Using Carbon-Containing Silicon Precursor

***Okhyeon Kim**, Tanzia Chowdhury, Mi-Soo Kim, Changgyu Kim, Hye-Lee Kim, Jeong Woo Han, Jae-Seok An, Jung Woo Park, Won-Jun Lee,* Sejong University, Republic of Korea

Silicon carbonitride (SiCN) offers a lower dielectric constant and better etch selectivity than silicon nitride (SiN), making it a promising alternative to SiN for semiconductor device fabrication. It is particularly suitable as a low-k barrier in copper interconnects and as a gate sidewall spacer in memory devices. However, an optimal deposition method to ensure conformality in high-aspect-ratio structures has not yet been established. SiCN is typically deposited by plasma-enhanced chemical vapor deposition (PECVD) or plasma-enhanced atomic layer deposition (PEALD) [1], but these methods have conformality limitations. In this study, we present the thermal ALD of SiCN using carbon-containing silicon precursors at 600–800°C. The maximum ALD temperature was determined based on self-limiting behavior with increasing precursor and ammonia exposure and confirmed by step coverage analysis in high-aspect-ratio patterns. Films deposited at the maximum ALD temperature were characterized by X-ray photoelectron spectroscopy (XPS) analysis. Carbon atoms bonded to silicon were observed in the film at concentrations of approximately 10–30%, resulting in a low dielectric constant of 4.9. In addition, density functional theory (DFT) calculations explain the mechanism of carbon incorporation. The thermal ALD approach of this study enables the deposition of conformal films of ternary SiCN compositions without the need for complex supercycle ALD processes of SiN and silicon carbide (SiC).

AF-MoP-47 Atomic Layer Deposition of High-Quality SnO Thin Films Using $Sn(EtCp)_2$ Precursor*, **Fumikazu Mizutani**, Nobutaka Takahashi,* Kojundo Chemical Laboratory Co., Ltd., Japan*; Tomomi Sawada,* National Institute for Materials Science,, Japan*; Toshihide Nabatame,* National Institute for Materials Science, Japan

Recently, SnO thin film has attracted attention because of an advantage of high hole mobility in the application of p-type oxide semiconductor. However, there are few reports of atomic layer deposition of conformal and defect-free SnO thin films.

Previously, we reported on ALD of SnO using a new Sn precursor (bis(ethylcyclopentadienyl) tin; $Sn(EtCp)_2$) [1]. Generally, ALD of SnO uses H_2O as a co-reactant for a divalent precursor, but no film growth was observed in ALD using $Sn(EtCp)_2$ and H_2O. To improve the adsorption of the precursor on the SnO surface, H_2O was used followed by H_2 plasma, which allowed the deposition of SnO thin films. However, when the elemental depth profile was analyzed, a small amount of Si was detected from the surface, indicating that a dense film had not been deposited.

To investigate the cause of this, the obtained SnO film was analyzed by XPS, and a small amount of Sn^0 signal was detected, indicating the presence of a metal component. This suggests that excessive reduction by the H_2 plasma occurred. In the previous report, SnO films were deposited on 150 mm Si wafers with native oxide films at a growth temperature of 200 °C, and saturation of reaction was confirmed with a H_2 plasma pulse time of 5 s. Therefore, this time we investigated whether it would be possible to deposit a dense film by shortening the H_2 plasma pulse time to 1 second.

FIG. 1 shows a comparison of film growth when the H_2 plasma time is 5 s and 1 s. As can be seen from FIG. 1, by shortening the H_2 plasma pulse time, the GPC became smaller, suggesting that the film became denser. The refractive index n at 380 nm of the SnO film deposited with 30 cycles, estimated by spectroscopic ellipsometry, was about 3.0 for both 5 s and 1 s H_2 plasma pulse times. However, for the film deposited with 100 cycles, the refractive index decreased to about 1.8 for the 5 s H_2 plasma pulse time, but only to about 2.6 for the 1 s H_2 plasma pulse time. This indicates that a dense film can be formed by shortening the H_2 plasma pulse time.

At the conference, we will report on the results of optimizing the H_2 plasma power and pulse time to deposit dense films and measure their electrical properties.

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AF-MoP-48 Damage-Free XPS Analysis of ALD HfO2, ZrO2 and HfZrOx Films Using Ar Cluster Ions*, **Seungwook Choi**, Ansoon Kim,* Korea Research Instutue of Standards and Science (KRISS), Republic of Korea

HfO_2, ZrO_2, and their mixture, $Hf_xZr_{1-x}O_2$ (HZO), are high-k materials widely studied and applied in various aspects such as gate dielectrics, charge trapping layers, doped oxides, and the formation of nanolaminated layers with other high-k materials[1]. Recently, there has been active research in applications such as resistive RAM (RRAM) and ferroelectric RAM (FeRAM)[2,3]. To achieve optimal properties as gate oxides, HfO_2 and ZrO_2 are typically deposited using Atomic Layer Deposition (ALD). Ideally deposited, these oxides exhibit a high dielectric constant and low defect characteristics, resulting in low leakage current. A critical technique for determining the composition ratio and impurities of HfO_2, ZrO_2, and HZO to optimize ALD deposition conditions is X-ray Photoelectron Spectroscopy (XPS). XPS analyzes photoelectrons emitted from the sample surface upon exposure to X-rays, providing detailed information on the surface's chemical composition.To fabricate ALD thin films with optimal gate oxide performance, it is essential to conduct comprehensive analyses. Specifically, evaluating oxygen vacancies, impurity levels, and chemical composition is crucial, as these factors significantly influence the dielectric constant, leakage current, and stability of the gate oxide device. XPS provides precise and surface-sensitive chemical composition analysis, enabling detailed characterization of ALD thin films.However, ex-situ XPS measurements expose samples to atmospheric contaminants (CO_2, H_2O, etc.), which can hinder accurate chemical characterization of HfO_2, ZrO_2, and HZO films. While Ar+ ion beam sputtering is commonly used to remove surface contaminants, it can damage the film surfaces, leading to inaccurate analysis of oxygen defects and chemical composition of the films.In this study, surface chemical analysis of HfO_2, ZrO_2, and HZO thin films was performed using XPS after removing surface contaminants using monatomic Ar+ and Ar2500+ cluster ions. It was found that even at the lowest monoatomic Ar+ ion beam energy, all films were damaged, leading to reduced films (HfO_{2-x}, ZrO_{2-x}, HZO_2-x) due to preferential sputtering. In contrast, sputtering with Ar2500+ cluster ions effectively removed surface contaminants without causing damage, allowing accurate characterization of oxygen defects and chemical composition. Furthermore, XPS combined with Ar cluster ion beam analysis enabled successful carbon impurity analysis of films fabricated by both PE-ALD and thermal ALD without damaging the films.[1] W. Banerjee et al., *Small*, 2022, **18**, 2107575.[2] A. Chen, *Solid-State Electron*. 2016, **125**, 25.[3] M. Lanza et al., *Adv. Electron. Mater.* 2019, **5**, 1800143.

AF-MoP-49 Steric Hindrance of Hf Precursors and Film Growth of HfO2 Atomic Layer Deposition: Comparative Kinetic Monte Carlo Simulation*, **Yanwei Wen**, Haojie Li, Bin Shan, Rong Chen,* Huazhong University of Science and Technology, China

Hafnia (HfO2)-based ferroelectrics have attracted considerable attention for next-generation memory devices due to their robust ferroelectricity at ultra-thin scales. We combine density functional theory and kinetic Monte Carlo simulations to investigate the atomic layer deposition of HfO_2 films from TEMA–Hf and $HfCp(NMe_2)_3$ precursors using O_3 as the oxidant.Our results show that both precursors decompose preferentially at 2-coordinate O sites on the HfO_2 surface, while 3-coordinate O sites present much higher energy barriers. Kinetic Monte Carlosimulations reveal that growth-rates per cycle (GPCs) of TEMA-Hf and HfCp(NMe2)3 with O3 are 0.094~0.109 nm/cycle and 0.081~0.096 nm/cycle from 150°C to 350°C, aligning closelywith experiments. The slower GPC observed forHfCp$(NMe_2)_3$ is attributed to the greatersteric hindrance of cyclopentadienyl ligand(Cp)compared to the dimethylamide(NMe_2) groups.Film morphology analysissuggests TEMA-Hf leads to smoother HfO_2 films.Nitrogen incorporation remains at about 1% for TEMA–Hf and $HfCp(NMe_2)_3$, consistent with experimental observations,while the concentration of O vacancies slightly decreases with the increase of deposition temperature. These findings provide insight into how precursor selection and atomic-level reaction pathways influence film growth and composition, thereby affecting the ferroelectric performance in HfO_2-based devices.

AF-MoP-50 In-Situ Spectroscopic Ellipsometry for Transition Metal Oxide Growth Control in Remote Plasma ALD Processes*, Yousra Traouli, Ufuk Kilic,* University of Nebraska - Lincoln*; Mathias Schubert, **Eva Schubert**,* University of Nebraska-Lincoln, USA

In this work, we investigate the real-time growth dynamics for transition metal oxide ultra-thin films (ZnO, WO_3, TiO_2) using Plasma-Enhanced Atomic Layer Deposition (PE-ALD) and in-situ spectroscopic ellipsometry (SE). Our primary focus is on characterizing the nonlinear growth regime during the initial nucleation phase and its transition into a stable, self-limiting layer-by-layer growth. By leveraging in-situ SE, we track the cyclic surface modifications, monitoring the evolution of film thickness and surface roughness throughout the deposition process[1]. The ALD growth utilizes organometallic precursors for the transition metals, with remote oxygen plasma and a water step as co-reactants to optimize film quality and uniformity. Additionally, we analyze the temperature dependence of the growth behavior to gain deeper insights into nucleation dynamics and film evolution[2]. Post-deposition structural and chemical characterization including scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) complements our in-situ findings. This study provides a comprehensive understanding of ALD growth mechanisms for transition metal oxides and offers valuable guidelines for optimizing deposition parameters to achieve high-quality, precisely controlled thin films.

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AF-MoP-51 Plasma-Enhanced ALD Process for Boron Carbide Films: Towards Tunable B:C Ratio, ***Catherine Marichy**, Neil Richard Innis, Abdhulhamid Afolabi,* Universite Claude Bernard Lyon 1, CNRS, LMI UMR 5615, Villeurbanne, F-69100, France; *Olivier Boisron,* Universite Claude Bernard Lyon 1, CNRS, ILM, Villeurbanne, F-69100, France; *Didier Leonard,* Universite Claude Bernard Lyon 1, CNRS, ISA, Villeurbanne, F-69100, France; *Colin Bousige, Catherine Journet,* Universite Claude Bernard Lyon 1, CNRS, LMI UMR 5615, Villeurbanne, F-69100, France

Boron carbide (B_xC) is a well-known ceramic material with high chemical and thermal stability, super-hardness, and a large neutron absorption cross-section. It is used in various applications such as refractory and cutting tool ceramics and neutron absorbers and detectors. Less explored are its electronic and optoelectronic properties. B_xC is a rather unknown semiconductor with tunable band gap[1,2] as a function of its B:C stoichiometry. Investigating its semiconductor properties requires its deposition as thin films with precise control over thickness, structure and composition. While PVD[3,4] and especially CVD[4–9] have shown potential for fabricating boron carbide thin films, ALD for B_xC remains largely unexplored[10] despite its advantages in terms of thickness control, uniformity and conformality.

In this study, amorphous B_xC thin films with atomic-level thickness control are successfully deposited by PEALD from triethylboron (TEB) and H_2 plasma[11]. A tunable B:C ratio is achieved by adjusting the process parameters. While the deposition temperature does not significantly affect the stoichiometry, special attention is given to the effect of plasma parameters, such as plasma mode (direct vs remote), H_2 flux and plasma power on the film composition. Plasma species not only remove the ethyl groups from TEB, but can also decompose by-products that may lead to additional carbon introduction into the film. A possible surface etching effect must also be considered.

The developed PEALD process of B_xC is discussed with a focus on the evolution of the film composition as a function of the plasma parameters. The plasma composition is monitored by in-situ optical emission spectrometry. The films are characterized in terms of thickness, morphology, structure and composition using various characterization techniques: ellipsometry, SEM and TEM, AFM, XPS, and ToF-SIMS. Attention is also paid to the physicochemical properties of the layers obtained, including their band-gap.

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AF-MoP-52 A Theoretical Study on High-Temperature ALD of TiN Using $CP(CH_3)_5Ti(Ome)3$ as a Precursor, ***Jae Min Jang,*** Hongik University, Republic of Korea; *Hye Won Park,* Incheon National University, Republic of Korea; *Soo-Hyun Kim,* Ulsan National Institute of Science and Technology, Republic of Korea; *Han-Bo-Ram Lee,* Incheon National University, Republic of Korea; *Bonggeun Shong,* Hongik University, Republic of Korea

In the field of semiconductor technology, titanium nitride (TiN) plays a critical role as a versatile material, serving as either diffusion barrier, adhesion layer, and conductor. As semiconductor devices continue to miniaturize, there is a demand for deposition methods of ultra-thin, easy thickness control, improved uniformity, and conformality, such as atomic layer deposition (ALD). For the above-mentioned applications of TiN, high temperature for the deposition process is often desirable. The precursors for high-temperature ALD of TiN, chlorine-containing Ti precursors may cast concerns regarding contamination and unwanted etching, while other Ti precursors often pose limitations in process temperature due to lack of thermal stability. In this regard, development of new ALD chemistry suitable for high temperature process is desirable. In this work, surface chemistry of $Cp(CH_3)_5Ti(OMe)_3$ (trimethoxy(pentamethylcyclopentadienyl)titaniumor TMPMCT)as a precursor for high-temperature ALDof TiNis investigated. Machine learning interatomic potential (MLIP) calculations are applied to elucidate the surface reaction mechanisms of TMPMCT. At high temperatures, the TiN surface is expected to have low coverage of H-containing functional groups due to desorption of NH_3 or H_2 [1]. Therefore, dissociative adsorption pathways of TMPMCT on the pristine TiN surface without surface functional groups are considered. The reactions under NH_3 exposure for removal of the ligands remaining on the surface are also elucidated. The changes in the Gibbs energy as functions of temperature are calculated as measure of the spontaneity of the reactions. Current work elucidates the chemistry of a potential new ALD process via molecular level theoretical investigations.

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AF-MoP-53 Adsorption of Hf Ald Precursor on Pristine HfO_2 Surface Without Hydroxyl Groups, ***Woong Pyo Jeon**, Miso Kim, Jinwoo Lee, Bonggeun Shong,* Hongik University, Republic of Korea

Hafnium oxide (HfO_2) stands as a prominent high-k dielectric material extensively employed as the gate oxide of nano-scale MOS devices. Atomic layer deposition (ALD) is a viable solution for the deposition of ultra-thin HfO_2 films with precise thickness control, enhanced uniformity, and conformality. Various oxygen sources are used for HfO_2 ALD, among which ozone or oxygen plasma can generate films devoid of surface functional groups such as hydroxyls (OH). Still, ALD of HfO_2 can occur on these surfaces, which may involve adsorption of the ALD precursors through ligand decomposition or ligand-mediated reactions [1]. In this study, the adsorption mechanism of TDMAH (tetrakis(dimethylamido)hafnium) on surfaces of pristine monoclinic HfO_2 without OHtermination is studied utilizing machine-learned interatomic potential (MLIP) and density functional theory (DFT) calculations. Accounting for potential byproducts arising from TDMAH adsorption and subsequent ligand desorption, diverse reaction pathways are explored, obtaining adsorption and activation energies for each scenario. To guide future experimental studies, vibrational spectra of the potential product structures are also calculated. Current study shows that ALD of oxides can proceed even without OH functional groups.

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AF-MoP-54 Sequential Adsorption of Dimethyl Zinc and Trimethylaluminum and Its Application to Zinc Aluminum Oxide Atomic Layer Deposition, *Haruto Suzuki, Satoshi Suzaki, Hibiki Takeda, Ryo Miyazawa, Bashir Ahmmad,* ***Fumihiko Hirose,*** Yamagata University, Japan

Zinc aluminum oxide films are applicable as wide-gap oxide semiconductors and for anti corrosion although the dependence of electronic properties on the zinc to aluminum atomic ratio is still unknown. In our laboratory, we have developed room-temperature atomic layer deposition of complex oxide using sequential adsorption where the two metal precursors are introduced to the surface sequentially to produce the mixed precursor saturated surfaces. This is assumed to allow for formation of perfectly atom dissolved oxide. In this experiment, we used dimethyl zinc (DMZ) as a Zn precursor and trimethylaluminum (TMA) as an Al precursor. The oxidizer was plasma excited humidified argon. We examined DMZ first introduction, followed by TMA adsorption. The atomic content ratio of Al to Zn was controlled by the exposure of the second gas of TMA. By using in-situ observation of IR absorbance spectroscopy, the TMA adsorption was modeled with one- and two-site adsorption models. Here TMA was assumed to adsorb on the DMZ-adsorbed surface with one or two unoccupied OH sites. Based on the dependence of TMA coverage on the DMZ exposure, the atomic ratio of Al to Zn was predicted. The related experimental results are presented, and the surface reaction mechanism is discussed in the conference.

AF-MoP-55 A Study on Laterally Controlled Distribution of Elements in InZnO Thin Films by Atomic Layer Modulation*, **Dong-Hyun Lim,*** Ajou University, Republic of Korea*; Kyung-Won Park, Ji-Hye Choi,* ATIK CO., LTD., Republic of Korea*; Il-Kwon Oh,* Ajou University, Republic of Korea

This study investigates the growth mechanisms and elemental distribution in InZnO (IZO) thin films using atomic layer modulation (ALM), a technique that enhances elemental distribution by sequentially introducing two precursors that react with a single counter reactant, thereby allowing for the formation of a monolayer multicomponent thin film. [1] A key finding is the conversion reaction where In metal transforms into Zn metal during the deposition process, as illustrated in Figure 1(a). The in-situ quadrupole mass spectrometry (QMS) analysis in Figure 1(b) confirms this reaction, showing that after feeding [3-(dimethylamino)propyl]dimethylindium (DADI) and pulsing diethylzinc (DEZ), In is converted into the ethyl ligand-bound $In(Et)_3$, indicating the formation of a zinc-rich film via ALM. Furthermore, the comparative analysis of homogeneous IZO films grown via ALM and laminate structures deposited by the supercycle method highlights the lack of research on how elemental distribution affects channel properties in oxide semiconductors. This comparison is expected to significantly contribute to the field of oxide semiconductor research. Lastly, it is noteworthy that ALM has primarily been studied for dielectric materials, with no prior investigations conducted on oxide semiconductors, marking a novel aspect of this research.

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AF-MoP-56 Comparative Study on the Impacts of Anhydrous and Hydrous H_2O_2 on ALD Hafnium Oxide Growth on Titanium Nitride Surface*, **Dan Le,*** RASIRC*; Jin-Hyun Kim, Thi Thu Huong Chu, Soubhik De, Dushyant Narayan, Minjong Lee,* University of Texas at Dallas*; Walter Hernandez, Josh Garretson, Adrian Alvarez, Jeffrey Spiegelman,* RASIRC*; Jiyoung Kim,* University of Texas at Dallas

HfO_2-based ferroelectrics have emerged as prominent materials for memory applications due to their unique electrical properties, even at the sub-nanometer scale. However, interface-related challenges, such as relaxation, imprint, fatigue, and breakdown, continue to pose significant concerns, especially for ferroelectric films thinner than 5 nm [1]. Previous studies have shown that the choice of oxidant sources during ALD HfO_2-based ferroelectrics plays a crucial role in oxide interface formation [2]. Therefore, selecting the appropriate oxygen source or developing effective interface engineering processes is essential to overcoming these interface-related challenges.

In our earlier studies, we observed that HfO_2-based ferroelectrics achieved using anhydrous H_2O_2 exhibited a higher growth rate and enhanced electrical properties [3]. However, our *in-situ* investigation of ALD HfO_2 on titanium nitride (TiN) substrate at 250 °C revealed that anhydrous H_2O_2 saturated the TiN surface with hydroperoxyl groups, leading to the formation of a limited interface, whereas H_2O formed little to no interface [2]. A key question remains whether a combination of H_2O and H_2O_2 may help reduce HfO_2–TiN interface formation while maintaining the enhanced properties of the HfO_2 layer. In this study, we focus on investigating the effects of hydrous H_2O_2 on interface formation and growth mechanism of ALD HfO_2 on TiN substrate. Using *in-situ* reflectance absorption infrared spectroscopy (RAIRS) and complementary analytical techniques, we aim to gain deeper insights into the underlying phenomena. Throughout the study, alongside TDMA-Hf as the metal precursor, the hydrous H_2O_2 (4:1 H_2O/H_2O_2 ratio) is delivered via a gas delivery system to ensure a stable and constant oxidant supply. While the IR results reveal some similarities, a distinct difference between anhydrous and hydrous H_2O_2 was observed, as the peak associated with hydroperoxyl groups was absent in the case of hydrous H_2O_2. The differences in the available surface species during the hydrous H_2O_2 pulse may influence the growth of HfO_2. In addition to IR analysis, the impacts of hydrous H_2O_2 on growth characteristics, and material properties, including chemical composition, density, ferroelectricity, etc. will also be carefully evaluated. Detailed experimental procedures and results will be presented.

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AF-MoP-57 Computation of Al_2O_3 ALD by Trimethylaluminum with Kinetic Monte Carlo and Neural Network Potential*, **Yichen Zou,** Yuxuan Wu,* The University of Tokyo, China*; Jun Yamaguchi, Noboru Sato, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

Atomic Layer Deposition (ALD) is widely utilized in semiconductor manufacturing owing to its method of alternately introducing a precursor and reaction gas, which relies on the surface saturation adsorption of the precursor. This approach ensures excellent uniformity in thickness and controls variations in processing conditions, but is challenged by its growth rate compared with other deposition methods. Investigation into the growth rate of ALD has drawn tremendous attention in the experiments but could be facilitated by emerging computation methods that cut the cost. Traditional computational methods, such as Density Functional Theory (DFT), offer insights into surface adsorption and reactions and are time-intensive when predicting the growth rate per cycle for ALD applications, particularly for large metalorganic compounds. To overcome these challenges, we are leveraging Kinetics Monte Carlo (KMC, an emerging time-scale reaction simulation method) and Matlantis^{TM} (a cutting-edge atomic-level simulator that utilizes neural network potentials) to investigate the adsorption of Trimethylaluminum (TMA) during Al_2O_3 ALD using H_2O as the reactant.KMC is a numerical simulation method based on stochastic processes, which is mainly used to study the dynamic evolution of complex systems. KMC is not only concerned with the equilibrium properties of the system but also directly simulates the time-dependent kinetic behavior, which is suitable for the study of non-equilibrium processes with multiple possible events such as the ALD process. The powerful Matlantis^{TM} calculates energies accurately and efficiently for multiple TMA molecules adsorption and reaction of multiple TMA molecules on the surface, and the energies are introduced into KMC to predict the growth rate of Al_2O_3 in each cycle. Both the KMC and Matlantis' calculations can be performed at extremely fast speeds, with time spent on a scale of minutes. In the following figures, we successfully predicted the adsorption kinetics of TMA during the TMA supply step, which showed a mass increase of 36 ng/cm^2 in approximately 0.3 seconds. Our TMA adsorption and growth simulations show strong agreement with previous DFT calculations and Quartz Crystal Microbalance (QCM) experimental results. In addition, our study revealed that some carbon remained inside the film. The KMC simulations were performed at different temperatures and water pulse times. The results show that both the temperature and water pulse time have important effects on the carbon residue in the film. Low temperature and short water pulse time significantly increased the carbon residue.

AF-MoP-58 Comparison of ALD SiN Film Properties Based on Synthesis Precursor, Process Temperature, and Conditions*, **Jaeyoung Lim,** Hanseong Kim, Sunki Min, Kang-sub Yim, Sun Jung Kim,* Samsung Electronics Semiconductor R&D center Semiconductor Processing Development, Republic of Korea

ALD SiN films play a crucial role in semiconductor processes, serving various applications. While different precursors are utilized for ALD SiN synthesis, the halogen-based precursor dichlorosilane (DCS) is widely adopted due to its cost-effectiveness and excellent film properties. However, its relatively low reactivity necessitates high-temperature plasma processing, posing limitations on film quality enhancement. In contrast, diIodosilane (DIS), another halogen-based precursor, exhibits higher reactivity, allowing for low-temperature plasma processing. This study compares the film characteristics of ALD SiN synthesized using DCS and DIS precursors under varying process temperatures and conditions. The findings aim to provide insights into optimizing ALD SiN synthesis methods for high-performance semiconductor logic devices.

Atomic Layer Etching
Room Event Hall - Session ALE-MoP
Atomic Layer Etching Poster Session

ALE-MoP-1 Study on High-Selectivity Atomic Layer Etching (ALE) of SiO_2/Si_3N_4 Using Ar/C_4F_6Plasma*, Kyongnam Kim,* Daejeon University, Republic of Korea*; **Jinwoo Choi,*** Deajeon University, Republic of Korea*; ByeongHo Song, Jeongwoon Bae,* Daejeon University, Republic of Korea

In the current semiconductor industry, the circuits being manufactured have reduced critical dimensions to a few nanometers, and the thickness of the materials requiring etching has also become exceedingly thin, increasing the necessity for highly precise plasma processes. Additionally, to etch materials with low plasma resistance, such as low-k materials, it is essential to conduct etching processes that do not damage the material's surface or sidewalls. This necessity has brought attention to Atomic Layer Etching (ALE) processes as a promising alternative. ALE is emerging as the next-generation etching technology because it allows for damage-free etching of surfaces and sidewalls and enables nano-scale control over etching depth.

In ALE processes, research is being conducted using PFCs (Perfluorocarbons) gases like C_4F_8 that can form an appropriate polymer layer to protect the sidewalls. However, most PFC gases, including C_4F_8, have extremely high Global Warming Potentials (GWP) ranging from thousands to tens of thousands, which poses a disadvantage as it does not align with the global trend of reducing carbon emissions.

This study explores the implementation of high-selectivity in the etching of SiO_2 over Si_3N_4 using the ALE process, a next-generation semiconductor etching technique, and C_4F_6, which is known to have a GWP of less than 100 and allows for easy control of the etching selectivity due to its high C/F ratio. To achieve precise real-time control of the etching rate, an ellipsometer capable of in-situ thin film thickness measurement was employed to analyze the Etch Per Cycle (EPC) according to changes in the etching process.

ALE-MoP-2 Improving Process Stability in Atomic Layer Etching for Next-Generation Microfabrication

***Suyoung Jang**, Junyeob Lee, Dohyeon Kim, Jeongwoon Bae, Taehyung Kim, Kyongnam Kim,* Daejeon University, Republic of Korea*; Jihyun Kim,* WONIK IPS, Republic of Korea

Abstract With the increasing integration density and miniaturization of semiconductor devices, the aspect ratio of patterns has been rising, emphasizing the importance of Atomic Layer Etching (ALE) technology for precise layer-by-layer control. Particularly, in physical adsorption-based ALE, the adsorption amount heavily depends on adsorption time, making it challenging to achieve accurate and stable EPC (Etch per Cycle).

This study systematically analyzes the impact of variations in physical adsorption amounts on EPC in ALE processes. To this end, a sensor capable of real-time monitoring of polymer quantities was employed to observe changes in polymer adsorption under various process conditions, and these data were compared with etching process outcomes. In particular, the study examined how changes in process variables-such as temperature, pressure, and gas composition-affect the amount of adsorbed polymers, the amount of polymer consumed during desorption processes, and unexpected variables occurring in each etching cycle. By identifying factors that influence process reliability and effectively monitoring such environments, this research proposes strategies to enhance the reliability of etching processes. This study is expected to contribute to the development of stable and precise ALE technologies for next-generation microfabrication processes.

ALE-MoP-3 Synergy in Thermal Atomic Layer Etching: Interplay between Individual Reactions

*Marcel Junige, **Andrew S. Cavanagh**, Steven M. George,* University of Colorado Boulder

The plasma-assisted atomic layer etching (ALE) community has long recognized that an ideal ALE sequence requires the favorable interaction of its individual, separated reaction steps [Kanarik *et al.*, *JVST-A* **33**, 020802 (2015)]. Ideal ALE synergy is characterized by self-limiting A and B half-reactions, whereas spontaneous etch pathways may continuously remove the targeted material. This work utilized *in situ* spectroscopic ellipsometry (iSE) to study and extend this synergy concept to thermal ALE processes:
ALE Synergy = $(EPC-\alpha-\beta)/EPC$
The digital etch per cycle (EPC) is the thickness loss derived from the A/B reaction sequence. The spontaneous etch rate αor βmay contribute a thickness loss during the individual A or B reaction. Synergy was evaluated for alumina (Al_2O_3), silica (SiO_2), silicon nitride (SiN_x), and silicon (Si) thermal ALE.

Al_2O_3 ALE using alternating hydrogen fluoride (HF) and trimethylaluminum (TMA) exposures [Lee *et al.*, *Chem. Mater.***28**, 2994 (2016)] exhibited an EPC of 2.61 Å/cycle at 275℃, whereas HF exposures alone gave a negligible Al_2O_3 spontaneous etch rate of less than 0.01 Å/min. This behavior corresponded to ideal synergy of 99.6%.

SiO_2 ALE using TMA/HF exposures [DuMont *et al.*, *ACS Appl. Mater. Interfaces* **9**, 10296 (2017)] exhibited an EPC of 0.20 Å/cycle at 275℃, whereas HF exposures alone displayed a minor SiO_2 spontaneous etch rate of 0.03 Å/min. This behavior corresponded to near-ideal synergy of 88%.

In contrast, SiN_x ALE using TMA/HF exposures exhibited an EPC of 1.06 Å/cycle at 275℃, whereas HF exposures alone caused a major SiN_x spontaneous etch rate of 1.72 Å/min. This behavior corresponded to no ALE synergy or predominant SiN_x spontaneous etching by HF alone [Junige & George, *Chem. Mater.* **36**, 6950 (2024)].

Si ALE using an oxygen (O_2)/HF/TMA exposure sequence at 290℃ has displayed complex behavior because of the interplay between three individual reactions. Si ALE has exhibited a controlled, linear EPC of ~0.4 Å/cycle [Abdulagatov & George, *Chem. Mater.* **30**, 8465 (2018)]. However, recent iSE and temperature-programmed quadrupole mass spectrometry experiments discovered that HF alone spontaneously etched Si at temperatures above 150℃. HF exposures caused a major Si spontaneous etch rate of 16.3 Å/min at 275℃ [Junige *et al.*, *AVS 70*, AP1+EM+PS+TF-TuM-3 (AVS: 2024)]. This Si spontaneous etching by HF could predominate Si ALE. But critically, the oxidation step during Si ALE formed a SiO_2 layer on the Si surface. Consequently, the synergy for Si ALE was determined by the near-ideal SiO_2 ALE synergy. The synergy definition needs to be modified here to account for the effect of each reaction in the A/B/C sequence.

ALE-MoP-4 Atomic Layer Etching of ZrO_2, HfO_2 and $HfZrO_4$ Thin Films via Metal-Free Ligand Exchange using Hydrogen Fluoride and Acetylacetone

***Kyoung-Mun Kim**, Joo-Yong Kim,* Merck KGaA, Darmstadt, Republic of Korea

Atomic Layer Etching (ALE) is a useful method for fabricating thin, crystalline films, especially high-dielectric materials. Gibbs free energy calculations were performed to identify suitable ALE precursors. Acetylacetone was selected as a promising candidate, as calculations indicated its potential to etch both ZrO_2 and HfO_2. ZrO_2, HfO_2, and $HfZrO_4$ films were etched at 250°C using a metal-free precursor via ALE, and their properties were compared. Crystalline ZrO_2 films were successfully etched without altering crystallinity or surface morphology (RMS roughness < 0.7 nm), consistent with the calculated Gibbs free energy (-14.19 kcal/mol). The metal-free precursor ensured the absence of metal impurities in the etched films. However, significant fluorine residue remained, which was reduced to approximately 4% through subsequent heat treatment. Conversely, crystalline HfO_2 (c-HfO_2) films exhibited limited etching, despite a favorable Gibbs free energy calculation (-8.88 kcal/mol). This discrepancy was attributed to the high density and corrosion resistance of c-HfO_2. To verify this hypothesis, amorphous HfO_2 (a-HfO_2), with lower density, was successfully etched, confirming the influence of density on the etching process. Partially crystallized $HfZrO_4$ films underwent partial etching, with amorphous regions being etched while crystalline regions remained unaffected. In conclusion, this study demonstrates a strong correlation between Gibbs free energy calculations and the feasibility of ALE for high-k dielectric materials. Additionally, the influence of factors such as crystallinity, density, and chemical resistance on the etching process has been elucidated. These findings provide valuable insights for optimizing ALE processes and achieving precise control over the thickness and properties of high-k dielectric films.

ALE-MoP-5 Isotropic Atomic Layer Etching of Crystalline HfO_2 Thin Films Using F Radical and $Al(CH3)_2Cl$

***Jehwan Hong**, Gyejun Cho, Changgyu Kim, Hye-Lee Kim,* Sejong University, Republic of Korea*; Byungchul Cho, Min Su Kim, Ju Hwan Park, Min Kim,* Wonik IPS, Republic of Korea*; Won-Jun Lee,* Sejong University, Republic of Korea

Hafnium oxide (HfO_2), a high-k material, has been extensively studied for semiconductor applications. Amorphous HfO_2 is commonly used as a gate dielectric in nano-CMOS devices due to its lower leakage current compared to other high-k materials. Doped crystalline HfO_2, which exhibits ferroelectricity even at thicknesses below 10 nm, is promising for FeFET and FeRAM applications. However, as the film thickness decreases, the surface roughness increases and the grain size in crystalline films becomes smaller. An isotropic atomic layer etching (ALE) process can be used to etch back thicker films to form smoother, larger grain thin films without ion bombardment damage. Previous studies have demonstrated isotropic ALE of HfO_2 using HF or SF_4 as the fluorinating agent and $Al(CH_3)_2Cl$ or $TiCl_4$ as the removal precursor [1]. However, the etching rate of the crystalline film was significantly lower than that of the amorphous film. While the use of XeF_2 as a more reactive fluorinating agent increased the etching rate, the etching rate of the crystalline film was still about half that of the amorphous films. In this work, we investigate the isotropic ALE of HfO_2 using fluorine radicals combined with $Al(CH_3)_2Cl$ as a removal precursor. The temperature dependence and reaction mechanisms of HfO_2 ALE were analyzed using an *in situ* quartz crystal microbalance, comparing etching rates and post-etch properties for both amorphous and crystalline HfO_2 films. At temperatures of 200°C or higher, the etching rate increased with increasing temperature. For both amorphous and crystalline films, higher etching rates were achieved than for HF, SF_4, and XeF_2, with no significant difference in etching rates between amorphous and crystalline films. After the ALE process, the surface roughness of amorphous thin films decreased, while crystalline films showed only a slight increase. This is attributed to the similar etching rates of grains and grain boundaries in the crystalline film. In addition, the leakage current can be improved for both amorphous and crystalline thin films by ALE etching back thicker films.

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ALE-MoP-6 Atomic Layer Etching of Al2O3 Film by Using Different Metal Precursor for Ligand Exchange

***Chan Lee**, Chang Kyu Lee, Byung Chul Cho, Ju Hwan Park, Min Kim,* WONIK IPS, Republic of Korea*; Misoo Kim, Khabib Khumaini, Hye-Lee Kim, Won-Jun Lee,* Sejong University, Republic of Korea

The atomic layer etching (ALE) is one of the advanced technology, which allows to delicate etch on complex pattern by atomic scale control.[1,2] In this study, the ALE of aluminum oxide (Al_2O_3) was proceeded by cyclic process composed of a surface modification by F radical, ligand exchange by metal precursor, which is trimethylaluminum (TMA) and dimethylaluminum chloride (DMAC). The Al_2O_3 surface is converted to $AlOF_x$ by F radical in the fluorination step, and the fluorinated layer is removed by a ligand exchange reaction with TMA and DMAC in the removal step. The etch amount of each precursor was analyzed by *in-situ* quartz crystal microbalance (QCM). Unlike DMAC, the etch amount of TMA decreased as cycle increased, which was caused by carbon absorption. It disturbed surface fluorination, and was confirmed by *in-situ* X-ray Photoelectron Spectroscopy (XPS). The ALE process was analyzed by transmission electron microscopy (TEM), atomic force microscopy (AFM), and time-of-flight secondary ion mass spectrometry (ToF-SIMS), X-ray diffraction (XRD). The crystallinity of Al_2O_3 film maintained after ALE process, which is totally different with same thickness as-depo film. Isotropic removal of Al_2O_3 thin films was observed on the trench patterns with an aspect ratio of >20. Finally, thesecharacteristics can be suggested application of high-k material in advanced memory device.

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ALE-MoP-7 Fabrication of Ultrathin Ruthenium Films via a Top-Down Approach Using Thermal Atomic Layer Etching

*Jeong Hwan Han, **Eun Ji Ju**, Jae Hyeon Lee,* Seoul National University of Science and Technology, Republic of Korea

Ruthenium (Ru) is considered a promising material for next-generation interconnects due to its low electron mean free path (EMFP) of 6.6 nm and bulk resistivity of 7.1 μΩ·cm. However, when Ru is deposited using conventional bottom-up processes, the significant difference in surface energy between the substrate and Ru promotes island growth, leading to discontinuous fine grains and increased surface roughness, which can elevate the resistivity of ultrathin Ru films. To address this issue, it is crucial to develop methods that improve the continuity of ultrathin Ru films and enhance their electrical properties.

In this study, thermal atomic layer etching (ALE) was explored to fabricate ultrathin Ru films. We investigated the etching behavior of Ru thin films, and self-limiting ALE conditions were achieved through surface modification and volatilization processes of Ru films. The effects of etching temperature and reactant gas injection time were systematically examined. To fabricate ultrathin Ru films with enlarged grains, thick (~20 nm) Ru thin films were initially grown by atomic layer deposition, followed by ALE. The continuity, electrical properties, and surface roughness of the Ru films were characterized using high-resolution field-emission scanning electron microscopy (FESEM), a four-point probe, and atomic force microscopy (AFM). By applying ALE to Ru, we successfully mitigated the degradation of electrical properties caused by discontinuities in the Ru ultrathin films, resulting in low-resistivity films.

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ALE-MoP-8 Thermal Atomic Layer Etching of ZrO_2 Using Chlorine-Based Precursor

*Sang-ik Lee, **Yong-won Kim**,* DNF Co., Ltd, Republic of Korea*; jun-hee Cho, Joong-jin Park,* DNF Co., Ltd., Republic of Korea

Atomic Layer Etching (ALE) has emerged as a critical thin-film processing technology that facilitates the advancement of next-generation semiconductor technology.

Research into ALE is focusing on various metal oxides, including Zirconium Dioxide (ZrO_2), Hafnium Dioxide (HfO_2), Titanium Dioxide (TiO_2), and Aluminum Oxide (Al_2O_3), among others. These materials are essential for developing capacitors and other electronic components that require high dielectric constants (k value).

In this study, we present the ZrO_2. ZrO_2 was deposited onto 8-inch silicon wafers through Thermal ALD process. The thickness of the deposited ZrO_2 layer was analyzed using spectroscopic ellipsometry,

ZrO_2 is utilized in capacitors due to its dielectric properties. To achieve a high dielectric constant, it is essential to obtain a thin, crystalline ZrO_2 film. However, when ZrO_2 is deposited thinly, it tends to form an amorphous layer, which does not fulfill the performance requirements for high-k applications. To overcome this challenge, we propose depositing ZrO_2 Thicker, which allows for the formation of a crystalline structure. The resultant crystalline ZrO_2 film can then undergo the ALE process to achieve an etching profile that retains the desired high-k characteristics.

A major problem when using fluorine-containing precursors for etching is the large amount of leftover fluorine on the surface after etching. This leftover fluorine can cause serious damage to the material. Therefore, we expect that Chlorine based Precursor will offer a good solution to this problem by lowering the risk of damage.

We used a mass flow controller (MFC) to adjust the amount and timing of Chlorine based Precursor input, and through various process concepts, we are exploring the etch rate per cycle (EPC) saturation and confirming its potential.

ALE-MoP-9 Highly Precise Atomic Layer Etching of SiO_2 with SF_6 Radicals and TMA Surface Modification

***Min Kyun Sohn**, Seong Hyun Lee, Jieun Kim, Sun Kyu Jung, Min-A Park, Jin Ha Kim, Jaeseoung Park, Jeong Woo Park, Dongwoo Suh,* ETRI, Republic of Korea

As next-generation semiconductor devices evolve from planar architectures to three-dimensional (3D) structures such as Gate-All-Around FETs and Complementary FETs, achieving isotropic etching with atomic-level precision has become increasingly critical. SiO_2, commonly used as an insulating layer or hard mask and also serving as an interface layer in nano-sheet channel gates, requires precise etch profile control to accommodate complex 3D device geometries. To meet these demands, Thermal Atomic Layer Etching (TALE) has emerged as a promising solution, offering high selectivity, low surface damage, and atomic-scale precision, thereby fitting the requirements of advanced 3D device fabrication.

However, most existing studies have employed Hydrogen Fluoride (HF)-based gases for TALE processes, raising concerns regarding corrosiveness, safety, and process control. Meanwhile, alternative fluorine-based gases generally exhibit low reactivity, making them inadequate for high-efficiency TALE. Consequently, there is a growing need for a radical-based ALE approach that retains the advantages of TALE while mitigating the issues associated with HF-based methods.

In this study, we propose a radical-based ALE process replacing HF gas with sulfur hexafluoride (SF_6) radicals, generated via a remote plasma source (RPS). We deposited approximately 700 Å of SiO_2 on a silicon wafer using TEOS through low-pressure chemical vapor deposition (LPCVD). The thickness of SiO_2 was measured via ellipsometry across a 6-inch wafer. Using this SiO_2 layer, we developed an optimized ALE process utilizing trimethylaluminum (TMA) for surface modification and SF_6 radicals for fluorination at 300 °C. Under the same temperature conditions, substituting SF_6 radicals with SF_6 gas alone resulted in no measurable etch, underscoring the necessity of radical-based reactions for effective etching. Our optimized process achieved an etch-per-cycle (EPC) of approximately 0.323 Å. Additionally, X-ray photoelectron spectroscopy (XPS) analysis clarified the chemical reaction mechanisms involved in both the TMA-induced surface modification step and the subsequent SF_6 radical etching step, thereby validating the reliability and stability of our method.

In conclusion, the SF_6–TMA radical-based ALE process presented here effectively preserves the core advantages of TALE while overcoming the drawbacks of HF-based approaches, satisfying the precision etching and process stability requirements crucial for 3D semiconductor manufacturing.

ALE-MoP-10 Plasma Atomic Layer Etching of SiO_2, Si_3N_4, and Si by Forming Ammonium Fluorosilicate Followed by Argon Ion Bombardment, *Heeyeop Chae, **Taeseok Jung**, Hyeongwu Lee, Hojin Kang, Minsung Jeon,* Sungkyunkwan University (SKKU), Republic of Korea

Plasma atomic layer etching (ALE) processes for SiO_2, Si_3N_4, and Si were developed with surface fluorination using NF_3/NH_3 plasma and Ar ion bombardment. The SiO_2, Si_3N_4, and Si surfaces were fluorinated by forming an ammonium fluorosilicate (AFS, $(NH_4)_2SiF_6$) layer. The AFS layer prevented continuous etching of SiO_2, Si_3N_4, and Si at an $NF_3/(NF_3+NH_3)$ gas ratio below 50 %. In this range, NH_x (x = 1 to 3) radicals were detected as major peaks compared to NF_x (x = 1 to 3) radicals as confirmed by quadrupole mass spectrometry (QMS).The formation oftheAFS layer was confirmed with N-H stretching (3330 cm^{-1}) and N-H bending (1454 cm^{-1}) in Fourier transform infrared (FT-IR) spectroscopy.The ALE window was observed in the range of 35 to 45 V for SiO_2 and 30 to 40 V for Si_3N_4 and 25 to 35 V for Si. The etch per cycle (EPC) was saturated to 3.7 nm/cycle for SiO_2 and 1.0 nm/cycle for Si_3N_4 and 0.5 nm/cycle for Si after 15 seconds of Ar plasma time at the NF_3/NH_3 plasma of 60 seconds. The higher EPC of SiO_2 is attributed to the stronger interaction of polar NH_4^+ and HF components with the more polarized Si-O bond than with the Si-N and Si-Si bonds.

ALE-MoP-11 Tailored Waveforms for Ion Energy Control in Ale Applications, *Sebastian Mohr,* Quantemol.Ltd, Germany*; **HyungSeon Song**,* Quantemol.Ltd, Republic of Korea

Atomic layer etching (ALE) is increasingly used in the manufacturing of semiconductor tools as they give more control over the resulting etching profiles than traditional etching techniques. While different approaches to ALE exist, many of them employ plasmas in one or more steps of the ALE process, be it to use the neutral radicals produced in the plasma to alter the surface or the ions to remove the altered top layer [1].

For such applications, independent control of ion flux and ion energy is highly desirable. Single frequency capacitively coupled discharges (CCPs) do not offer this, as the input power affects both flux and energy. Dual frequency discharges allow this to some extent, but it is limited due to, for example, increased ionization by secondary electrons at high powers of the low frequency. Furthermore, traditional CCPs usually produce bimodal ion energy distribution functions which can cover several 10s to 100s of eV with sharp peaks at either end, so the ion energy cannot be easily limited to a small interval of energies, which is desirable especially for ALE applications, so that the ions remove the top layer of the surface but do not damage the underlying bulk [1].

An alternative approach to achieve this desired control are tailored waveforms. These can range from so-called asymmetric waveforms combining a fundamental frequency with even multiples [2] to non-sinusoidal waveforms typically consisting of sharp voltage peaks [1] followed by a relatively long interval of an almost constant voltage. While it has been demonstrated that these type of CCPs offer independent control of ion flux and energy and/or are able to limit the ion energy to narrow energy intervals, they have not yet been well studied in industrial applications.

This presentation will show continued efforts to simulate industrial applications of tailored waveform CCPs using the well-established 2D plasma simulation code HPEM [3]. In these discharges, the plasma is sustained via ICP coupling, while the tailored waveforms are applied to an rf-electrode staging the wafer. Former simulations have shown the intended effect in case of blank metal electrodes.

ALE-MoP-12 Understanding Fluorocarbon Thin Film Growth through CF_xRadical Adsorption on Amorphous Si_3N_4, ***Mihyeon Jo**, Sangheon Lee,* Ewha Womans University, Republic of Korea

Fluorocarbon thin films play a crucial role in semiconductor and display manufacturing processes, particularly in plasma-enhanced chemical vapor deposition (PECVD) and plasma etching. To gain a fundamental understanding of the thin film growth mechanism, this study investigates the adsorption behavior of CF, CF_2, and CF_3 radicals on an amorphous Si_3N_4 surface using Density Functional Theory (DFT) calculations. By comparing the adsorption energies and structural stabilities of individual radicals, we aim to elucidate the role of each species in fluorocarbon film formation.

To achieve this, we modeled an amorphous Si_3N_4 surface and systematically adsorbed CF, CF_2, and CF_3 radicals to analyze the resulting surface modifications and bonding structures. Additionally, we examined the formation of C-F, C-C, C-N, and C-Si bonds, as well as changes in the electronic structure through Density of States (DOS) analysis. These investigations provide insights into the contributions of different radicals to thin film growth and help determine the conditions under which a stable fluorocarbon layer can form.

This study contributes to the atomic-level understanding of fluorocarbon thin film growth mechanisms and provides fundamental knowledge that can aid in controlling radical composition in plasma processes to achieve desired thin film properties.

ALE-MoP-13 Study of Low GWP Gas Decomposition and Fluorocarbon Film Created gas Deposition on SiO_2, ***Minji Kim**, Sangheon Lee,* Ewha Woman's University, Republic of Korea

Global warming is one of the serious problems about the earth's environment and the biggest cause of global warming is CO_2 released into the atmosphere, which has increased in concentration in proportion to the development of the industry, but other greenhouse gases such as perfluorocarbons (PFCs) and hydrofluorocarbons (HFCs) have also been shown to have a much stronger greenhouse effect than carbon dioxide.

Because hydrofluorocarbons (HFCs) have a high infrared absorbency and long atmospheric lifetimes. The Global Warming Potentials (GWPs) which shows the degree to which other greenhouse gases contribute to global warming based on the impact of carbon dioxide on global warming, is 1,000 to 10,000 times as high as that of CO_2 (whose GWP is 1). CHF_3 molecule which is the simplest molecule among HFCs gases has 11,700 GWP index.

These HFCs gases are used in various device-fabrication processes in the semiconductor industry, CHF_3 is used in the etching process of SiO_2 films. Since semiconductors are an indispensable part of modern technology. it is time to discover alternative gases with a low GWP index that can be used in the etching process.

Thus, C3F6O, one of several precursor gas candidates for fluoro-ketone, will be investigated for several radical species decomposed during the etching process compared to the reference etching gas CHF3, which is deposited on SiO2 to form a fluorocarbon film. This work will use the Vienna ab initio simulation package (VASP) to perform the calculation details of quantum chemistry calculations, Gaussian09 and density functional theory (DFT) to calculate the energy of the decomposition path.

ALD for Manufacturing
Room Event Hall - Session AM-MoP
ALD for Manufacturing Poster Session

AM-MoP-1 Low-Temperature Atomic Layer Deposition of Silicon Nitride Films Using Space-Division Equipment, ***Jae-Min Park**, Taeho Jeon, Sung-Eun Lee, Hojin Nam, Hyeong Wook Kim, Hyunsik Hwang, Changhee Han, Heonhyeong Lim, Sangjoon Park,* WONIK IPS Co., Ltd., Republic of Korea

Silicon nitride (SiN) films have been widely applied in microelectronics, optoelectronics and other fields due to their excellent dielectric properties, chemical inertness and mechanical strength. The increasing demand for low-temperature SiN deposition is driven by the need for reduced thermal budgets in advanced device fabrication. Atomic layer deposition (ALD) offers precise thin film deposition with excellent film quality and uniformity, even at low temperatures. This study investigates low-temperature SiN ALD using CORBIT NITRAD, a space-division equipment capable of rotation and revolution that uses a microwave plasma source. We designed multi-step plasma enhanced atomic layer deposition process using CORBIT NITRAD. The sequence of the multi-step PEALD process consists of the Dichlorosilane feeding step, the H2/Ar plasma step, the NH3/Ar plasma step, Thermal NH3 step and N2/Ar plasma step. The H radicals in H2 plasma and NH3 plasma efficiently remove the ligands from the precursor, and the N2 plasma removes the surface hydrogen atoms to activate the adsorption of the precursor. This multi-step PEALD approach is a major advantage of space-division ALD system, allowing the deposition of highly uniform, high quality SiN films at low temperatures while maintaining high throughput. The SiN film deposited at 430°C showed a step coverage of about 98% and a growth rate of ~0.7 Å/cycle, and showed excellent wet etching resistance especially in the low sidewall region.

AM-MoP-2 Assessing the Potential of Non-Pyrophoriczn(Dmp)$_2$ for the Fast Deposition of ZnO Functionalcoatings by Spatial Atomic Layer Deposition, ***David Muñoz-Rojas**,* CNRS, France*; Liam Johnston,* LMGP, France*; Jorit Obenlüneschloß,* RUB, Germany*; Anjana Devi,* IFW, Dresden, Germany*; Daniel Bellet,* Grenoble INP, France

Spatial atomic layer deposition (SALD) is a promising thin film deposition technique that enables fast, large-scale deposition and nanoscale thickness control by utilizing spatially separated precursor vapors and a substratespecimen relative motion, while being feasible in atmospheric pressure conditions. This study explores the use of a non-pyrophoric precursor, $Zn(DMP)_2$, in open-air SALD to produce ZnO, and compares the SALD processing speed, and thin film properties, as well as the environmental impact of using this precursor *versus* the more conventional diethylzinc (DEZ), whose pyrophoricity discourages open-air processing. For this purpose, a life cycle analysis (LCA) study was carried out. Our investigation shows that $Zn(DMP)_2$ open-air SALD can yield ZnO films faster than conventional ALD using DEZ, producing high purity ZnO films with a growth per cycle of 0.7 Å at 180 °C, which corresponds to 184 Å min^{-1} maximal growth rate. Emphasizing practical applications, the conformality of the ZnO coating produced around silver nanowire (AgNW) networks by $Zn(DMP)_2$ open-air SALD and the functionality of these protective coatings has also been demonstrated. The resulting transparent conductive nanocomposites had a substantially improved durability on par with their DEZ-synthesized counterparts.

reference

Assessing the Potential of Non-pyrophoric Zn(DMP)2 for the Fast Deposition of ZnO Functional Coatings by Spatial Atomic Layer Deposition

Liam Johnston, Jorit Obenlüneschloß, Muhammad Farooq Khan Niazi, Matthieu Weber, Clément Lausecker, Laetitia Rapenne, Hervé Roussel, Camilo Velasquez Sanchez, Daniel Bellet, Anjana Devi, David Muñoz-Rojas*.

RSC Applied Interfaces, 2024, 1, 1371-1381

AM-MoP-3 A Novel Microwave ECR Plasma System for Damage-Free PEALD, ***Paul Dreher***, *Dominik Hartmann,* Evatec AG, Switzerland*; Julian Pilz,* Silicon Austria Labs, Austria*; Jörg Patscheider,* Evatec AG, Switzerland

While most materials will not suffer radiation damage at ion energies below ~20 eV, some crucial compounds do show deterioration already at lower energies. Examples for ion irradiation-sensitive materials are many group III nitrides such as GaN, InN etc., but also sputter-sensitive oxides, e.g. ITO, MoO_3 and other transition metal oxides, as well as sulfides like MoS_2 and other 2D materials [1] [2]. Microwave-excited plasmas can reach these favorable conditions due to low sheath voltages. Such a microwave-excited electron cyclotron resonance (ECR) plasma has been successfully integrated into a novel plasma-enhanced atomic layer deposition (PEALD) system. In this study, we investigate the electronic and structural properties of the produced Al_2O_3 and AlN films *in-situ* as well as *ex-situ* with Ellipsometry, AFM, FIB-SEM, XRR and XPS.

In-situ diagnostics, including optical emission spectroscopy (OES), residual gas analysis (RGA) and retarding field energy analysis (RFEA) were employed to study the deposition processes of Al_2O_3 and AlN films. These studies provided central information on precursor decomposition and reaction kinetics during the different process steps, which can be used to optimize the materials properties. At 250°C a growth-per-cycle (GPC) of 1.3 Å/cycle was achieved for alumina films, with thickness non-uniformity below 0.5% on 200 mm silicon wafers (see Fig. 1). The 60 nm thick alumina films have a refractive index of 1.65 at 633 nm (see Fig. 2). XPS measurements showed carbon contents below 1 atomic percent.

In further investigations the influence of substrate biasing with RF power and its influence on the materials roughness and density, as measured with AFM and XRR, were studied. The ion energies and flux were monitored with an RFEA system during the process. As the ion energy in microwave discharges is typically small, the energy range can be modified from a few eV without RF power up to >200 eV ion energy using an RF bias.

The findings show that microwave ECR plasma is indeed a versatile type of plasma source, which can be beneficial for high quality PEALD processes to deposit for damage-free films. The possibility to combine this new PEALD module in an Evatec cluster system with separate modules for PECVD, sputter deposition and etching opens up new paths to investigate and develop innovative processes and devices.

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AM-MoP-4 Optimization of the showerhead for Atomic Layer Deposition by Computational Fluid Dynamics, ***Seungheon Lee***, *Dongkun Song, Gyeongwon Min, Doyoung Jung, Jungeon Park, Jeongmin Han, Dahye Geum, Hyeondo Han, Seungwan Bae, Hyoeun Lee, Guyoung Cho,* Dankook University, Republic of Korea

Atomic Layer Deposition (ALD) is widely used in many fields that require high-quality thin films, such as semiconductor and display. These industries also need precise controlled thin film thickness. The ALD generally satisfies these requirements – defect free thin film, impurity free thin film, superior uniformity, angstrom level thickness control and such on. However, the ALD process generally has the disadvantage of slow process speeds and difficulty in controlling the proper process conditions. The superior uniformity and the high-quality thin films which are powerful strong points of ALD are significantly related with the optimized shape of process chamber.

In this study, we focused on improving the uniformity of the deposition by modifying the flow distribution inside the process chamber. Computational fluid dynamics (CFD) was carried out at a fixed working pressure of 1 Torr and a fixed temperature of 250℃. Gas flows inside the reactor were assumed as the continuum flow during all process steps. Simulations were performed for various showerheads to obtain optimized internal flow distributions. And the optimized showerhead geometry was selected using an approximation method in the commercial program.

For each flow direction obtained, the deposition on Al_2O_3 was simulated. All simulations were performed under same conditions to check uniformities of Al_2O_3 thin films.The result allowed us to determine which direction of flow should be changed to improve the uniformity of the thin film.In addition, the distribution of flow and chemical species along with the direction were investigated to confirm the influence of each distribution on the deposition.

Acknowledgements

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AM-MoP-5 Very High Frequency Plasma-Enhanced ALD: System Configuration and Thin Film Property Analysis, ***Jae Yeon Han***, *Hyung Min Kim, Da Eun Bae, Jae Ho Choi, Jae Hack Jeong,* CN1 Co., Ltd, Republic of Korea

The atomic layer deposition (ALD) process is required in semiconductor manufacturing due to its advantages, such as high step coverage, atomic-level thickness control, and uniform film deposition. 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 silicon nitride (SiN_x), aluminum nitride (AlN), titanium nitride (TiN), and tantalum nitride (TaN), leading to active development of the plasma-enhanced ALD (PE-ALD) processes.

However, depositing thin films at high temperatures can cause damage to the substrate. To solve this problem, a technology is needed that can maintain the quality of thin films while reducing damage to the substrate at low temperature. Currently, extensive research is being conducted on very high frequency (VHF) plasma as a method to mitigate damage to the substrate. VHF plasma shows significantly higher plasma density and lower substrate damage at the same plasma power as radio frequency (RF)

We developed a PE-ALD system capable of uniformly applying VHF plasma and analyzed the characteristics of thin films according to plasma frequency. A multi-contact matcher system was applied to the VHF plasma PE-ALD system, enabling the application of plasma from RF to VHF. Additionally, a B-matcher system was implemented in the VHF plasma PE-ALD system to maintain process reproducibility, as shown in Fig. 1. The silicon nitride (SiN_x) was deposited using VHF PE-ALD process shown in Fig. 2 at low temperatures (≤200°C) and varying the plasma frequency according to the B-matcher position. Thickness and refractive index were measured using ellipsometry. Impurity content was measured through X-ray photoelectron spectroscopy (XPS) depth profiling. Thin film density and interface roughness were measured by X-ray reflectivity (XRR).

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AM-MoP-6 Pneumatic Optimization Utilizing Predictive Analytics Within Embedded Systems for Dose Control of Fast Pulsing Valves.*, Frank Horvat,* Swagelok Company

Precision valve timing is a necessary need for proper chemical dosing within the Atomic Layer Deposition (ALD) process. The affect of dosing has a direct influence on the consistency and overall wafer yield in high volume manufacturing. There are various elements within a pneumatic system which if not properly addressed can affect the overall actuation time of a process valve, therefore directly influencing chemical dosing. Investigation into identifying these various elements within a pneumatic system and its overall influence on valve timing is performed. Additionally, research utilizing time based predictive algorithms were employed to specifically designed embedded hardware to allow for the mitigation of these pneumatic inefficiencies. The adaption of an embedded architecture has allowed for seamless integration within pneumatic systems. The use of real time, process information from valves has allowed for improved valve timing, valve to valve repeatability and hence more control of chemical dosing.

AM-MoP-7 Fast Deposition of High-Quality ALD Materials Using the PlasmaPro ASP System*, Yi Shu,* *Arpita Saha, Dmytro Besprozvannyy Besprozvannyy, Michael Powell Powell, Agnieszka Kurek,* Oxford Instruments Plasma Technology, UK*; Harm Knoops,* Oxford Instruments Plasma Technology, UK, Eindhoven University of Technology, Netherland, UK

With the fast evolution of device design and fabrication, the ability of manipulating materials and layers at atomic scale has become more important.[1] Due to its ability to deposit high-quality materials layer-by-layer, Atomic Layer Deposition (ALD) has been started to utilise in novel fabrications for the latest applications including CMOS gates,[2] SiC Power,[3] GaN RF and microLEDs[5]. One of the main challenges in integrating ALD processes with these applications is the relatively high cost of development time due to the slow growth rates and long cycle times. This limits R&D cycles to focusing on ALD chemistries that deliver high growth rates or can be thin (<10 nm) for the application, as the time required to deposit the material becomes a significant bottleneck to device development.

To enable ALD techniques for a wider range of applications, it is fundamental to deposit ALD layers at a higher dep rate, whilst maintaining the desired high-quality of the deposited materials. To this end, we have designed an ALD platform, PlasmaPro ASP (PPASP), for research and development customers. The novel remote capacitively coupled plasma (CCP) source and compact chamber design enable fast deposition rates for a variety of ALD chemistries, whilst maintaining control over plasma conditions to deliver low damage.[6,7]

Here, we show how the PPASP can deposit dielectric oxides and nitrides films with significant improvements in deposition rates, whilst maintaining excellent material properties and conformality. We also illustrate the ability to run super-cycles for doping/ternary material deposition. These improvements can therefore enable fast development of ALD processes for devices by rapid comparisons of different recipe conditions, which would open an entire new space for ALD exploration to realise the ambition of utilising ALD across a wider range of devices and research space.

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AM-MoP-8 Non-Destructive Characterization of Alumina Film Thickness and Fractional Coverage Utilizing XPS and StrataPHI Modeling*, Amy Ferryman,* *Norb Biderman, Kateryna Artyushkova,* Physical Electronics

Atomic layer deposition (ALD) is widely used due to its precise deposition capabilities, allowing for the creation of very thin, conformal, and high-quality films on the nanometer scale. These films are ideal for applications requiring precise barrier layers, passivation layers, or protective coatings in complex geometries, particularly in microelectronics, sensors, and medical devices. ALD deposition of alumina offers several advantages, including uniform coating on complex 3D structures, precise thickness control, high purity, and suitability for sensitive substrates due to its low deposition temperature. The self-limiting behavior of ALD cycles allows for controllable film growth in which a homogenous film can be achieved at the lowest film thickness. To control the thickness in a range of few nanometers, it is important to understand the interaction between the reactants and substrate during the nucleation period, or the first few cycles. X-ray photoelectron spectroscopy (XPS) is a well-established technique for non-destructive analysis of the chemical composition of thin layers and interfaces. By analyzing a material at varying takeoff angles between the sample and analyzer, angle dependent XPS (ADXPS) can be utilized to probe the thickness and chemical composition of thin films without creating ion beam-induced damage associated with destructive sputter profiling. The spectral results obtained by ADXPS can be furthered evaluated by *Strata*PHI, a software product designed by Physical Electronics, to calculate not only the thickness of thin films but also provide an estimate of fractional coverage, which is of great importance for high-throughput metrology of thin-film structures. This presentation will highlight the benefits of utilizing angle dependent XPS in combination with StrataPHI modeling software to non-destructively characterize and simultaneously calculate the layer thickness and fractional coverage of a series of aluminum oxide films deposited on glass substrates throughout the nucleation period by the ALD process.

AM-MoP-9 Optimization of Liquid Fluidization Design for Temperature Control on the Showerhead*, Eunsun Jung,* *Tae S Cho, Eungseo Kim, Bonuk Koo,* WONIK IPS, Republic of Korea

Additive manufacturing(AM) is well-suited for creating complex functional parts that cannot be realized through traditional machining technology, and its applications have been rapidly increasing across various industries. It is expected to play a significant role in enhancing the performance of key components in semiconductor equipment. Specifically, the showerhead, which uniformly sprays process gases onto the wafer surface, requires a highly complex structure to prevent performance degradation caused by structural deformation from heat and uneven temperature. However, due to the limitations of traditional machining processes, its design is constrained.To optimize the showerhead design, we implemented the following structure. The process gas flows through a cylindrical hole inside the showerhead, while a temperature compensation channel is added to the outer wall of the cylinder. A cooling gas or liquid can flow through the multi-stage baffle from a single supply port through nozzles branched out toward the center and outward of the showerhead. For efficient cooling and heat exchange, the gap and shape of the baffles were adjusted, such as circular, elliptical, and curved baffles. The cooling channel was added only to the exact location that need to be cooled.Finite element analysis was performed using Ansys Fluent to analyze the showerhead. A reference endplate was divided into triangular meshes, resulting in an analysis model consisting of a total of 4,467,043 nodes and 25,799,364 elements. To reflect actual process conditions, 630℃ radiative heat was applied to the lower part of the endplate, and 155℃ radiative heat was applied to the upper part to set the internal surface temperature to 225℃.To analyze the effect of the cooling fluid, Solvay Galden HT 200 fluid provided by Ansys Fluent was used. The physical properties of this fluid are density 1790 kg/m^3, specific heat 960 J/(kg·K), thermal conductivity 0.065 W/(m·K), and viscosity 0.0043 kg/(m·s). The inlet temperature of the cooling fluid was fixed at 175℃ through a heat exchanger, and the flow rate was changed to 10 LPM, 2 LPM, and 1 LPM, respectively, to analyze the temperature change inside the showerhead.When there was no cooling fluid (reference), the average temperature inside the showerhead was 227.1℃ with a range of about 15℃. On the other hand, when the flow was set at 10 LPM, 2 LPM, and 1 LPM, the average temperature decreased to 180.9℃, 180.7℃, and 180.8℃, respectively, with a range reduced to 1.2℃, 4.3℃, and 8.97℃. It was confirmed that the temperature uniformity improved significantly as the flow rate of the cooling fluid increased, as clearly shown in the attached figure.

AM-MoP-10 XPS Metrology for Area Selective Deposition Applications in Semiconductor Manufacturing*, Kangwon Kim, Hyung Keun Yoo,* Samsung Electronics, Republic of Korea*; Heechang Yang, Sunho Kim,* Nova Measuring Instruments Korea, Ltd., Republic of Korea*; Wei Ti Lee, Torsten Stoll,* Nova Measuring Instruments, Inc.

Propelled by the relentless miniaturization of integrated circuits, area selective deposition (ASD) process has emerged as an important enabling deposition technique in the semiconductor industry. Traditional processing methods are sometimes being hampered by shrinking design rules in 2D features, as well as the challenges of three-dimensional architectural designs. As in every deposition step in the semiconductor manufacturing process, ability to do process control is essential to maintain stability and to maximize yield. Over the past decade, through adoption in high volume manufacturing fabs across the globe, X-ray Photoelectron Spectroscopy (XPS) has established itself as a reliable metrology of choice for ultra-thin films measurements.

In this paper, we will describe the use of XPS as a versatile yet sensitive metrology technique for developing, measuring, and monitoring the ASD deposition process. Due to its specificity to elements or species of interest, and combining with its surface sensitivity, XPS is a powerful metrology for ASD thin film applications. Examples of ASD applications will be presented.

One traditional ASD process is via self-assembled monolayer (SAM), where SAM is selectively adsorbed on the nongrowth area before deposition of the desired material [1]. XPS is shown to be able measure the selectivity of SAM and its effectiveness to enable a defect-free ASD process. Selectivity of SAM is also evaluated as a function of linewidth. Another example is the selective deposition process aiming for a bottom-up growth in trenches or vias. XPS is demonstrated to measure thicknesses of selectively deposited material at the bottom via. Excellent repeatability and consistency of XPS ASD thin film measurements on a full 300mm wafer will also be presented.

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AM-MoP-12 A Remote Plasma Spectroscopy Diagnostic for Monitoring of Atomic Layer Deposition Processes*, Marcus Law,* Gencoa Ltd., UK

Effective and robust monitoring of individual gas concentrations during ALD processes offer a unique insight into the condition of the process. Analysis of the gaseous environment can be used to assess reaction saturation and help to quickly establish optimum cycle and purge times. In addition, precursor delivery can be monitored and quantification of vacuum quality in terms of leaks and contamination is imperative to achieve optimum and repeatable results.

Conventional quadrupole residual gas analysers have difficulty monitoring ALD processes due to the high process pressures and the presence of contaminating hydrocarbons contained within many ALD precursors. In this work, a compact remote plasma optical emission spectroscopy (RPOES) gas sensor that operates over a wide pressure range (0.5 – 1 E-7 mbar) without filaments or the need for differential pumping was employed, providing robust, fast measurement of gaseous species.

In this contribution, we report on the real-time monitoring of by-product release and precursor consumption determined using this method. Examples of this sensing technique’s practical uses for ALD processes are discussed; this includes detection of contaminants, optimising purge cycle length and monitoring the reaction dynamics in terms of precursor gas intake. Furthermore, the use of RPOES for measurement of vacuum quality and leak detection prior to process start is discussed in combination with analysis of ALD reaction dynamics and optimisation and control of the full ALD cycle.

AM-MoP-13 Early Detection of Process Window Shifts in ALD processes by PillarHall Lateral High Aspect Ratio Test structures*, Jani Karttunen,* Chipmetrics Oy, Finland*; Anish Philip,* Aalto University, Finland*; Jussi Kinnunen, Kalle Eskelinen, Feng Gao, Mikko Utriainen,* Chipmetrics Oy, Finland

The increasing complexity of 3D DRAM and 3D NAND demands precise control over atomic layer deposition (ALD) to ensure high yield and reliability. Ultra-high aspect ratio (AR >100) structures pose challenges for thin film conformality, making early detection of process shifts crucial. ALD tool qualification is particularly complex for ultra-thin dielectric films, widely used in 3D memory channel holes, where process deviations are difficult to detect using blanket monitor wafers, requiring more sensitive qualification methods. This study evaluates whether the PillarHall® Lateral High Aspect Ratio (LHAR) test chip can serve as a high-sensitivity ALD monitoring tool, capable of detecting precursor decomposition, temperature drift, pressure fluctuations, and other process instabilities before they impact device production.

ALD process evaluations were conducted using PillarHall® LHAR5 test chips (Chipmetrics) with 500 nm and 100 nm gap heights, enabling analysis of cavity aspect ratios >1000. TiO_2 was deposited using titanium isopropoxide (TTIP) and water, while Al_2O_3 was grown from trimethylaluminum (TMA) with water and ozone. The LHAR method provides film penetration depth profiles, offering direct insight into step coverage and deposition behavior across ultra-high aspect ratio cavities.

To evaluate industrial applicability, LHAR test structures were integrated into FEOL-compatible pocket wafers, allowing wafer-level ALD tool qualification and comparison across different reactor systems.

Our results demonstrate that LHAR test structures effectively detect process deviations across multiple ALD chemistries and tool configurations, proving invaluable for process development, optimization, and industrial tool qualification. Ultra-thin dielectric films in HAR structures require advanced qualification methodologies, as blanket wafers fail to capture critical process shifts.

By integrating LHAR test chips into ALD qualification workflows, fabs and tool manufacturers can benchmark ALD reactors, enhance process control, and accelerate tool qualification, ensuring optimized ALD performance for next-generation semiconductor architectures.

AM-MoP-14 Optical Monitoring of MoCl5 and MoOCl4 Vapor Delivery for Atomic Layer Deposition Applications*, Berc Kalanyan,* *James Maslar,* NIST-Gaithersburg

Ultrathin Mo is a candidate material for interconnects in advanced logic and gate metallization in flash memory applications. Hydrogen reduction of molybdenum pentachloride ($MoCl_5$) is one of several ALD routes for preparing metallic Mo films[1]. While $MoCl_5$ is an attractive precursor, it presents challenges for manufacturing due to its low volatility, its tendency to form oxychlorides, and self-etching[3]. Solids are especially problematic for high-volume manufacturing because their delivery characteristics can depend on vessel design, operating conditions, and packaging. Further, volatile oxychlorides are also precursors for film deposition[2]. Therefore, a detailed understanding of $MoCl_5$ delivery and subsequent deposition behavior requires quantitative metrology to measure the partial pressures and flow rates of $MoCl_5$ and reactive impurities such as $MoOCl_4$.

To address this need, we have demonstrated direct absorption measurements in the visible and UV wavelengths to monitor the partial pressures and delivery rates of $MoCl_5$ and $MoOCl_4$ under ALD conditions. Using spectral signatures[4] of $MoCl_5$ and $MoOCl_4$, we designed high-speed in-line gas analyzers to simultaneously detect both species during flow. Calculations using the spectral response of the analyzers show detection limits of 0.35 Pa and 0.90 Pa for $MoCl_5$ and $MoOCl_4$, respectively[5]. However, spectral overlap between $MoCl_5$ and $MoOCl_4$ in the UV wavelengths makes quantitative determination of each species difficult. We have recently expanded upon this work by independently measuring $MoOCl_4$ species using a non-dispersive IR analyzer installed on the ALD chamber. In addition to the gas analyzers, the measurement system also incorporates a high-speed UV-vis spectrometer to monitor gas phase spectral changes over time.

This presentation will discuss precursor delivery and composition data obtained from both non-dispersive and spectroscopic measurements performed during $MoCl_5$ injections. We will show that it is possible to simultaneously obtain high-speed quantitative measurements of $MoCl_5$ and $MoOCl_4$ partial pressures and flow rates. We will compare the sensitivity and selectivity of different analyzer designs toward $MoCl_5$ and $MoOCl_4$. Further, we will apply the measurements to characterize $MoCl_5$ delivery and $MoOCl_4$ generation from a small diameter 300 mL vessel and a wider 1.2 L vessel suitable for HVM.

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AM-MoP-15 Process Monitoring via Time-of-Flight Mass Spectrometry based on Isotopic Patterns, *Hye-Young Kim,* ***Sung Kyu Jang****, Seul-Gi Kim, Yoonjeong Shin, Jong Hyun Choi, Hyeongkeun Kim,* Korea Electronics Technology Institute, Republic of Korea

Although Time-of-Flight Mass Spectrometry (ToF-MS) is widely used to monitor semiconductor processes such as Atomic Layer Deposition (ALD) and Etching (ALE) in real time, there always remains uncertainty in naming byproducts and their quantities due to a number of candidate chemical compounds with the same masses. This, accordingly, leads to the difficulty in making use of resultant mass spectra for practical applications such as fault detection and classification.

To ensure reliability of ToF-MS analysis, we have devised a method based on isotopic patterns, which mainly consists of the following two steps: constructing basis matrices given stable isotopes and their relative abundances, and finding a non-negative weight vector associated with each basis matrix by solving a Non-Negative Least Squares (NNLS) problem.

To be concrete, at first, basis matrices are roughly formulated by listing chemical elements expected to appear during processes provided materials in use together with process parameters and performing convolution of the distributions of their isotopes. A following filtering, which excludes unreasonable combinations of atoms and singles out representative patterns of atoms, increases confidence in the matrices.

At the next step, an original MS data is split into time intervals to closely track the dynamics of elements in consideration. By solving a series of corresponding NNLS problems, which take the basis matrices and the mass spectra split into time intervals as input, weight vectors at each interval are obtained. It stands to reason that these vectors would coincide with relative composition ratios of chemical compounds and therefore act as indicators to determine process abnormality. The weight vectors are then optimized by taking their statistical properties into account and solving a set of modified NNLS problems. Here, in order to alleviate high computational demands of dealing with NNLS problems, distributed GPU computing is adopted.

In conclusion, this analysis method for ToF-MS based on isotopic patterns opens up a new and reliable way to deal with ToF-MS data and to monitor semiconductor processes. It is, furthermore, expected to facilitate application of ToF-MS to practical purposes to detect process abnormality or to optimize processes.

Nanostructure Synthesis and Fabrication
Room Event Hall - Session NS-MoP

Nanostructure Synthesis and Fabrication Poster Session

NS-MoP-1 Structural Modifications of Porous Templates with Pbte ALD Coatings*, Haifeng Cong,* ***Helmut Baumgart,*** Old Dominion University

Porous silicon templates have attracted increasing attention because of their controllable geometry, tunable nanoporous structure, large pore volume/high specific surface area, and versatile surface chemistry. Porous templates show significant advantages and application potential in microfluidics, electro-osmotic pumps, biomedical drug delivery, sensing, photonics, integrated opto-electronics, energy conversion, thermoelectrics, thermo-acoustics, electronics and Lab-on-a-chip technology for biomedical, pharmaceutical and environmental monitoring. For this study we have focused on energy conversion with ALD lead chalcogenide PbTe film coatings since PbTe is a useful narrow band gap thermoelectric material that can operate at comparatively higher temperatures in the range of 600~850 K due to its better chemical stability and high melting point. PbTe thin films have been synthesized inside of porous silicon templates with native oxide by Atomic Layer Deposition (ALD) using lead (II)bis(2,2,6,6-tetramethyl-3,5-heptanedionato) ($Pb(C_{11}H_{19}O_2)_2$), (trimethylsilyl) telluride ($(Me_3Si)_2Te$) as ALD precursors for lead, and tellurium. The Si native oxide surface was functionalized before ALD PbTe thin film deposition to ensure reproducible chemisorption of the ALD precursor compounds. The growth temperature during ALD was varied over a range from 135°C to 170°C. The Lead precursor was volatilized at a temperature of 140 °C and the Tellurium precursor was heated at 40 °C. The chamber base pressure was kept at 40 mTorr.Several physical characterization techniques have been employed to determine the ALD PbTe thin film characteristics. The crystal structure and phase purity of samples of PbTe films were analyzed by X-ray diffraction (XRD). The film morphology and structure of the products were determined by field emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HR-TEM). The surface roughness was analyzed by atomic force microscopy (AFM). The analysis of the composition and stoichiometry of the ALD coatings were carried out by Energy dispersive X-ray spectroscopy (EDS). The experimental evidence revealed the ALD growth of lead telluride followed the Vollmer-Weber Island growth model. We found a strong dependence of the nucleation process of the polycrystalline grain distribution on the temperature.We report a systematic study of all ALD parameters required to optimize the coating of the interior walls of porous membranes which open front and backside, straight pores of varying diameter and porosity with dead endings in the substrate and pores with spatially modulated ondulating cross sectional shapes.

NS-MoP-2 Area-Selective Solid-State Synthesis of Nickel Silicide Nanostructures*,* ***Gabriele Botta,*** Nanogune, Italy*; Mato Knez,* nanogune, Croatia

Over the past decade, metal silicides have been re-discovered for their significant potential across various fields of nanotechnology. [1,2,3] However, integrating them into modern devices continues to pose challenges, primarily due to limited control over phase formation during their synthesis. [4] Additionally, since they are typically grown as continuous layers, their structuring often relies on complex top-down patterning techniques, which significantly limit their practical applications. [5] This study addresses these issues by proposing a method for Area-Selective (AS) silicidation (Fig. 1a SD). Our approach ensures that during material synthesis, the resulting silicide nanostructures acquire a predefined morphology and nucleate exclusively in the targeted regions of the substrate.

The AS silicidation process is demonstrated through the formation of $NiSi_2$ structures on Si(100) and Si(111) substrates (Fig. 1b SD), and its broader applicability is further illustrated with the successful AS synthesis of Cu_3Si (Fig. 1c SD). To direct growth, the silicon substrates are patterned using ion beams, which create surface defects that promote silicide nucleation in the desired areas. Unlike conventional Solid State (SS) synthesis, which involves annealing a metal thin film on silicon, our method begins with an ALD deposited metal oxide. Silicidation is performed by annealing in the presence of a reductant (H_2), which reduces the metal oxide to its metallic state. The resulting metal then reacts with the underlying silicon, forming a metal silicide. During this two-step reaction, the material re-arranges along surface defects, which act as templates, guiding both the shape and positioning of the forming silicide crystals.

The effectiveness of this multi-step fabrication method, coupled with its adaptability to various metal-silicide systems, underscores its potential to create functional, structured silicides without the need for post-synthesis nanopatterning.

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NS-MoP-3 Atomic Layer Deposition by Pressure-Driven Convective Flow Through 3D Nanocomposite Structures*,* ***Austin Cendejas,*** *Benjamin Greenberg, Kevin Anderson, Boris Feygelson,* US Naval Research Laboratory

Conformal coating of high aspect ratio tortuous 3-dimensional nanostructures has been shown to require careful consideration of dose and purge times to achieve uniform ALD coatings of high quality.[1,2] Specifically, through static-dosing of ALD precursors cycle times for complete surface saturation are often in excess of 10s of minutes for macroscopic substrates.[2] Recently our group has demonstrated an order of magnitude reduction in saturation dose times by forcing precursor flow through the compact via a pressure gradient of 50-100 Torr across the 3D nanocomposite. In this work, diethylzinc (DEZ) and water were pulsed sequentially to deposit conformal films of ZnO completely through the ~2mm thickness of nanocomposite compacts comprised of 200 nm SiO_2 nanoparticles. Due to the nonuniform pressure across the nanocomposite compact, precursors undergo a transition from convective to diffusive transport. Preliminary modeling of the internal pressure gradients of the compacts was utilized to determine the relative contributions of these two transport modes in addition to structural nonuniformities (i.e. cracks, large pores, etc.). It was found that uniformity in the internal pore structure and structural integrity of the initial, uncoated, nanoparticle compact was crucial in achieving uniform coatings on the entire surface. Additionally, the effect of precursor partial pressure during doses on saturation dose times and the extent to which the diffusive transport could be enhanced was studied. Saturation dose times were measured via *in-situ* quadrupole mass spectrometry of the effluent gas and film uniformity and conformality were studied via *ex-situ-* cross-sectional scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDXS), and X-ray diffraction (XRD).

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NS-MoP-4 Atomic Layer Deposition for Novel Nanocomposite Solids with New Functionalities*, **Boris Feygelson**, Benjamin Greenberg, Kevin Anderson, James Wollmershauser,* U.S. Naval Research Laboratory*; Austin Cendejas,* American Society of Engineering Education, postdoc residing at U.S. Naval Research Lab*; Sarshad Rommel, Mark Aindow,* Department of Materials Science and Engineering, Institute of Materials Science, University of Connecticut

Scaling grains down to nanometer size enhances many properties of polycrystalline solids due to an increase in the grain boundary interfacial volume fraction. Sintering of nanoparticles is the most versatile way to produce nanocrystalline solids of various materials. A crucial prerequisite for achieving advanced, size-dependent properties in these nanocrystalline solids is removing porosity by sintering while preserving nanoscale morphology and grain size. Using our environmentally controlled pressure-assisted sintering (EC-PAS) technique, we have successfully produced fully dense ceramics with grain sizes down to 4 nm [1,2].

By engineering nanoparticle building blocks with designed core/shell structures using particle atomic layer deposition (ALD) [3], we can fabricate novel nanocomposite solids with properties controlled by rationally designed core/shell geometries, constituent properties, and the resultant vast network of interfaces. We refer to such nanocomposites as artificial interfacial solids (AIS). For instance, when the core/shell nanoparticle structure is preserved during EC-PAS, the resulting nanocomposite comprises isolated nanoparticles (cores of initial core/shells) embedded in a host material (a continuous 3D percolated network of shells from adjacent core/shells merged together).

We have further developed the EC-PAS process to produce percolated AIS (PAIS) nanocomposite solids with two separate and interconnected 3D paths for electron and/or heat transport. The process involves creating a porous compact from nanopowder, followed by ALD infiltration and conformal deposition of a second material on all available surfaces within the porous compact [4], and finally, a sintering stage. The nanopowder in the sintered nanocomposite forms the first 3D percolated network, which becomes surrounded by the deposited and merged 3D network of the second material. Both networks are strongly bonded to each other through sintering.

Examples of AIS and PAIS nanocomposites for various applications will be presented and discussed, highlighting their potential properties, applications, and versatility.

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NS-MoP-5 Nanostructure and Conductivity of SiO2/ZnO:Al Nanocomposites Fabricated by ALD Infiltration and Pressure-Assisted Sintering*, **Benjamin Greenberg**, Kevin Anderson, Alan Jacobs, Joseph Prestigiacomo, Zoey Warecki, Todd Brintlinger,* U.S. Naval Research Laboratory*; Austin Cendejas,* ASEE Fellow Residing at U.S. Naval Research Laboratory*; Eric Patterson, James Wollmershauser, Boris Feigelson,* U.S. Naval Research Laboratory

Over the past decade, environmentally controlled pressure-assisted sintering (EC-PAS) has been established as a reliable technique for producing dense, nanocrystalline ceramics with exceptional mechanical properties due to their low porosity (less than 1%) and small grain size (as small as 4 nm). Examples include transparent Mg_2AlO_4 with hardness up to 22 GPa[1] and WC with hardness up to 39 GPa[2]. Recently, our group has demonstrated that EC-PAS can also be combined with ALD infiltration to produce nanocomposites with unique combinations of optical, electrical, and thermal properties, which are tunable via the sintering conditions and the number of ALD cycles.

In this work, we examine the nanostructure and electrical properties of SiO_2/ZnO:Al nanocomposites fabricated by this combination of EC-PAS and ALD with the aim of understanding how to maximize electrical conductivity. In an air-free process chain, porous compacts of SiO_2 nanoparticles are infiltrated with ZnO:Al using diethylzinc, trimethylaluminum, and water (15:1 ZnO:Al_2O_3 cycle ratio) prior to sintering at 450 °C and 2 GPa to produce monolithic nanocomposites with ~1 mm thickness and ~100 nm SiO_2 domain size. 16 or 32 ALD cycles yields conductive ZnO:Al channels comprising 16% or 27% of the nanocomposite's volume with nominal channel width of ~6 or ~12 nm and average zincite crystallite size of ~4 or ~6 nm, respectively. Based on theoretical predictions and experimental measurements of the metal-insulator transition criterion for networks of ZnO nanocrystals,[3] these channel widths are expected to be sufficient for metallic/band-like charge transport. Temperature-dependent resistance measurements down to as low as 0.4 K, however, reveal negative temperature coefficients characteristic of non-metallic charge transport. Specifically, for 16 cycles of ZnO:Al ALD, the charge transport mechanism appears to be Efros-Shklovskii variable-range hopping, and for 32 cycles, the temperature dependence is weaker but still clearly negative. To investigate whether this lack of metallic conduction is due to deviations from the ideal ZnO:Al geometry (percolating channels with uniform thickness), we characterize the nanocomposites' micro- and nanostructure via scanning electron microscopy (SEM) and scanning transmission electron microscopy with energy-dispersive x-ray spectroscopy (STEM-EDS). We also compare the nanocomposites' electrical properties to those of ALD ZnO:Al films on SiO_2 wafers and explore the influence of the SiO_2/ZnO:Al interface on conduction.

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NS-MoP-6 Creation of Nanowire-Bundled Grain Boundaries in Bi_2Te_3-Based Thermoelectric Materials via Atomic Layer Deposition*, **Gwang Min Park**, Seunghyeok Lee,* Korea Institute of Science and Technology (KIST), Republic of Korea*; Jinseok Hong, Seokho Nahm,* Hanyang University, Korea*; Seung-Hyub Baek, Jin-Sang Kim,* Korea Institute of Science and Technology (KIST), Republic of Korea*; Seung-Yong Lee,* Hanyang University, Korea*; Seong Keun Kim,* Korea Institute of Science and Technology (KIST), Republic of Korea

Improving thermoelectric material performance is essential for energy harvesting and solid-state cooling applications. This study demonstrated a novel structure of Bi_2Te_3-based thermoelectric materials with ZnO nanowire-bundled grain boundaries, realized via atomic layer deposition (ALD) and subsequent spark plasma sintering (SPS). The ZnO nanowires formed at the interfaces due to the rearrangement of the ALD-grown ZnO ultrathin layer over $Bi_{0.4}Sb_{1.6}Te_3$ powder, driven by localized heating during the SPS process and the anisotropic nature of ZnO. The nanowire-bundled interfaces enhanced phonon scattering, thereby reducing lattice thermal conductivity while maintaining excellent electronic transport. This structural innovation achieved a high figure-of-merit, $zT_{max} = 1.69 \pm 0.09$ at 373 K and an average zT of 1.55 over the range of 300–473 K. A thermoelectric module fabricated with 127 p–n pairs achieved a record-high conversion efficiency of 6.57% at a temperature difference of 163 K. These findings highlight the potential of nanowire-bundled interfaces to enhance the thermoelectric material performance and pave the way for scalable next-generation energy conversion technologies.

NS-MoP-7 Surface Engineered Polymeric Membranes for Improved Fouling Resistance and Superior Oil-Water Separation*, Bratin Sengupta, Yining Liu, Seth Darling,* ***Jeffrey Elam,*** Argonne National Laboratory

Fouling is a grand challenge which severely degrades membrane system performance, especially for applications in water treatment. Polyvinylidene fluoride (PVDF) is widely used for membrane fabrication due to its inertness and stability. However, PVDF is extremely susceptible to fouling due to its inherent hydrophobicity. Post-synthetic functionalization of PVDF membranes can increase the membrane-foulant interaction energy and reduce fouling. In this regard, vapor phase functionalization is particularly promising since it can produce ultrathin films (<5 nm) which do not alter the membrane pore structure and morphology. For example, thin metal oxide layers impart hydrophilicity and are often positively charged at the pH of the wastewater, realizing high membrane – foulant interaction energy. Atomic layer deposition (ALD) can produce ultrathin metal oxide layers on polymers, but the inert PVDF surface inhibits nucleation necessitating a prohibitively large number of ALD cycles to impart fouling resistance. In this presentation, I describe a novel pretreatment step that dramatically accelerates the nucleation of metal oxide ALD on PVDF. Using this pretreatment, we create highly effective anti-fouling surfaces using one ALD cycle compared to >150 ALD cycles on the pristine PVDF membranes. This strategy is effective for a range of ALD metal oxides including Al_2O_3, TiO_2, and ZnO. We employ a suite of in situ and ex situ analytical techniques to elucidate the surface chemical mechanism for the enhanced nucleation. We perform extensive characterization and testing of the surface-engineered PVDF to quantify the benefits for water filtration and demonstrate >99% flux recovery with only ~1% irreversible flux loss during operation. We also demonstrate the efficacy of our surface engineered PVDF membranes for oil-water separation. Efforts are underway to perform this surface treatment using our roll-to-roll, atmospheric pressure spatial ALD system.

NS-MoP-8 Interface Engineering of 2D MoS_2 Devices through ALD Oxidant Selection*,* ***Si Eun Yu****, Thi Thu Huong Chu, Minjong Lee, Dushyant M. Narayan, Doo San Kim, Dan N. Le,* University of Texas at Dallas*; Rino Choi,* Inha University, Republic of Korea*; Jiyoung Kim,* University of Texas at Dallas

Two-dimensional transition metal dichalcogenides (2D TMDCs) have emerged as promising semiconductor materials for next-generation electronic devices due to their high mobility within atomic-scale thickness. To preserve the superior performance of 2D semiconductors in field-effect-transistor (FET) applications, gate dielectrics should be deposited via physisorption to prevent chemical reactions between the atomic-scaled 2D surface and ALD precursors.[1] A straightforward approach to achieving this is reducing the deposition temperature; however, this is often accompanied by the formation of lower-quality gate dielectrics. It is thus essential to establish alternative strategies for gate dielectric deposition, such as exploring precursors and/or employing advanced ALD techniques.

This study will present a promising approach utilizing H_2O_2 as an oxidant source for gate dielectric deposition, along with a strategy to achieve uniform deposition without damaging 2D materials. Comparative studies were conducted using H_2O, O_3, and H_2O_2 for high-k HfO_2 growth on 2D MoS_2. Each oxidant exhibited distinct growth behaviors. While O_3 facilitated uniform HfO_2 deposition, its strong oxidation effect led to Mo-S bond conversion into Mo-O bonds, inducing damage to the MoS_2 surface. The resulting surface damage led to degraded FET device performance, indicating that O_3 cannot be a viable candidate for high-k dielectric deposition on 2D semiconductors. For H_2O and H_2O_2, achieving fully conformal coverage remains a significant challenge. To address this limitation, stop-valve techniques were employed to extend oxidant exposure time and dosage, effectively enhancing dielectric coverage while maintaining interface integrity. The interface properties were further analyzed using a top-gate FET structure,[2] providing insights into the interface trap density associated with different oxidants.

This presentation will cover material characterization, ALD techniques, and electrical performance, offering a comprehensive evaluation of oxidant effects on 2D semiconductor integration.

This work was supported by Samsung Electronics through GRO program (IO240612-10229-01). We gratefully acknowledge TMEIC for ozone generator (OP-250H) and RASIRC for BRUTE® Peroxide. S. E. Yu acknowledges KIAT/MOTIE (RS-2024-00435406).

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ALD Applications
Room Tamna Hall A - Session AA1-TuM
Memory Applications II

Moderators: Pinyen Lin, TSMC, **Seung Wook Ryu**, SK Hynix

8:00am **AA1-TuM-1 Effect of Ga Doping on Coercive Field Reduction and Endurance Enhancement in Atomic Layer Deposited HfO2-based Thin Film for FeRAM Applications***, **Zi-Ying Huang**, Yu-Chun Li,* Fudan University, China*; Ming Li,* Peking University, China*; Ye Zhu,* Hong Kong Polytechnic University, China*; David Wei Zhang, Hong-Liang Lu,* Fudan University, China

HfO_2-based ferroelectric memory (FeRAM) has emerged as a promising candidate for next-generation nonvolatile memories, owing to its remarkable compatibility with CMOS processes and scalability. However, the reliability of HfO_2-based materials remains a significant challenge, primarily due to their limited endurance and easy dielectric breakdown. These issues can be attributed to their large coercive field, which not only increases the operating voltage but also enhances the risk of dielectric breakdown. In this work, Ga-doped HfO_2 ferroelectric capacitors with varying concentrations and annealing temperatures are prepared by atomic layer deposition (ALD) technique for the first time, and their ferroelectric properties, crystal structure, polarization switching kinetics, and endurance characteristics have been systematically investigated. The results indicate that the Ga-doped HfO_2 ferroelectric films exhibit finely modulated coercive fields (E_c) ranging from 1.1 MV/cm (HfO_2/Ga_2O_3 = 32:1) to a very low 0.6 MV/cm (HfO_2/Ga_2O_3 = 11:1). Notably, under 650°C rapid thermal annealing, the W/Ga:HfO_2/W capacitors achieve a comprehensively good ferroelectricity, including a large remnant polarization ($2P_r$) of 32.0 μC/cm^2 and a small coercive electric field (E_c) of 0.8 MV/cm. Moreover, the capacitors exhibit robust breakdown reliability, including high breakdown electric field (E_{BD}, >4.5 MV/cm), large breakdown voltage (>2.7 V) for ten-year time-dependent dielectric breakdown (TDDB) lifetime, and surpassing endurance (>10^{10} cycles). The study introduces Ga doping as a viable strategy to enhance the reliability of HfO_2-based FeRAM.

*Corresponding Author: honglianglu@fudan.edu.cn

8:15am **AA1-TuM-2 Realizaton of Selector-Only Memory via Supercycle Atomic Layer Deposition of Ge-Sb-Se Ternary Alloy***, **Jeongwoo Seo**, Minu Cho, Inkyu Sohn,* Yonsei University, Korea*; Youngjae Kang, Jong-bong Park, Kiyeon Yang, Wooyoung Yang,* Samsung Advanced Institute of Technology, Republic of Korea*; Hyungjun Kim,* Yonsei University, Korea

In recent years, storage class memory (SCM) has been considered as a promising next-generation memory technology, combining fast data processing speed of dynamic random access memory (DRAM) with the non-volatility of NAND flash memory. Among SCMs, ovonic threshold switch (OTS) material-based selector-only memory (SOM) has emerged as a pivotal memory technique, presenting outstanding device performances in terms of power consumption, operational speed, and cycling endurance [1]. In addition, owing to the dual functionality (simultaneous memory and selector operation) of OTS material, its simple memory cell structure exhibits superior scalability, offering cost-effectiveness [2].

To meet the ever-increasing demands for lower fabrication cost and higher memory density, however, it is mandatory to devise vertical SOM based on three-dimensional vertical cross point (3DVXP) array structure. To fabricate vertical SOM devices, thin film deposition technique that guarantees conformal deposition of thin films on high aspect ratio structure is required. In this context, atomic layer deposition (ALD) is a promising thin film deposition technique for the realization of the vertical SOM devices.

In this study, Ge-Sb-Se ternary alloy was synthesized by supercycle ALD process using methanol as co-reactant to enhance the reactivity of precursors. ALD Ge-Sb-Se served as a dual functional material for the memory cell of SOM devices. The material properties of ALD Ge-Sb-Se were thoroughly investigated using various measurement tools. Controlling the sub-cycle ratio during supercycle ALD process, we were able to precisely control the chemical composition of Ge-Sb-Se ternary alloy and determine the optimal composition for the vertical SOM devices. Fabricated SOM devices exhibited average threshold voltage of 2.37 V and average memory window of 1.04 V. Our research results suggest ALD Ge-Sb-Se ternary alloy as an outstanding memory cell component for the next-generation vertical SOM technology.

Acknowledgement

This work was supported by Samsung Electronics.

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8:30am **AA1-TuM-3 Atomic-Scale Thickness Control of Antiferroelectric ZrO_2 via Morphotropic Phase Boundary Engineering for Enhanced Ferroelectricity***, **Chun-Ho Chuang**, Ting-Yun Wang, Yu-Sen Jiang, Miin-Jang Chen,* Department of Materials Science and Engineering, National Taiwan University, Taiwan

This studydemonstrates the enhancement of dielectric and ferroelectric properties in sub-6 nm ZrO_2-based thin films by precisely modulating the atomic-scale thickness of the underlying HfO_2 seeding layer to engineer the morphotropic phase boundary (MPB) effect. By precisely tuning the seeding layer thickness to control the grain size and induce the in-plane tensile stress, the antiferroelectric (AFE, $P4_2/nmc$) to ferroelectric (FE, $Pca2_1$) phase transformation is triggered. Consequently, a high dielectric constant (ε_r ~ 38), low effective oxide thickness (EOT ~ 0.54 nm), and a high remanent polarization (P_r ~ 30 μC/cm^2) are achieved, while eliminating wake-up treatment and lowering the processing temperature to 400°C, which are highly favorable for integration with advanced semiconductor technology nodes. A novel application of helium ion beam microscopy (HIM) combined with Gwyddion software enables high-resolution imaging and quantitative analysis of nanoscale grain evolution during the AFE-MPB-FE transition. Compared to conventional scanning electron microscopy (SEM), HIM offers a sub-nm beam size, higher secondary electron yield, and minimal charging effects, enabling high-precision characterization of non-conductive ultrathin films without a heavy metal coating. This work overcomes critical scaling challenges — performance degradation in sub-6 nm FE films and high annealing temperatures — positioning ZrO_2 as a strong candidate for high-K dielectric layers and nonvolatile memory in AI, IoT, and neuromorphic computing.

8:45am **AA1-TuM-4 Metastable Rutile TiO2 Growth on Non-Lattice-Matched Substrates via a Sacrificial Layer Strategy***, **Jeon Jihoon**, Kim Seong Keun,* Korea Institute of Science and Technology (KIST), Republic of Korea

Metastable materials possess unique properties critical for advanced technologies; however, their synthesis is significantly challenging. Among the TiO_2 polymorphs, rutile TiO_2 stands out for its exceptional dielectric properties; however, its film growth typically requires high temperatures or lattice-matched substrates, limiting its practical applications. This article presents a novel sacrificial layer strategy for the atomic layer deposition (ALD) of pure-phase rutile TiO_2 films on diverse substrates, including amorphous Al_2O_3, HfO_2, and ZrO_2. This approach employs ultrathin Ru sacrificial layers to facilitate the formation of rutile TiO_2 seed layers via the in-situ generation of a rutile-matched RuO_2 lattice. At the same time, it is completely removed as volatile RuO_4 under exposure to O_3 during the ALD process. This approach eliminates the need for high-temperature annealing and substrate restrictions, enabling low-temperature formation of rutile TiO_2 on diverse substrates, including amorphous oxides. Comprehensive characterization revealed the structural stability of the films and their enhanced dielectric performance. Stabilizing rutile TiO_2 independently of the underlying layer opens new possibilities for its integration into memory capacitors. Furthermore, this strategy provides a versatile framework for stabilizing other metastable material phases, thereby offering opportunities for diverse applications.

9:00am **AA1-TuM-5 EWF Modulation and Electrical Performance Enhancement Using Fluorine Surface Treatment in Yttrium Oxide-based Dipole-First Gate Stack***, **Sangkuk Han**, Changhwan Choi, Wonjae Choi,* Hanyang University, Korea

Effective work function (EWF) tuning through dipole engineering is crucial for enabling multi-Vt options in advanced logic devices such as Gate-All-Around (GAA) nanosheets and Complementary-FET (CFET). The dipole-first approach is one of the most promising candidates for enabling multi-Vt engineering in next-generation logic devices. However, a primary challenge in this scheme is achieving precise Vt fine-tuning [1]. To address this, advanced shifter materials must provide fine-tunable EWF modulation to support diverse Vt flavors. In this study, Y_2O_3 was utilized as a dipole material to enable fine-tunable EWF modulation, while Fluorine Surface Treatment (FST) was applied to passivate defects in the high-k layer to improve electrical performance. Y_2O_3 exhibits strong resistance to fluorine-containing plasma, which prevents IL/channel degradation caused by fluorine plasma incorporation [2].

In this work, nMOS capacitors were fabricated to evaluate V_{FB} shift and electrical characteristics in dipole-first gate stack. By modulating the thickness of ultra-thin lanthanide oxide films (La_2O_3, Y_2O_3) from 2 Å to 4 Å using atomic layer deposition (ALD). As shown in Fig. 1, V_{FB} reduction of pristine and fluorine-treated Y_2O_3 at 4 Å was observed at 200mV and 330mV, respectively. In contrast, La_2O_3 at 4 Å exhibited a large V_{FB} negative shift of 635mV, indicating a significantly broader tuning range. These results demonstrate that Y_2O_3 offers improved EWF fine-tunability, making it a more beneficial alternative to La_2O_3 in dipole-first gate stack. I-V characteristics show a consistent reduction with increasing thickness up to 4 Å for pristine Y_2O_3, whereas La_2O_3 exhibited a decrease only up to 3 Å, followed by an increase at 4 Å. This increase is attributed to IL regrowth and sub-oxide formation, potentially affecting the interfacial properties. Fluorine treated Y_2O_3 shows over an order of magnitude reduction in leakage current compared to pristine Y_2O_3 as shown Fig. 2. The improvement results from defect passivation within the high-k layer, particularly oxygen vacancies, while the strong resistance of Y_2O_3 to fluorine containing plasma helps prevent IL/channel degradation caused by fluorine incorporation.

Our results show that Y_2O_3 exhibits greater potential for fine-tuning compared to La_2O_3, while FST Y_2O_3 also showed improved electrical performance by maintaining a controlled negative V_{FB} shift with reduced leakage current. Our findings suggest that Y_2O_3 is a promising alternative dipole material for matching the threshold voltage requirements of next-generation advance logic devices such as a CFET architectures.

9:15am **AA1-TuM-6 Reconfigurable Memristor Crossbar for Graphlet Computing***, **Kyung Seok Woo,*** Sandia National Laboratories*; Nestor Ghenzi,* Seoul National University*; Hyungjun Park,* Seoul National University, Republic of Korea*; A. Alec Talin,* Sandia National Laboratories*; Cheol Seong Hwang,* Seoul National University, Republic of Korea*; R. Stanley Williams, Suhas Kumar,* Sandia National Laboratories

In-memory computing approaches using memristor crossbars have been proposed as a paradigm shift to overcome the von Neumann bottleneck by combining memory and processing functions. Memristors are considered one of the most promising devices for in-memory computation due to their low power consumption, high switching speed, and scalability. However, sneak paths and stochastic behavior are two critical issues that limit their practical implementation. There have been transformative designs of in-memory computing using either stochasticity or sneak paths, but the combined potential of memristor crossbars remains unexplored. Here we propose a graphlet computing platform that synergistically utilizes both phenomena using a tunable hybrid memristor with a bilayer of insulator fabricated via plasma-enhanced atomic layer deposition (PEALD). By controlling the O_2 plasma power of PEALD, two oxide layers have different oxygen vacancy concentrations that allow for tunable switching behaviors under different switching conditions (Fig. 1). The tunable memristor was integrated into a crossbar, which was used to map a graph by assigning each device as either a node or an edge. Then, we performed graphlet computing by utilizing inherent sneak paths and stochastic behavior of the crossbar (Fig. 2). While the sneak paths are used to count graphlet structures for analyzing complex graphs, the stochasticity is implemented in a random walk process to efficiently solve computationally expensive problems. This newly proposed computing scheme demonstrates the advancement of memristor-based in-memory computing hardware by addressing the inherent issues of memristor technology.

9:30am **AA1-TuM-7 Tuning of Effective Work Function in Cl Free TiAlN ALD Through Fine Al Doping Process for Gate Electrode Application***, **Gyeong Min Jeong**, Hae Dam Kim, Jin-Seong Park,* Hanyang University, Republic of Korea

In the advancement of semiconductor device fabrication, integrating high-κ dielectrics and metal electrodes is essential to overcome the limitations of traditional silicon-based MOSFETs. Titanium nitride (TiN) is a pivotal material, effectively mitigating diffusion-induced oxidation at polycrystalline silicon electrode interfaces. TiN have metallic properties like low resistivity and exceptional physical and chemical stability, render it indispensable in applications such as electrodes, surface coatings, and diffusion barriers. Work function of metal electrodes critically influences MOSFET electrical characteristics, including threshold voltage and leakage current. However, Fermi-level pinning in high-κ materials leads to deviations from intrinsic work function values, necessitating the consideration of effective work function values. For TiN, the effective work function typically ranges between 4.6 and 4.8 eV, aligning well with p-MOSFET. In contrast, n-MOSFET require lower work function values, prompting extensive research into methods for reducing TiN's work function to meet these requirements. Atomic layer deposition (ALD) has emerged as a cornerstone technique in semiconductor shrinking, offering unparalleled control over film thickness and composition. TiN thin films are commonly deposited via thermal ALD processes utilizing precursors such as titanium tetrachloride ($TiCl_4$) and ammonia (NH_3). This approach reliably yields high-quality films with low resistivity. However, the incorporation of chlorine residues necessitates post-deposition at temperatures exceeding 400 °C. Alternatively, metal-organic precursors like tetrakis(dimethylamido)titanium (TDMAT) can be employed; nevertheless, achieving low resistivity with TDMAT often requires plasma-enhanced processes or subsequent high-temperature annealing. In this study, we developed a thermal ALD process using TDMAT and NH_3 as precursors, incorporating trimethylaluminum (TMA) cycles to deposit TiAlCN thin films at a relatively low temperature of 300 °C. This method achieved films with a resistivity of approximately 5000 μΩ·cm, lower than previously reported values for thermal ALD TiN films deposited from TDMAT without post-deposition annealing. Furthermore, by doping aluminum concentrations below 10%, we successfully tuned the work function from 4.9 eV to 4.5 eV. Compared to conventional $TiCl_4$-based processes, our method offers advantages including reduced carbon contamination and lower deposition temperatures, thereby minimizing potential adverse effects on adjacent thin films. This makes the process particularly suitable for the fabrication of MOSFETs with increasingly complex architectures.

9:45am **AA1-TuM-8 Optimizing Grain Structure in Mo-Ru Alloys for High Conductivity***, Changhwan Choi, **Hyunjin Lim**, Youngseo Na, Yeh Been Im,* Hanyang University, Korea

As the demand for continuous miniaturization in semiconductors increases, the search for new interconnect materials has become a key area of innovation. Conventional materials such as copper (Cu) face challenges related to increased resistivity, electron mobility limitations, and electromigration issues [1]. In addition, modern semiconductor processes impose stringent requirements on thermal stability, process compatibility, and interconnect reliability. Against this backdrop, molybdenum (Mo) and ruthenium (Ru) have emerged as promising candidates for next-generation interconnect materials [2]. Their high thermal stability, adaptability to ultrathin film deposition, and compatibility with advanced fabrication environments suggest the potential for a paradigm shift in interconnect design.

Mo and Ru have similar atomic radii, which minimizes lattice distortion when alloyed, thereby suppressing the increase in electrical resistivity [3]. Furthermore, the combination of Mo's superior oxidation resistance and Ru's ability to address barrier layer challenges enhances the reliability of interconnect structures. However, successfully integrating MoRu alloys into semiconductor interconnect technology requires reconsideration of nanoscale deposition techniques, including precise thickness control and uniform deposition on high-aspect-ratio structures. To address these challenges, plasma-enhanced atomic layer deposition (PE-ALD) plays a crucial role. Compared to conventional thermal ALD, PE-ALD provides additional reaction energy, enhancing surface reactivity and enabling deposition at lower temperatures, making it particularly suitable for back-end-of-line (BEOL) applications.

In this study, we employ PE-ALD to deposit MoRu thin films, investigating the control of alloy composition, grain growth mechanisms under plasma conditions, and the effect of plasma on film crystallinity. Furthermore, we evaluate the electrical resistivity of the films and conduct reliability tests under high-temperature annealing and current stress conditions. Mo films deposited by ALD exhibited a resistivity of 1167 μΩ·cm at 2 nm and 146 μΩ·cm at 8 nm, while Ru demonstrated an excellent resistivity of 20 μΩ·cm at 7 nm (Fig. 2). To investigate the size effect behavior, an MoRu alloy was fabricated and analyzed. By optimizing the deposition process and material properties, this study aims to assess the feasibility of MoRu as a viable alternative to Cu and W-based interconnects and provide fundamental data for its potential industrial implementation in future semiconductor manufacturing.

ALD Applications
Room Tamna Hall A - Session AA2-TuM
EUV and Patterning Applications

Moderators: Jiyoung Kim, University of Texas at Dallas, **Hanjin Lim**, Samsung Electronics Co., Inc.

10:45am **AA2-TuM-12 Defect-free Carbon based EUV Pellicle by using Bi-layer Capping with Atomic Layer Deposition***, **Park Jihoon,** Yoon Hwi,* Yonsei University, Korea*; Wi Seong Ju, Lee Yunhan, Lee Byunghoon, Bae Sukjong, Choi Jin,* Samsung Electronics, Republic of Korea*; Kim Hyungjun,* Yonsei University, Korea

For several decades, semiconductor device scaling down has been steadily progressing. Therefore, lithography technology has also been developed to engrave smaller patterns into circuits. Extreme ultraviolet lithography (EUVL) technology which uses a wavelength of 13.5 nm, which is significantly shorter than conventional lithography, has emerged as a solution. However, the increased light source power of EUV causes the chamber to become harsher and high temperature. These conditions accelerate mask damage and require frequent mask replacement. So, as EUV equipment advances, demand for pellicle increases.

Carbon-based pellicles are considered as EUV pellicle materials because they have high transmittance, good thermal stability, high emissivity, and good mechanical properties. However, they have low durability against hydrogen plasma in EUV equipment, so a capping layer is essential. Therefore, in this study, we attempted to deposit a very thin and uniform film of MoN with low EUV absorption coefficient and H_2 plasma durability through ALD. However, plasma pre-treatment or PEALD was required to perform ALD on graphite with an inert surface, which caused graphite damage.

In this study, we greatly improved the adsorption using physisorption on the graphite surface at high precursor vapor pressure. An oxide thin film less than 2 nm was deposited as the first layer, and the coverage was confirmed by comparing the I_d/I_g peak ratio of Raman spectrum before and after H_2 plasma treatment. After full coverage of the oxide thin film, a defect-free graphite capping layer was successfully deposited by depositing a MoN film less than 5 nm. Next, we conducted a characteristic evaluation as an EUV pellicle. Our research will be a basic experiment for a carbon-based pellicle capping layer.

11:00am **AA2-TuM-13 Three-Step Plasma-Enhanced ALD of Ultra-Thin SiNx with Enhanced Etch Resistance for EUV Pellicle Applications***, **Hye-Young Kim,** Hyun-Mi Kim, Yoonjeong Shin, Jonghyuk Yoon,* Korea Electronics Technology Institute, Republic of Korea*; Ji-Beom Yoo,* Sungkyunkwan University (SKKU), Republic of Korea*; Seul-Gi Kim, Hyeongkeun Kim,* Korea Electronics Technology Institute, Republic of Korea

Silicon nitride (SiN_x) thin films are widely recognized for their hardness, chemical inertness, and exceptional barrier properties, making them indispensable as passivation layers and gate insulators in semiconductor devices. Recent studies have shown that enhancing film density through optimized deposition parameters can significantly reduce the etch rate in hydrofluoric acid (HF). To build on this concept, an optimized ALD process was developed, using SiN_x as a capping material to protect the base materials of extreme ultraviolet (EUV) pellicles. A three-step ALD process, consisting of Si_2Cl_6 (precursor) - NH_3 plasma (reactant 1) - N_2 plasma (reactant 2), was developed to enhance resistance to potassium hydroxide (KOH), which is crucial for pellicle capping, and to protect the base material from hydrogen plasma generated in the EUVL chamber. A detailed investigation was conducted by comparing SiN_x films deposited using NH_3 plasma alone, N_2 plasma alone, and their sequential combination. The NH_3 plasma–N_2 plasma sequence resulted in the highest film density of 3.10 g/cm^3, compared to 2.85 g/cm^3 for films deposited using NH_3 plasma alone. This increase in density correlated well with the improved etch resistance in KOH, as the etch rate was significantly reduced from 3.3 Å/h (NH_3 plasma alone) to 1.8 Å/h in the three-step ALD process. Additionally, the formation of Si etch pits was nearly eliminated, further confirming the enhancement in etch resistance. Further analysis was conducted to investigate how the additional N_2 plasma in the three-step process influenced film density, composition, and hydrogen bonding. To this end, XPS and FT-IR analyses were performed to examine changes in these properties. Additionally, to determine whether ion bombardment played a primary role in densification, a modified three-step process incorporating Ar plasma instead of N_2 plasma was implemented for comparison. Furthermore, in situ Optical Emission Spectroscopy (OES) was conducted during the plasma exposure step and resultant emission signals were matched with dissociated reaction products to investigate the reactive species generated in each process and their impact on the final film properties.

11:15am **AA2-TuM-14 Mo_2C-Coated CNT with Hydrogen Radical Resistance for EUVL Pellicles***, Hyeongkeun Kim, **Su Min Lee**, Yongkyung Kim Kim, Jonghyuk Yoon, Kihun Seong, Heongyu Lee, Sun Gil Kim, Hyun-Mi Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea*; Gu Young Cho,* Dankook University, Republic of Korea*; Seul-Gi Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea

Extreme ultraviolet lithography (EUVL) is a key technology in advanced semiconductor manufacturing, enabling precise patterning at the nanoscale. However, mask contamination poses a major challenge, necessitating the use of EUV pellicles to protect the mask while ensuring high transmission of EUV light. To meet performance requirements, EUV pellicles must achieve over 90% transmission and maintain mechanical stability at thicknesses of just a few nanometers. [1]

Single-walled carbon nanotube (SWCNT) membranes are promising for EUV pellicles due to their high transmittance, thermal stability, and mechanical strength. However, their vulnerability to hydrogen radical etching at higher EUV source powers limits their durability. [2] To address this, we developed a molybdenum carbide (Mo_2C)-coated CNT membrane with enhanced resistance to hydrogen plasma. [3]

The Mo_2C capping layer was synthesized using atomic layer deposition (ALD) of molybdenum carbide (MoC_x) with molybdenum pentachloride ($MoCl_5$), followed by carbidization in a methane (CH_4) atmosphere. This process enabled uniform Mo_2C capping while preserving the CNTs' intrinsic properties.

Results demonstrated that Mo_2C-coated CNT membranes exhibit superior resistance to hydrogen plasma etching compared to uncoated CNTs. This study highlights the potential of Mo-$_2$C-coated CNTs as high-performance EUV pellicles, paving the way for improved lithography processes in semiconductor fabrication.

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11:30am **AA2-TuM-15 ALD Outstanding Presentation Award Finalist: Vapor-Phase Infiltration of Hafnium in Poly(Methyl Methacrylate) Thin Films for Extreme Ultraviolet Lithography Applications***, Md Istiaque Chowdhury, Xinpei Wu,* Brookhaven National Laboratory*; Won-Il Lee, Mueed Ahmad,* Stony Brook University*; J. Anibal Boscoboinik, Kim Kisslinger, Aaron Stein, Nikhil Tiwale,* Brookhaven National Laboratory*; Jiyoung Kim,* University of Texas at Dallas*; **Chang-Yong Nam,*** Brookhaven National Laboratory

Vapor-phase infiltration (VPI), an organic-inorganic hybridization technique derived from atomic layer deposition (ALD), has demonstrated the ability to generate novel hybrid photoresists for extreme ultraviolet EUV lithography applications. In this study, we investigated hafnium (Hf) infiltration in poly(methyl methacrylate) (PMMA) via VPI using tetrakis(dimethylamido)hafnium (TDMA-Hf) as a precursor. Unlike typical metal oxide VPI, we employed a metal precursor-only VPI approach, capped by a short water pulse at the end of the procedure, under various VPI temperatures ranging from 85 °C to 150 °C.

Using in-situ mass gain measurement by quartz crystal microbalance (QCM) and a suite of ex-situ characterizations including polarization-modulated infrared reflection-absorption spectroscopy (PM-IRRAS), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS), we discovered that: (a) TDMA-Hf could infiltrate PMMA uniformly over the tested thickness of approximately 30 nm despite its relatively large molecular size; (b) the carbonyl (C=O) group in PMMA primarily interacted with infiltrating TDMA-Hf, most likely forming weak coordination bonds; however, at temperatures above 120 °C, a new unidentified bond was formed, likely resulting from stronger covalent interactions; and (c) VPI protocols needed optimization to minimize the inadvertent introduction of oxidants (e.g., water, oxygen) and subsequent formation of undesired Hf oxides within PMMA.

The synthesized Hf-PMMA thin films were subjected to a lithographic patterning study using 100 kV electron-beam lithography (EBL), revealing that VPI temperature directly influenced EBL sensitivity. By employing an appropriate developer, Hf-PMMA infiltrated below 100 °C demonstrated up to a ~60% improvement in EBL sensitivity compared to the un-infiltrated PMMA control. However, at higher infiltration temperatures, sensitivity decreased, which we attribute to the stronger chemical binding between the infiltrated Hf precursor and PMMA. These results highlight the critical importance of understanding and controlling precursor-polymer interactions during VPI to generate organic-inorganic hybrid thin films for advanced lithography applications, including EUV lithography.

The research was funded by the U.S. Department of Energy Office of Science Accelerate Initiative Award 2023-BNL-NC033-Fund. The research used the Materials Synthesis and Characterization, and Electron Microscopy Facilities of the Center for Functional Nanomaterials, which is a U.S. Department of Energy Office of Science User Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.

11:45am **AA2-TuM-16 Atomic Layer Deposition and Atomic Layer Etch cycles to minimize "Mushroom Growth" effect in Area Selective Atomic Layer Deposition***, **Birol Kuyel**, Joe Alex,* NANO-MASTER

Area-Selective Atomic Layer Deposition (AS-ALD) is a bottom-up thin-film deposition technique that enables selective growth on targeted regions while preventing deposition on adjacent areas. This method has gained significant interest due to its self-aligning and self-inhibiting properties, which help mitigate edge placement errors inherent in traditional top-down fabrication processes. However, the isotropic nature of Atomic Layer Deposition (ALD) can lead to undesirable lateral growth, commonly referred to as the "mushroom growth" effect. In this study, we aim to experimentally develop an integrated ALD and ALE cycle to mitigate this effect in the area-selective deposition of SiO_2 and Si_3N_4. To achieve this, we utilize the NANO-MASTER NLE-4000 hybrid system, which enables both Plasma-Enhanced ALD (PEALD) and Plasma-Assisted ALE (PAALE) within the same chamber.

ALD Fundamentals
Room Halla Hall AB - Session AF1-TuM

Mechanism and Theory I

Moderators: Christophe Vallée, University of Albany, **Charles H. Winter**, Wayne State University

8:00am **AF1-TuM-1 The Mechanism of Thermal ALD of Silicon Carbonitride from Chloroalkylsilanes and Ammonia – Theory Meets Experiment***, **Simon Elliott**,* Schrödinger, Ireland*; Jiyeon Kim, Paul Lemaire, Dennis Hausmann,* Lam Research

Carbon-doping of silicon nitride or silicon oxide results in a lowering of the dielectric constant and etch rate. The C-doped derivatives are therefore being used to replace the parent films in many applications in FEOL semiconductor manufacturing, such as for spacers and gap fill. Traditionally these C-doped films are deposited by CVD methods, but recently ALD methods have been formulated using silicon precursors with Si-CHx bonds. Maintaining the Si-CHx bond has been challenging due to its propensity to cleave under plasma conditions or at high temperatures. For these reasons, precursors that can be used in a low temperature thermal ALD process are highly desired.In this work we investigate whether ammonia is viable as a thermal ALD co-reagent for this application and what mixture of chloro and alkyl ligands are most favorable in the silicon precursor.

We use density functional theory (DFT) to compute the atomic-scale structure of surface intermediates and the mechanism of potential ALD reactions and complement this with detailed characterization during substrate exposure experiments.

Looking first at the co-reagent, we investigate the kinetics of proton transfer from ammonia to a model silyl fragment on an aminated surface. Four proton transfer pathways are obtained for HCl elimination, all with high barriers (>1.2 eV) that are indicative of low Bronsted acidity and suggest that side-reactions will compete with the ALD process. Three pathways are obtained for CH4 elimination with even higher barriers (>2.5 eV). Therefore, up to moderate temperatures, terminal-CH3 is likely to survive ammonia treatment and be incorporated into the film, and this could be a route to C-doping. Residual gas analysis (RGA) and quartz crystal microbalance is used to monitor whether HCl or CH4 is in fact evolved during each half reaction.

The second part of the study looks at the effect of various combinations of chloro and methyl ligands in candidate Si precursors, both monomers (SiCl4, SiHCl3, SiCl3Me, SiH2Cl2, SiHCl2Me, SiCl2Me2) and dimers (Si2Cl6, Si2Cl4Me2). Structural models are generated efficiently of the >100 surface intermediates that can potentially occur through physisorption, chemisorption via ligand elimination and etching by exchange with surface amines. For each precursor, DFT-based thermodynamics reveal that the most favorable intermediate is surf-SiCl3 up to about 250C, surf-Cl2 up to 450C and surf-Cl at higher temperatures, with associated predictions of ALD growth rate. Film composition and growth rate is then validated experimentally by ellipsometry (SE) and infrared red spectroscopy (ATR-FTIR), ex-situ but with an inert atmosphere glove box.

8:15am **AF1-TuM-2 Mechanistic Studies on Area Selective ALD of Iridium***, **Heta-Elisa Nieminen**, Matti Putkonen, Mikko Ritala,* University of Helsinki, Finland

The importance of self-aligned film deposition processes is obvious when considering the complexity of the devices being currently manufactured. Every process that can directly deposit only on selected areas may decrease the number of processing steps needed. When the growth is dictated by surface chemistry also issues related to pattern misalignment can be avoided. Finding new self-aligned thin film deposition processes becomes yet more important as the device dimensions are shrinking. Understanding the mechanism behind the selectivity helps in finding new process and surface combinations. In this work, the reason behind a selective growth of iridium on a set of substrates that are chemically alike is studied. The surface reactions and the selectivity mechanism are studied with ALD-UHV cluster tool by using *in vacuo* XPS, LEIS and TPD together with *in situ* QCM.

Excellent area selectivity in ALD of metallic iridium on a wide selection of substrates was initially found by Zhang et al. (*Chem. Mater.* 2022, 34, 8379-8388). The depositions were done with iridium(III) acetylacetonate, $Ir(acac)_3$, and O_2 as precursors. The growth is believed to start with a ligand exchange reaction between surface -OH group and the $Ir(acac)_3$ precursor. Initial hypothesis for the selective growth is that the weakly acidic byproduct formed in the ligand exchange reaction, Hacac, adsorbs preferably on more basic surfaces passivating them. In the current work, two surfaces on which iridium was deposited successfully, native SiO_2 terminated Si and *in situ* deposited Al_2O_3, are compared to two surfaces on which the deposition did not succeed, Al_2O_3 and HfO_2. The latter mentioned oxides as well as the native SiO_2 terminated Si were exposed to air and airborne hydrocarbons prior to the iridium deposition.

The passivation of the non-growth surfaces was clearly confirmed with the analysis methods used and details of the nature of the passivating compounds were resolved. Also, the possible role of the adventitious hydrocarbons in the beginning of the film growth was studied. The increased knowledge about the surface reactions can guide the thinking when selectivity is aimed on new process and surface combinations.

8:30am **AF1-TuM-3 ALD Outstanding Presentation Award Finalist: Like Boots or Hearts: The Kinetics of Precursor Decomposition***, **Sean Barry**,* Carleton University, Canada

One of the main differences between Chemical Vapor Deposition (CVD) and atomic layer deposition (ALD) is gas-phase reactivity: we anticipate precursors to react together or independently in the gas phase in CVD but generally expect ALD precursors to arrive at the substrate intact. However, thermal activation of a precursor in the gas phase can benefit ALD saturation by producing a more active chemical species.

Our group often uses an *in-situ* solution-phase method to discover thermal behaviour and track the kinetics of decomposition. Samples are flame-sealed in a glass tube with an appropriate solvent and monitored by nuclear magnetic resonance (NMR) spectroscopy. This characterization method is common in synthetic chemistry and can be used to analyse a variety of nuclei independently, and this technique can commonly and easily assess protons. Using this technique in conjunction with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), we can build structure-function relationships to help design better precursors.

The framework $Mo(VI)(=N^tBu)_2Cl_2.(L\text{-}L)$ (where L-L is a chelating ligand) allows us to easily investigate the role of chelate ligands in precursor design due to the thermal stability of the imide/chloride core. This talk will center on measuring the thermodynamics of precursor thermolysis through Eyring analysis and detail the implications of β-H versus γ-H elimination, as well as differentiating *inter*-molecular vs. *intra*-molecular reactivity. The presentation will show detailed reaction coordinates and different mechanistic thermolysis pathways for a growing family of Mo(VI) compounds.

8:45am **AF1-TuM-4 Reaction Mechanism of Atomic Layer Deposition of Zirconium Oxide Using Tris(dimethylamino)cyclopentadienyl Zirconium**, ***Yong Richard Sriwijaya***, *Hye-Lee Kim, Okhyeon Kim, Khabib Khumaini,* Sejong University, Republic of Korea*; Romel Hidayat,* PT PLN, Indonesia*; Won-Jun Lee,* Sejong University, Republic of Korea

A promising strategy for the development of advanced atomic layer deposition (ALD) precursors is the design of heteroleptic metal-organic compounds in which multiple ligand types are attached to a metal center. These heteroleptic precursors offer advantages over homoleptic counterparts, such as improved thermal stability while maintaining high reactivity. A notable example is tris(dimethylamino)cyclopentadienyl zirconium ($CpZr(NMe_2)_3$), which has successfully replaced the homoleptic precursor tetrakis(ethylmethylamino)zirconium ($Zr(NEtMe)_4$) in the fabrication of zirconium oxide (ZrO_2) films for dynamic random-access memory (DRAM) devices. Compared to Zr(NEtMe)4, CpZr(NMe2)3 exhibits better thermal stability, enabling better conformality at high process temperatures of 300°C with a growth per cycle of ~0.9 Å [1]. However, the competition between the NMe_2 and Cp ligands during surface reactions complicates the identification of the final chemisorbed species, which is important for designing the precursor for high-temperature ALD. In this study, we investigated the reaction mechanism of ZrO_2 ALD using a combined approach of *ab initio* calculations and *in situ* characterization. Density functional theory (DFT) calculations were performed to model the stepwise surface reactions of $CpZr(NMe_2)_3$ on a ZrO_2 surface, while *in situ* quartz crystal microbalance (QCM) analysis was used to study the ALD process with alternating precursor and ozone (O_3) exposures. DFT results indicate that the first two NMe_2 ligands are readily released during chemisorption of the Zr precursor with low activation energies of 0.22 eV and 0.16 eV. In contrast, the release of the Cp ligand or the third NMe_2 ligand is thermodynamically unfavorable due to its endothermic nature and high activation energy. As a result, the final chemisorbed surface species is predicted to be $O_2ZrCp(NMe_2)^*$. QCM analysis confirms the release of two NMe_2 ligands during the first ALD half-cycle, which agrees with the DFT results. This study demonstrates the effectiveness of integrating DFT calculations with QCM analysis to gain mechanistic insight into ALD reactions, especially when heteroleptic precursors are involved.

References [1] J. Niinisto et al., J. Mater. Chem. 18, 5243 (2008).

9:00am **AF1-TuM-5 A Study on the Correlation of Surface Chemistry to Electrical Properties of Ultra-thin Oxide Semiconductors by Atomic Layer Deposition: A Case Study of Indium Oxides Thin Films**, ***Joohyeon Lee***, Ajou University, Republic of Korea*; Dohee Kim, Ja Yong Kim, Jong Young Lee, Seung Wook Ryu,* SK Hynix, Korea*; Il Kwon Oh,* Ajou University, Republic of Korea

Atomic layer deposition (ALD)-grown ultra-thin In_2O_3 offers promising solutions with amorphous films at sub-3 nm thicknesses, allowing effective tuning of mobility and V_{th} based on thickness [1].

Materials and electrical properties of ultra-thin ALD films are significantly dependent on surface chemistry. For example, $HfCl_4$, with simple chlorine ligands, achieves a higher growth per cycle (~1.3 Å/cycle), lower interface trap density (1.86×10^{11} eV^{-1} cm^{-2}), and reduced leakage current density (3.94×10^{-7} A/cm^2 at $V_{FB} = -1V$). This is due to efficient oxidation and minimal steric hindrance, resulting in stoichiometric films with fewer oxygen vacancies. In contrast, $Hf(N(CH_3)_2)_4$, with bulky dimethylamino ligands, exhibits slightly lower GPC (~1.2 Å/cycle) and higher oxygen vacancy concentrations, leading to increased D_{it} (8.96×10^{11} eV^{-1} cm^{-2}) and leakage current (2.25×10^{-6} A/cm^2). Steric hindrance limits oxidant access, resulting in sub-stoichiometric HfO_{2-x} phases [2]. This highlights the critical role of ligand structure in determining film stoichiometry, defect density, and electrical performance, emphasizing the need for a comparative study for ultra-thin film formation using ALD.

In this study, we investigate the reaction mechanisms and surface chemistry of two indium precursors, [3-(dimethylamino)propyl]dimethyl indium (DADI) and trimethyl indium (TMI), for ALD-grown ultra-thin In_2O_3 films using O_3 as the reactant. DADI, containing dimethylamino and methyl groups, introduces greater steric hindrance compared to TMI, which has only methyl groups. This difference affects adsorption density, oxidizer accessibility, and oxygen deficiency during film growth, leading to variations in film composition, density, and electrical properties. To evaluate these differences, quadrupole mass spectrometry (QMS) will analyze ALD byproducts, X-ray photoelectron spectroscopy (XPS) will assess impurity levels and oxygen vacancies, and transmission electron microscopy (TEM) will confirm film uniformity. Physical properties such as morphology and density will be analyzed using atomic force microscopy (AFM) and X-ray reflectometry (XRR). Finally, a bottom-gate TFT will be fabricated to correlate these properties with electrical performance, providing a comparative evaluation of the precursors for BEOL integration into monolithic 3D devices.

References [1] Si et al., Nano Lett., 21, 1, 500–506 (2021) [2] Oh et al, J. Mater. Chem. C 6, 7367 (2018).

9:15am **AF1-TuM-6 Catalytic Role of Silane(SiH4) in Enhancing Titanium Nitride(TiN) Atomic Layer Deposition(ALD)**, ***Hu Li***, Tokyo Electron America Inc.*; Taichi Monden, Masaaki Matsukuma,* Tokyo Electron Technology Solutions Ltd., Japan*; Jianping Zhao,* Tokyo Electron America Inc.*; Yoshitada Morikawa,* Osaka University, Japan*; Peter Ventzek,* Tokyo Electron America Inc.

Titanium nitride (TiN) films are crucial for microelectronics applications due to their exceptional electrical conductivity, thermal stability, and barrier properties. Atomic layer deposition (ALD) has emerged as a preferred method for TiN fabrication, offering precise thickness control and superior conformality, particularly important for nanoscale structures. In this study, first-principles calculations based on density functional theory (DFT) were employed to investigate the catalytic role of silane (SiH_4) in the $TiCl_4/SiH_4/NH_3$ ALD process, with a focus on the removal of chlorine (Cl) atoms from the substrate surface. The results demonstrate that SiH_4 effectively promotes Cl desorption by reducing surface-bound Ti–Cl species, thereby enhancing surface reactivity and increasing the availability of active sites for improved precursor coverage. Detailed analyses of reaction pathways, activation energy barriers, and adsorption energies reveal that SiH_4 significantly lowers the energetic cost of Cl elimination, leading to a more efficient ALD process with higher growth-per-cycle (GPC) rates. These findings provide valuable insights into the catalytic mechanisms of SiH_4 and underscore its critical role in producing high-quality TiN films with reduced impurity levels. This work offers practical guidance for optimizing precursor combinations and process parameters in ALD technology.

9:30am **AF1-TuM-7 Correlation of Hydroxyl Group and Growth Characteristics in Atomic Layer Deposition of Ternary Oxide Depending on Growth Temperature**, ***Sanghun Lee***, Yonsei University, Republic of Korea*; Il-Kwon Oh,* Ajou University, Republic of Korea*; Hyungjun Kim,* Yonsei University, Republic of Korea

Atomic layer deposition (ALD) of doped or alloy materials has been intensively investigated with recent advances in nanotechnology applications. However, ALD of multicomponent materials is challenging because the growth characteristics often deviate from what is expected due to the difference in surface characteristics of heterogeneous and single materials, resulting in undesired thickness or properties. For metal oxides, the growth characteristics highly rely on the surface hydroxyl groups, which play a role as the reactive site. Thus, studying the reaction mechanism of a precursor on hydroxyl-terminated heterogeneous surfaces is important for understanding the nonideal growth of ternary oxide. This work provides understanding of how growth characteristics of ALD $TiSiO_x$ are deviated according to process temperature. Here, we investigated the correlation between hydroxyl and the growth of ALD $TiSiO_x$ depending on temperature, analyzing infrared spectra, and chemical compositions. The results show that large amounts of hydroxyl are detected in $TiSiO_x$ deposited at 100 °C, where the adsorption of H_2O on Ti–O–Si bonds is favorable. It leads to higher growth per cycle (GPC) than the estimated value. In contrast, hydroxyl disappears at 200 °C due to dehydroxylation, resulting in lower GPC. Differences in hydroxyl also influence the film density as revealed in x-ray reflection spectra, which is related to the film qualities (e.g., elastic modulus and dry etch rates). This work provides insight into how to control hydroxyl in the ALD of ternary oxides, which is susceptible to hydroxyl incorporation, leading to undesired growth characteristics.

9:45am **AF1-TuM-8 Atomistic Modeling of Oxygen Recombination Reactions in the ALD of SiO_2 and Al_2O_3**, *Suresh Kondati Natarajan,* Synopsys Inc., Denmark*; Rafshan Ul Atik,* Synopsys India Pvt. Ltd., India*;* ***Yong-Ju Kang***, Synopsys Korea Inc., Republic of Korea*; Jess Wellendorff, Søren Smidstrup,* Synopsys Denmark ApS, Denmark

Atomic layer deposition (ALD) has been a key enabling technology for atomically fine-tuned manufacturing of cutting-edge semiconductor devices. Depending on the underlying chemical mechanism of the ALD process, growth rates can vary significantly from process to process. In semiconductor gate stacks, Al_2O_3 is considered as interface dipole inducer and SiO_2 has been used as gate oxide. It has been shown that plasma enhanced ALD (PEALD) growth rate of SiO_2 is orders of magnitude larger than that of Al_2O_3 [1]. In these processes, O_2 plasma is used as the source of oxygen. O_2 plasma includes reactive species such as O radicals which can, in principle, recombine with the previously deposited O species on the growth surface and form O_2 gas. It has been proposed that the growth rate difference between SiO_2 and Al_2O_3 can be attributed to the differences in the oxygen recombination rates at the respective growth surfaces [1].

In this talk, we present evidence from atomic scale modeling in terms of thermochemical, kinetic and dynamic analysis of reactions taking place at the SiO_2 and Al_2O_3 growth surfaces using industry-grade simulation frameworks within the QuantumATK software [2,3] developed by Synopsys. Dynamic simulations with Synopsys QuantumATK have been previously utilized to get insights and determine mechanisms of ALD of HfO_2 [4] and ALE of 2D TMD materials [5].

In this study, we employed Density Functional Theory to calculate the thermochemical and kinetic properties of oxygen recombination reactions at both SiO_2 and Al_2O_3 growth surfaces. Using thermochemical modelling, we computed the free energy change associated with oxygen recombination. Using kinetic modelling, we extracted the activation barrier for the recombination reaction and derived the corresponding reaction rates. MACE universal machine learned force field is chosen for dynamic simulations as *ab initio* methods are very time-consuming for such studies. Using dynamic modelling, we explicitly simulated the plasma species-surface interaction and compared the probability of recombination at both growth surfaces. From the results generated at different levels of atomic-scale modelling, we provide a comprehensive understanding of the oxygen recombination leading to growth rate differences observed in the PEALD of the two materials.

[1] K. Arts et al., J. Phys. Chem. C, 123, 27030−27035 (2019).

[2] QuantumATK V-2024.09, Synopsys. (https://www.synopsys.com/quantumatk)

[3] S. Smidstrup et al., J. Phys.: Conden. Matter 32, 015901 (2020).

[4] J. Schneider et al., ALD/ALE 2022, Ghent, Belgium.

[5] S. K. Natarajan et al., ALD/ALE 2024, Helsinki, Finland.

ALD Fundamentals
Room Halla Hall AB - Session AF2-TuM

Mechanism and Theory II

Moderators: Atsushi Sakurai, ADEKA CORPORATION, **Tania Sandoval**, Technical University Federico Santa Maria

10:45am **AF2-TuM-12 Screening Volatile Metal Complex for ALD Precursor by Modified COSMO-SAC Method and Estimating Its Reactivity by Atomistic Simulator Using Neural Network Potential***, **Noboru Sato,*** The University of Tokyo, Japan*; Naoyuki Hoshiya, Akiyoshi Yamauchi, Shigehito Sagisaka, Yosuke Kishikawa,* DAIKIN INDUSTRIES, LTD., Japan*; Yuxuan Wu, Jun Yamaguchi, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

The film growth characteristics of ALD vary greatly depending on the precursors; therefore, there are many attempts to develop novel metal complexes. We are developing a method to predict and measure metal complexes' vapor pressure and adsorption equilibrium constants for the ideal ALD precursor. As ALD utilizes the saturated chemisorption of the precursor, high vapor pressure and equilibrium constant are required. We established a method for accurately estimating the vapor pressures of metal complexes by modifying the COSMO-SAC (COnductor-like Screening MOdel - Segment ACtivity) method proposed by Lin et al [1, 2]. In this presentation, we report the results of predicting and developing metal complexes with high vapor pressures, and we analyze the reactivity of candidate compounds using an atomistic simulator based on neural network potential (Matlantis™). Calculations were performed using the PBE+D3 level of theory.

When investigating the conditions for high-vapor-pressure complexes, we found that the lower the polarizability and dielectric constant, the higher is the vapor pressure (Figure 1). Accordingly, we predicted the vapor pressure of Co complexes with a polarizability of 220 or less and a dielectric constant of 2.1 or less, the results are shown in Figure 2. When we synthesized $CpCo(C_2F_4)CO$ and measured its vapor pressure, we found it to be 8 Torr at 85°C, which is sufficiently high for ALD applications (Figure 3). Thus, by utilizing the COSMO-SAC method, it is possible to design metal complexes with high vapor pressures.

To evaluate whether $CpCo(C_2F_4)CO$ can be used for ALD, we used Matlantis™ to calculate the chemisorption process on the Cu(111) surface, which served as the growth substrate (Figure 4). The metal complex physisorbed with an energy of 90kJ/mol, and the Cp ligand dissociated with a low activation barrier of 10–25kJ/mol, suggesting that it can be readily adsorbed on a clean Cu(111) surface at 200–300°C. When calculating the adsorption energies of the CO, C_2F_4, and Cp groups, we found that while the CO and C_2F_4 groups have adsorption energies of 90kJ/mol, the Cp group exhibits a very high adsorption energy of 245kJ/mol. This indicates that removal of the Cp group is likely to be the rate-determining step. The effective removal of Cp groups from the surface remains a challenge for future work.

References

1. Lin S.T., et. al., *J. Phys. Chem. A*, **108** (2004) 7429-7439.
2. Sato, N., et. al., AVS 24th International Conference on Atomic Layer Deposition, Helsinki, Finland (2024), AF1-TuM-2.

11:00am **AF2-TuM-13 Ion Effects on Plasma-induced Surface Composition Changes during SiCN Atomic Layer Deposition: A Combined Ab-Initio and Monte Carlo Approach***, **Ting-Ya Wang,*** University of Texas at Austin, Taiwan*; Hu Li,* Tokyo Electron America, Inc., China*; Peter Ventzek, Jianping Zhao,* Tokyo Electron America, Inc.*; Gyeong Hwang,* University of Texas at Austin, Korea (Democratic People's Republic of)

Plasma-enhanced atomic layer deposition (ALD) is an effective method for reducing deposition temperatures, particularly during nitridation. However, plasma can also introduce adverse effects, such as altering chemical composition and causing densification, which significantly influence key material properties like the dielectric constant. Understanding plasma-induced changes in surface morphology and composition is therefore critical. While experimental techniques for surface analysis face inherent limitations, theoretical methods also present challenges, particularly in modeling ALD processes where primary surface reactions are rare events.

Integrating kinetic Monte Carlo (kMC) with density functional theory (DFT) offers a powerful approach for simulating ALD. However, a key challenge in kMC lies in the need for a predefined list of permissible events. Traditionally, researchers manually compile a set of reactions deemed most significant. Yet, the vast number of possible events on a surface, combined with the importance of rare events in ALD, raises concerns about the authenticity and completeness of outcomes derived from manually curated reaction lists.

We developed an atomistic, off-lattice, three-dimensional simulator that integrates kMC with DFT. We employed a strategic approach to construct a comprehensive event list, capturing a broad spectrum of potential surface reactions. Our study focused on investigating the effects of ions in N_2 plasmas on silicon carbonitride (SiCN) materials, with particular emphasis on the roles of ion energy and flux.

SiCN is a low-k material critical for semiconductor manufacturing, where low dielectric constants are essential to minimize capacitive coupling in integrated circuits. The dielectric properties and mechanical strength of SiCN are strongly influenced by the elemental composition, bond types, and bond orders. Variations in these parameters can lead to significant differences in film quality and functionality, highlighting the importance of understanding and controlling these characteristics. By utilizing our simulator to model surface reactions and the evolution of SiCN films during ALD, we aim to validate and refine our approach while identifying strategies to optimize the material's properties for industrial applications.

11:15am **AF2-TuM-14 Benchmarking Large Language Models for Atomic Layer Deposition***, **Angel Yanguas-Gil,** Matthew Dearing, Jeffrey Elam, Jessica Jones, Sungjoon Kim, Adnan Mohammad, Chi Thang Nguyen, Bratin Sengupta,* Argonne National Laboratory

In this work we introduce an open-ended question benchmark, ALDbench, to evaluate the performance of large language models (LLMs) in the field of atomic layer deposition. Our benchmark comprises questions with a level of difficulty ranging from graduate level to domain expert current with the state of the art in the field. Human experts reviewed the questions along the criteria of difficulty and specificity, and the model responses along four different criteria: overall quality, specificity, relevance, and accuracy. We ran this benchmark on an instance of OpenAI's GPT-4o using an API interface. This allows us to fine tune hyperparameters used by the LLM for text generation in a way that is not possible using conventional chat-based interfaces.

The responses from the model received a composite quality score of 3.7 on a 1 to 5 scale, consistent with a passing grade. However, 36% of the questions received at least one below average score. An in-depth analysis of the responses identified at least five instances of suspected hallucination. We also observed statistically significant correlations between the following question and response evaluation criteria: difficulty of the question and quality of the response, difficulty of the question and relevance of the response, and specificity of the question and the accuracy of the response. Finally, we will address other issues such as reproducibility, impact of hyperparameters on the quality of the response, and possible ways in which the performance of the LLMs can be further improved.

[1] Yanguas-Gil et al, Benchmarking large language models for materials synthesis: the case of atomic layer deposition, arXiv:2412.10477 (2024). Submitted to JVSTA

11:30am **AF2-TuM-15 Adsorption State Study of Trimethylaluminum Using Neural Network Potential Computation and High Accuracy in-situ Quartz Crystal Microbalance***, **Yuxuan Wu**,* The University of Tokyo, Japan, China*; Jun Yamaguchi, Noboru Sato, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

Atomic layer deposition (ALD) is primarily applied in ULSI fabrication because of its characteristics of alternately supplying the precursor and reaction gas, relying on saturation of surface adsorption. This results in excellent uniformity and stability of the film thickness against fluctuations in fabrication conditions. Detailed results from previous studies have constructed a well-defined adsorption and reaction pathway for TMA ALD by in-situ characterization and computational simulation. The growth of Al_2O_3 could be understood by the adsorption amount and structures of TMA and H_2O at each step, where the $-CH_3$ and -OH densities on the surface significantly determine the characteristics of deposition. Understanding such termination on the surface can reveal the thermodynamic and kinetic factors for the reaction, where the quality and efficiency of the reaction can be controlled.

Conventional methods, such as Density Functional Theory (DFT) and Quartz Crystal Microbalance(QCM), examine the surface adsorption and reaction of precursors. However, the challenges of time-consuming and inapplicable for the steric hindrance prediction with a large slab size remain for DFT, and the insufficient accuracy of QCM (1 ng/cm^2) limits the measurement of small molecule adsorption. These limitations influence the analysis of the surface adsorption of TMA.

Using a state-of-the-art simulator (Matlantis^{TM}) with the Preferred potential (PFP) and high-accuracy in-situ QCM with a calibrated frequency counter and resonator, we explored the adsorption and reaction of TMAon the Al_2O_3 surface. Because of the precise neural network potential (PFP) developed by advanced machine learning-based techniques, it can easily predict the adsorption behavior of precursors on large adsorption surfaces in an extremely short time (minutes). We calculated the adsorption state and energy for TMA using Matlantis^{TM} and found good agreement with previous DFT calculations, as shown in Fig.1 (<0.07 eV). The adsorption calculation later expanded to multiple TMA molecule adsorption on the surface and predicted surface coverage for TMA by the steric hindrance effect due to the methyl group as 0.75, compared with the reference predicting surface coverage of 70%–80%. The adsorption amount of TMA on the Al_2O_3 surface with predicted surface coverage is 34.7 ng/cm^2, which is close to the experimental results from modified in-situ QCM, which shows 40 ng/cm^2 with a crystal roughness of 15%. The results from jMatlantis^{TM} were predicted well and precisely compared with both experiment results from QCM and computational DFT.

11:45am **AF2-TuM-16 Atomistic Insights into the Surface Chemistry Driving ALD of IGZO Films from First-Principles and Machine-Learning Simulations***, **Alex Watkins**,* University of Warwick, UK

The quaternary oxide semiconductor In-Ga-Zn-O (IGZO) has gained attention in recent years due to its promise in key properties: high optical transparency, high electron mobility, and low fabrication costs. These properties make it an exciting candidate for several applications including thin-film transistors (TFTs) in next-generation OLEDs, flexible electronic devices, advanced CMOS, and AI hardware.[1] One technique that has become indispensable for thin-film fabrication such as this is ALD, due to its exceptional conformality and control. The ALD process of IGZO requires a complex supercycle consisting of three single-component steps, each requiring a three-step process. This complexity requires significant optimisation to have success, this is where understanding the underlying surface chemistry is key, and atomistic simulations can provide great assistance.

In ALD the initial nucleation of a precursor on a target substrate is key to the overall quality of the deposited film, this requires effective precursor binding to the surface. Molecular dynamics (MD) simulations and minimum-energy reaction pathway analysis, enabled by *ab initio* Density Functional Theory (DFT) offer valuable insights into reaction chemistry, shedding light onto kinetics and thermodynamics factors.[2,3,4,5,6,7,8] Most recently machine-learned interatomic potentials (MLIPs) offer a major boost to the capabilities of these simulations, in bridging the gap between atomistic simulations studying binding of a single precursor and the kinetic Monte Carlo simulations studying larger scale properties such as rates of deposition and surface coverage.

In this contribution, we will present key atomistic insights into the ALD nucleation and growth mechanisms of IGZO on silicon oxide (SiO_2) substrate, as predicted by DFT and MLIPs, considering the different ALD sub-cycles, e.g. InOx, GaOx and ZnOx depositions. In particular, we will discuss the effect of simultaneous substrate binding of multiple precursors/co-reactants on the nucleation and growth behaviour, and the effect of temperature on the adsorption and surface coverage properties.

[1] *ACS Applied Electronic Materials* **2024,** 6 (8), 5694-5704; [2] *ACS Nano* **2017**, 11, 9, 9303–9311; [3] *Chem. Mater*. **2019**, 31, 4, 1250–1257; [4] *Chem. Mater*. **2017**, 29, 3, 921–925; [5] *Nanoscale*, **2021**, 13, 10092-10099; [6] *Chem. Mater*. **2017**, 29, 5, 2090–2100; [7] *Nanoscale*, **2016**, 8, 19829-19845; [8] *Solar Energy Materials and Solar Cells* **2017**, 163, 43-50.

ALD Fundamentals
Room Tamna Hall B - Session AF3-TuM
Precursor Chemistry II

Moderators: Venkateswara Pallem, AirLiquide, **Paul Williams**, Pegasus Chemicals

8:00am **AF3-TuM-1 ALD of SnO_2 Thin Films using Tin(IV) Acetate as a Novel Precursor***, **Anjan Deb**, Miika Mattinen, Mikko J. Heikkilä, Mykhailo Chundak, Anton Vihervaara, Kenichiro Mizohata, Mikko Ritala, Matti Putkonen,* University of Helsinki, Finland

Tin dioxide (SnO_2), with an exceptional combination of high transparency, conductivity and stability in harsh chemical environments, has gained a lot of attention as a potential material for various optoelectronic applications including transparent electrodes for solar cells, anode materials for batteries, smart windows and displays, gas sensing and catalysis. Many of these applications require scalable, highly uniform and conformal thin films with superior quality and performance. The atomic layer deposition (ALD) technique offers a unique combination of scalability, uniformity and conformality with angstrom level thickness control.

Most of the previously studied ALD precursors for SnO_2 require highly oxidizing coreactants, such as O_3, H_2O_2, and O_2 or H_2O plasma. These processes are unsuitable for various sensitive applications, including biological systems and polymeric substrates. Among the available precursors, $SnCl_4$ and tetrakis(dimethylamino)tin(IV) react with water; however, $SnCl_4$ presents challenges due to the high deposition temperatures (300–600°C) and formation of corrosive by-products. Consequently, development of new precursors and processes are essential to fully explore the potential applications of ALD SnO_2 thin films.

In this work, we present a new ALD process for SnO_2 thin films with tin(IV) acetate as a novel precursor and water as a co-reactant. We studied the film deposition over a temperature range of 150-250°C. The growth rate decreased from 0.8 to 0.4 Å/cycle as the deposition temperature increased from 150 to 250 °C. All the as-deposited films were amorphous. Crystallization of the amorphous SnO_2 thin films was studied with high temperature grazing incident X-ray diffraction (HT-GIXRD) technique in air and nitrogen environments. Crystallization started at 275 °C in air, whereas in the N_2 environment it was delayed until 325 °C. In both annealing environments phase pure SnO_2 with the tetragonal cassiterite (rutile-type) structure was obtained. X-ray photoelectron spectroscopy (XPS) analysis of the as-deposited SnO_2 films confirmed that all the tin existed in the Sn^{4+} state at all the deposition temperatures. The as-deposited films exhibited a transparency of 72-87% in the visible range, with a slight decrease observed as the deposition temperature increased. Time-of-flight elastic recoil detection analysis (ToF-ERDA) indicated small amounts of carbon (~2.8 at-%) and hydrogen (~2.2 at-%) impurities in the films which decreased with the post-deposition annealing.

8:15am **AF3-TuM-2 Bridging the Gap: Volachem's Mission to Advance ALD Precursor Development***, **Martin Wilken**, Dominik Naglav-Hansen, Andreas Ostendorf,* Ruhr Universität Bochum, Germany*; Anjana Devi,* Leibniz Institute for Solid State and Materials Research, Germany

The development of new precursors is essential for expanding atomic layer deposition (ALD) applications in microelectronics and beyond.[1-2] However, a persistent challenge remains: the limited availability of precursors that combine high volatility, high reactivity and thermal stability, and while meeting industrial scalability requirements. The transition from cutting-edge scientific research to commercially available precursors is particularly difficult, with only a few dedicated R&D projects and companies addressing this gap. This is where VolaChem steps in.

VolaChem, founded by Dr. Dominik Naglav-Hansen and Dr. des. Martin Wilken, is a science-to-market transfer project dedicated to the development of volatile chemicals for technical applications. A key focus is the research, development, and up-scaling of ALD precursors, ensuring their applicability in the processing of advanced materials. By employing a database-driven approach for synthesis R&D, specialized precursor analytics, and consulting services, VolaChem aims to accelerate the transition of novel precursor concepts from academia to industry.

In this presentation, the authors will introduce their business concept and service offerings as well as innovative methodologies, while fostering a scientific dialogue on the needs, challenges, and opportunities related to volatile compounds in both research and industrial settings.

VolaChem is built upon the founders' extensive academic research and expertise in designing tailored compounds for use as volatile precursors in technical processes.[3-6] By bridging the gap between laboratory innovation and industrial application, VolaChem aspires to become a driving force in the next generation of ALD chemistry.

8:30am **AF3-TuM-3 Revealing the Effect of Defect and Hydrogenation on Borazine-based Atomic Layer Deposition using First Principles Calculations***, **Tsung-Hsuan Yang**,* Tokyo Electron America*; Gyeong Hwang,* University of Texas at Austin*; Hu Li, Jianping Zhao, Peter Ventzek,* Tokyo Electron America

Borazine ($B_3N_3H_6$) has emerged as a promising precursor for synthesizing high-quality hexagonal boron nitride (h-BN) and amorphous boron nitride (a-BN), particularly after the groundbreaking work of Hong et al. (Nature 582, 511–514 (2020)), where they claimed to grow ultralow dielectric amorphous boron nitride using chemical vapor deposition method. Leveraging its intrinsic B_3N_3 ring, borazine enables facile atomic layer deposition (ALD) without the need for additional nitrogen sources. In this work, we utilize density functional theory (DFT) to investigate the reactivity of borazine with diverse surfaces, including those with defects, hydrogen terminations, and varying degrees of hybridization (sp2 and sp3). Our findings emphasize the critical roles of surface defects and hydrogenation in governing the deposition process. Furthermore, we will discuss the self-limiting behavior observed during ALD using borazine, a key characteristic for achieving precise film thickness control.

8:45am **AF3-TuM-4 Novel Heteroleptic Precursors for Oxide Semiconductor Films (In-, Ga-, Zn-, Sn-Ox), Aimed at Co-dosing Process and Cocktail Precursor***, **Nana Okada**, Ryota Fukushima, Keisuke Takeda, Masaki Enzu, Tomoharu Yoshino, Atsushi Yamashita, Yoshiki Oe, Akio Saito, Yutaro Aoki, Akihiro Nishida, Atsushi Sakurai,* ADEKA CORPORATION, Japan

Vertical channel transistors (VCT) with InGaZnO[1] and InGaZnTinO[2] channels deposited by ALD have been gaining attention for the 3D integration of devices, especially DRAM. A supercycle ALD with homoleptic alkyl metal precursors is commonly used: multiple metal precursors and reactants are injected step by step. It allows very controlled components, yet the process is long, and the precursors are pyrophoric[3]. Overcoming a long process, alternative approaches have been suggested such as co-dosing, which supplies multiple precursors simultaneously, and cocktail precursor, which combines precursors in one canister. However, these are challenging because all precursors must have similar volatility and mixing stability, and no precursors satisfy both requirements.

In this study, we developed new heteroleptic In, Ga, Zn, and Sn precursors: $In(Me)_2[^sBuNC(Me)C(H)C(Me)N^sBu]$ (DKI-6), $Ga(Me)_2[^sBuNC(Me)C(H)C(Me)N^sBu]$ (DKG-6), $Zn(Et)[^sBuNC(Me)C(H)C(Me)N^sBu]$ (DKZ-6), and $Sn(N^iPr_2)[^tBuNC(Me)N^tBu]$ (HTP-7) (Fig. 1). All precursors showed high volatility and non-pyrophoricity. A key feature of these materials is that they exhibit a vapor pressure difference of less than 10 °C at one torr (Fig. 2). Additionally, these materials remain stable and non-reactive when all mixed in equal moles. TGA of the mixture showed a smooth curve and no residue: 99.9% volatility (Fig. 3). ^1H NMR of the mixture had no byproduct peaks: the peaks came from each precursor (Fig. 4). Depositions of DKI-6 and DKZ-6 were done individually with H_2O on SiO_2 substrates at 150 to 300 °C. Both precursors showed ALD behavior and around 200 °C will be promising for a co-dosing and cocktail process (Fig. 5). DKI-6 and DKZ-6 at 200 °C growth rates were 0.1 and 0.2 Å/cycle respectively. X-ray photoelectron spectroscopy (XPS) indicated that impurity-free In_2O_3 and ZnO films were obtained successfully (Fig. 6). In contrast to In_2O_3, ZnO film did not have stoichiometry. This is believed to be caused by the difference in the sputtering ratio between Zn and O atoms. Moreover, DKI-6 and DKZ-6 were also reacted with O_3, and higher growth rates and impurity-free films were detected. This further investigation will be discussed at the conference.

These novel materials are promising for co-dosing and cocktail methods, offering significant process advantages like reducing flammable concerns and time consumption. The deposition of multi-component films is under investigation.

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9:00am **AF3-TuM-5 Investigation of Fluorinated Copper and Gold Alkoxides as Precursors for Atomic Layer Deposition***, **Nick A. Hoffman**, David J. H. Emslie,* McMaster University, Canada

This research focuses on the development of new precursors and processes for thermal atomic layer deposition (ALD) of elemental copper and gold thin films. Most previously reported copper thermal ALD processes require deposition temperatures in the range of 100-500 °C, which can result in agglomeration and discontinuous ultra-thin films.[1] Meanwhile, there have only been three reported processes[2] for Au thermal ALD – two of these use ozone (O_3) as a co-reactant, which limits substrate compatibility, while the minimum deposition temperature for the third process using $[AuCl(PEt_3)]$ with 1,4-bis(trimethylgermyl)-1,4-dihydropyrazine is limited by the volatility of the precursor and co-reactant. Thus, precursors which offer increased reactivity, thermal stability and volatility compared to those currently available, as well as the development of new reaction chemistries which might facilitate deposition at temperatures lower than previously reported, are of particular significance.

Herein we present a new family of fluorinated alkoxides, $[\{M(OR^F)(L)\}_n]$ (M = Cu, Au; OR^F = fluorinated alkoxide; L = PR_3, CNR), as potential precursors for thermal ALD of Cu and Au. Complexes were synthesized by straightforward and scalable methodologies, and were crystallographically and spectroscopically characterized. The thermal properties of these complexes were evaluated, displaying a wide range of thermal stability and volatility, with some precursors possessing the required characteristics for use in ALD. Solution-state reactions of these precursors with various ALD co-reactants support the thermodynamic feasibility of potential ALD reaction chemistry, yielding the target metal and volatile by-products. Select precursors were chosen for preliminary studies on a custom-built ALD reactor, leading to deposition of metallic thin films.

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9:15am **AF3-TuM-6 ALD of Al_2O_3 for Gas Barrier Applications: Impact of Al Precursors***, **Jean-Pierre Glauber**,* Leibniz Institute for Solid State and Materials Research, Germany*; Maximilian Gebhard, Lukas Mai,* Ruhr University Bochum, Germany*; Harish Parala, Anjana Devi,* Leibniz Institute for Solid State and Materials Research, Germany

Al_2O_3 is a versatile material system and due to its unique properties, thin films of Al_2O_3 find a range of applications in electronics, aerospace, automotive industry, anti-reflective coatings[1] packaging, gas barrier layers (GBLs)[2] etc. Especially for packaging and encapsulation of degradable goods, which are typically encapsulated by polymers such as polypropylene

(PP) and polyethylene terephthalate (PET), low temperature processing of dense and amorphous Al_2O_3 thin films is required.[2] These prerequisites render atomic layer deposition (ALD) as a favorable thin film fabrication method. Trimethylaluminum (TMA) is the most commonly precursor for ALD of Al_2O_3.[3] However, the high reactivity towards moisture requires expensive safety measures and the possible formation of TMA dimers leads to difficulties in predicting and controlling the process characteristics. Combined with the lack of a defined ALD window in TMA/H_2O ALD processes, alternative Al precursors that are non-pyrophoric, but still volatile and reactive to enable low temperature ALD processes with various co-reactants including H_2O and O_2 plasma are of great interest.

We have explored [3-(dimethylamino)propyl]-dimethyl aluminum (DMAD)for PEALD of Al_2O_3 thin films on polymer substrates. The influence of the two precursors on Al_2O_3 thin film growth and film properties was investigated and compared. Thin layers of Al_2O_3 and dyads of Al_2O_3 and SiO_2 were deposited (Figure 1a) with the aim of using them as GBLs on PP substrates. Interestingly, the dyads on PP containing SiO_2 and Al_2O_3 significantly outperformed the Al_2O_3 grown with TMA in terms of barrier properties (Figure 1 b).[4]

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9:30am **AF3-TuM-7 Atomic Layer Deposition of Nb_2O_5 using New Nb Precursor***, **Daehyeon Kim**, Suhyun Kim, Jinhyung Park,* Air Liquide, Republic of Korea

Niobium Oxides (Nb_2O_5) have been extensively utilized in various fields of technology. Traditionally these oxides have been applied as resistive films used as high-k materials for insulating layers. For instance, a thin layer of Nb_2O_5 between two ZrO_2 dielectric layers is expected to help significantly reduce leakage current and stabilize the cubic/tetragonal phases of the ZrO_2, affording higher k values in the current MIM capacitor of a DRAM. Furthermore, the application range of Nb_2O_5 expanded as HZO (HfZrO), which has ferroelectric properties, began to be applied to dielectric materials for DRAM capacitors. It is recently being studied as an interlayer between electrodes and HZO to enhance ferroelectricity of HZO.

Today, there is a growing need for a highly volatile, thermally stable, ideally low-viscosity liquid niobium precursor that allows to deposit films at high temperature in the Atomic Layer Deposition (ALD) process with a low film growth rate for precise thickness control. However, in general, thermal stability has a trade-off relationship with vapor pressure and viscosity, making it challenging to develop an ideal precursor with excellent properties across all these aspects.

To address these requirements, Air Liquide developed three Nb precursors (Nb1, Nb2, Nb3). Among them, Nb3 exhibited the most promising physical properties including not only high vapor pressure (1Torr at 105℃) and low viscosity (6.5cP at 24℃) but also high thermal stability (decomposition onset at 340℃ by DSC). It demonstrated a moderately low film growth rate of 0.4 Å/cycle, enabling precise control of film thickness. Furthermore, Nb3 showed exceptional ALD performance, achieving 100% step coverage at 350℃ and 375℃ (A/R: 1:30) and an ALD window extending up to 350℃, which is superior to the commercially available precursor in the industry.

9:45am **AF3-TuM-8 Atomic Layer Deposition of Mo Thin Film using Metal Organic Mo Precursor***, Han-Bo-Ram Lee, Bonwook Gu,* Incheon National University, Republic of Korea*; T. Barry Sean, Kieran Lawford,* Carleton University, Canada*; **Kwangyong An**,* incheon National University, Republic of Korea

The increase in integration and nanostructuring of semiconductor devices requires precisely controlled processes and improved materials properties. Molybdenum (Mo) has been actively studied as an alternative to W for the interconnects of semiconductor devices because of its low resistivity below the electron scattering regime. However, the Mo precursors reported thus far, such as $MoCl_2O_2$ and $MoCl_5$, often present challenges such as high melting points, line clogging, and particle formation. Additionally, Mo reacts easily with oxygen, making it difficult to form pure metal Mo thin films. To address these challenges, we investigated a Mo ALD process using a liquid MoCp precursor, which remains liquid at 70 °C and has a high vapor pressure of 1 Torr at 119 °C. Using hydrogen as a reactant, we successfully deposited Mo thin films at deposition temperatures below 500 °C and further improved resistivity by annealing at 950 °C for 1 hour in N_2 to reduce impurities. The lowest resistivity of the ALD Mo thin films obtained in this study was 14 μΩcm. X-ray photoelectron spectroscopy (XPS) was used to analyze the atomic concentration and bonding structure of the thin film and X-ray diffraction (XRD) was employed to evaluate its crystallinity. This study demonstrates that the MoCp precursor overcomes the limitations of conventional solid-state precursors, enhancing the reliability of Mo ALD processes. These results confirm its viability for use in advanced semiconductor technologies.

Atomic Layer Etching
Room Samda Hall AB - Session ALE1-TuM

Thermal Gas Phase ALE

Moderators: Steven M. George, University of Colorado at Boulder, **Chanmin Lee**, Samsung Electronics

8:00am **ALE1-TuM-1 Thermal Atomic Layer Etching in Next Generation 3D Devices***, **Younghee Lee**,* Lam Research Corporation **INVITED**

Thermal atomic layer etching (ALE) enables precise material removal with atomic-level precision through sequential, self-limiting surface reactions. This study explores the use of ALE and atomic layer deposition (ALD) in 3D devices, focusing on applications in full release, partial recess, and etch-back processes. Key challenges such as selectivity, surface roughness, and potential damage or contamination are addressed with new chemistries, processes, and hardware. We discuss the mechanisms behind selectivity, efforts to control roughness, and methods to minimize damage and contamination using non-metal reactants and novel chemistries.

8:30am **ALE1-TuM-3 Atomic Layer Etching of SiCO Films with Surface Modification by O_2 and CF_4/NH_3/Ar Plasmas and Desorption by IR Annealing***, **Nicholas McDowell**,* Hitachi High Technologies America Inc.*; Nobuya Miyoshi,* Hitachi, Ltd., Japan*; Phuc Phan, Ritchie Scott-McCabe,* Hitachi High Technologies America Inc.*; Hiroyuki Kobayashi,* Hitachi High Technologies, Japan

Thermal atomic layer etching (ALE) is one promising method to achieve atomic level precision and high conformality over three-dimensional structures and can further enable the manufacturing of gate-all-around (GAA) devices. Initially, an ALE process using a CF_4/NH_3/Ar remote plasma exposure followed by infrared (IR) annealing was studied on SiCO films. The process showed self-limiting behavior and achieved an etch per cycle (EPC) of 0.2 nm/cycle. To increase the EPC, an O_2 remote plasma exposure step was added before the CF_4/NH_3/Ar plasma exposure in the ALE cycle. The process achieved an EPC of 1.0 nm/cycle. Measurements of the EPC of the SiCO film showed self-limiting behavior in both the O_2 and CF_4/NH_3/Ar steps. X-ray photoelectron spectroscopy (XPS) results showed an increase in atomic concentration (A.C.) of Oxygen while the A.C. of Carbon decreased following the exposure of the film to an O_2 remote plasma. The results indicate that the methyl groups (-CH_3) in the top layers of the film are being replaced by hydroxyl (-OH) groups and Si-O-Si bonding. The N1s spectrum showed the formation of an ammonium fluorosilicate $(NH_3)_2SiF_6$-based surface-modified layer following exposure to a CF_4/NH_3/Ar remote plasma. IR annealing of the film showed desorption of the ammonium fluorosilicate surface-modified layer and the return to an as grown SiCO film surface composition.

8:45am **ALE1-TuM-4 Thermal Atomic Layer Etching of Mo with $NbCl_5$ and O_2***, **Juha Ojala**, Mykhailo Chundak, Anton Vihervaara, Marko Vehkamäki, Mikko Ritala,* University of Helsinki, Finland

With the constant demand to decrease component sizes in integrated circuits, the lowest level metal interconnects are approaching the performance limits of copper as a conductor. Molybdenum has been considered as an alternative material due to its lower resistivity at the nano scale and its potential for barrierless interconnects. In manufacturing future interconnects, highly controlled and selective etching processes such as atomic layer etching (ALE) will be beneficial, especially as 3D integration becomes more common. ALE can be used to pattern metal thin films, fine tune interconnect dimensions, and as a corrective step in area-selective deposition.

We present a new thermal ALE process for etching of Mo, where the surface of Mo is oxidized with O_2 and the resulting oxide etched with $NbCl_5$.

The ALE process was studied using XRR thickness measurements and *in vacuo* XPS studies. The films were characterized before and after etching using XRD, EDS, SEM, AFM, and four-point probe.

Etching temperatures of 225–400 °C were studied and etching was seen at temperatures as low as 250 °C. Maximum etch per cycle (EPC) of around 5 Å was seen at 400 °C. Saturation with O_2 pulses is slow, but the increase of EPC slows down with longer pulses, indicating diffusion limited oxidation. The saturation of $NbCl_5$ is faster, taking only 2 s at 300 °C. *In vacuo* XPS studies revealed that $NbCl_5$ etches Mo^{6+} very quickly. The lower oxidation states of molybdenum are not completely etched at 300 °C, but the intensity of the peaks diminishes significantly. Oxidation of the surface to Mo^{6+} is also slow with O_2, which in part explains the slow saturation.

Effect of the etching on film properties is minimal. The crystal structure of the film is unchanged after partial etching, and no increase in resistivity was observed that could not be attributed to the decreasing film thickness. AFM and XRR showed that during etching the roughness of the film R_q increases slightly from around 3 nm to at most 4 nm. This is accompanied by the grain structure becoming clearer in AFM and SEM. XPS showed that after partial etching small amounts of Nb and Cl are left on the surface, but these are below the detection limit of EDS. After complete etching of the film no Mo, Nb, or Cl could be detected on the substrate with XPS.

9:00am **ALE1-TuM-5 Film and Surface Stress During Thermal Atomic Layer Etching of Al_2O_3 and Tungsten***, **Ryan B. Vanfleet**, Steven M. George,* University of Colorado at Boulder

Film and surface stress were measured during thermal atomic layer etching (ALE) using in situ wafer curvature techniques in a custom reactor. Aluminum oxide (Al_2O_3) thermal ALE using hydrogen fluoride (HF) and trimethylaluminum (TMA) as the reactants was employed as a model system. Al_2O_3 ALE was explored at different temperatures ranging from 225 to 285°C using initial Al_2O_3 ALD films. The initial Al_2O_3 ALD film was under tensile stress of 400 MPa. Therefore, Al_2O_3 ALE led to an apparent compressive film stress resulting from the removal of the Al_2O_3 ALD film. Additionally, the initial fluorination of the Al_2O_3 surface resulted in a pronounced compressive stress.

The surface stress from the individual TMA and HF surface reactions was also measured by the high sensitivity wafer curvature measurements. The TMA exposure resulted in a compressive surface stress of -0.5 N/m. This compressive stress can be attributed to repulsion between the methyl species left on surface after the TMA ligand-exchange reaction. The HF fluorination reaction then removed the surface methyl species and released the compressive stress. The surface stress changes resulting from the TMA and HF reactions were large compared with the apparent compressive stress resulting from one Al_2O_3 ALE cycle during the removal of the Al_2O_3 ALD film.

Thermal tungsten (W) ALE using O_3/O_2 and tungsten hexafluoride (WF_6) as the reactants was explored at 285°C by additional in situ measurements. The initial W ALD film was under tensile stress of 1000 MPa. Consequently, W ALE led to an apparent compressive film stress resulting from the removal of the W ALD film. The surface stress was also measured resulting from the individual O_3/O_2 and WF_6 surface reactions. The O_3/O_2 exposure resulted in a compressive surface stress of -6.0 N/m. This compressive stress can be attributed to volume expansion resulting from W oxidation. The WF_6 exposure then released the compressive stress. These in situ wafer curvature measurements of film and surface stress during Al_2O_3 ALE and W ALE are providing new insight into the details of thermal ALE.

9:15am **ALE1-TuM-6 The Invention of Atomic Layer Etching: on the Conception of Cycled Exposures of Silicon to Halogens and Pulses of Heat, Ions, and More, by Seiichi Iwamatsu***, Fred Roozeboom,* University of Twente, Netherlands*; **Dmitry Suyatin**, Jonas Sundqvist,* AlixLabs A.B., Sweden*; Kuniyuki Kakushima,* Tokyo Institute of Technology, Japan

While the history of Atomic Layer Deposition (ALD) has been reported in excellent reports on the VPHA-project (www.vph-ald.com/) initiated in 2013 by Puurunen (1), and in articles by Malygin(2) and Parsons *et al*. (3), the "reverse" process, Atomic Layer Etching has lagged behind. For long (4,5) the first patent published on ALE was thought to have been initiated by Max Yoder (6), who in 1987 conceived the idea on etching diamond by "flooding" its surface with intermittent pulses of NO_2 and noble gas ions mixed with H_2 gas. This date of conception still holds for plasma-assisted ALE of diamond. However, from extensive AI-assisted patent searches we found that thermal ALE of silicon was conceived by **Seiichi Iwamatsu** (Fig. 1) of Seiko Epson, Japan. In 1981 he filed an application on Si-etching by repeated exposure to iodine (I_2) vapor at moderate temperatures (20-100 °C), followed by a light or heat pulse up to ~300 °C (7); see Fig. 2. Several other patents on ALE in his name followed (8). One of them disclosed plasma-assisted quasi-ALE, named "digital etching" (9) via Si-surface modification by “lamination” with a single Cl-atomic layer from exposure to Cl_2 gas, followed by a removal step carried out by Ar^+-ion bombardment to etch off "one atomic layer or at most three atomic layers by controlling the kinetic energy". Soon after, other researchers in Japan published on the digital etching of GaAs, with similar two-step physico-chemistry recipes(10). Today, ALE has come to maturity, fueled by early-leading groups, who worked on thermal and plasma ALE of metals, metal oxides, metal nitrides, semiconductors, and their oxides; see the reviews in refs. (11,12).

This presentation will highlight the groundbreaking work and background of the Japanese inventor Seiichi Iwamatsu. Born in 1939 in Kyoto to a family of physicians, he grew up and studied in Osaka, after which he spent many years as a "master inventor" (over 1200 patents filed in his name) for Seiko Epson (~1970-1990) and others afterwards. He played key innovative roles in thin-film technology and e-beam lithography, and contributed also this way to the success story of Seiko’s quartz watch (13), a masterpiece in micromachining and heterogeneous integration with electronics. We conclude that Dr. Iwamatsu, now 86 years old, can be recognized as the original inventor of Atomic Layer Etching of silicon.

<u>Acknowledgement</u>

The authors would like to thank Prof. R. Puurunen (Aalto University, Finland) for extensive consultations, and Dr. Masanobu Honda (Tokyo Electron Miyagi Ltd., Japan) for his support in retrieving some of the historic facts mentioned here about Dr. Iwamatsu.

9:30am **ALE1-TuM-7 Isotropic Atomic Layer Etching of HfO-$_2$ using Plasma Fluorination with NF_3 and Ligand Exchange with BCl_3***, **Hyeongwu Lee**, Heeju Ha, Daeun Hong, Heeyeop Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Isotropic atomic layer etching (ALE) for HfO_2 was developed with plasma fluorination using NF_3 plasma followed by ligand-exchange using BCl_3.Hf-O-F bond was observed by X-ray photoelectron spectroscopy (XPS) after the plasma fluorination. The fluorinated layer of HfO_2 was selectively removed by ligand-exchange using BCl_3 without affecting the underlying HfO_2 layer. No etching was observed below 80°C, and 0.3 ~ 3.5 Å/cycle of etch per cycle (EPC) was observed in the range of 100 ~ 220°C. Self-limiting characteristic was confirmed after BCl_3 dose time of 15 seconds at a fixed fluorination time at the temperature of 200 °C. The surface roughness of amorphous HfO_2 film slightly decreased from 0.372 to 0.322 nm, but the surface roughness of crystalline HfO_2 film was increased from 0.375 to 0.675 nm after the 30 ALE cycles. The monoclinic phase of crystalline HfO_2 film was confirmed by X-ray diffraction (XRD), and the different facets have different etch rates after the ALE process.The maximum intensity of (-111), (111), (020), and (200) facets decreased by 58 %, 36 %, 37 %, and 25 %, respectively, after 30 ALE cycles, and this result attributed a rougher crystalline HfO_2 surface afterthe ALE. The similar EPC was confirmed in amorphous HfO_2 film on Si-trench patterns having aspect ratio of 6.8 by scanning electron microscope (SEM) analysis after the ALE process.

Atomic Layer Etching
Room Samda Hall AB - Session ALE2-TuM

ALE Applications I

Moderators: Eric A. Joseph, IBM Research Division, T.J. Watson Research Center, **Jonas Sundqvist**, BALD Engineering AB

10:45am **ALE2-TuM-12 Enhancing 3D NAND Flash Memory Production: Addressing High Aspect Ratio Etching Challenges with Atomic Layer Etching***, **Jaewon Lee**, Huichan Seo,* SK hynix Inc., Republic of Korea **INVITED**

The fabrication of 3D NAND flash memory presents significant challenges in the etching process, particularly as device architectures scale to higher layer counts. Key issues include achieving precise etch profiles in high aspect ratio (HAR) structures, maintaining uniformity across large wafer areas, and ensuring high selectivity between different materials. Atomic Layer Etching (ALE) has emerged as a promising technique to address these challenges by enabling atomic-scale precision in material removal. However, traditional ALE processes are often limited by slow etch rates, which can impede throughput in high-volume manufacturing. Recent advancements in plasma-enhanced ALE have demonstrated potential in increasing etch rates while preserving the inherent precision of the technique. This abstract discusses the current challenges in 3D NAND etching and explores the development of ALE processes, focusing on enhancing etch rates, improving profile control, and ensuring uniformity across wafers. By advancing ALE technology, it is possible to meet the stringent requirements of next-generation 3D NAND fabrication.

11:15am **ALE2-TuM-14 Controlled Electron-Enhanced Silicon Etching with H_2 Background Gas and Positive Sample Voltage***, Sumaira Yasmeen,* University of Colorado at Boulder*; Harsono Simka,* Samsung Semiconductor*; **Steven George,*** University of Colorado at Boulder

Controlled electron-enhanced silicon etching can be achieved with H_2 background gas and positive sample voltage. Electrons impinged on the silicon surface at normal incidence at currents of ≥200 mA over surface areas of ~4 cm^2. The electron energy was ~140-240 eV defined by the grid bias on the hollow cathode plasma electron source and positive sample voltages. The H_2 pressures were <3 mTorr. The silicon etching for Si(100) and a-Si at room temperature was measured using in situ spectroscopic ellipsometry. The etched silicon thickness was linear versus time during electron-enhanced etching. The etch rates increased progressively with larger positive sample voltages (Figure 1). Si(100) etched slower than a-Si. For example, the etch rates were ~2.6 Å/min for crystalline Si(100) and 9.9 Å/min for a-Si under the same conditions at an incident electron energy of 140 eV with a positive sample voltage of +90 V.

Without the positive sample voltage, the silicon etch rates were negligible. In addition, electron-enhanced Si etching was not accomplished using a D_2 background gas instead of a H_2 background gas. These results support the proposed mechanism for electron-enhanced Si etching where H_2 produces H^- via dissociative electron attachment (DEA) according to $H_2 + e^- \rightarrow H_2^- \rightarrow H + H^-$. The positive voltage on the sample stage then pulls the H^- negative ions to the silicon sample to react with silicon to produce SiH_4 as an etch product (Figure 2). The low energy electrons required for DEA are secondary electrons produced by the primary electrons impinging on the silicon surface.

The energy of secondary electrons from silicon peaks at ~2-3 eV and drops off rapidly at higher energies approaching 10 eV. The peak of the DEA cross section for H_2 is 3.75 eV. In comparison, the peak of the DEA cross section for D_2 is 14.0 eV. The D_2 background gas may not be effective for silicon etching because D^- is not produced by DEA because the secondary electron energy from silicon is too low. These results demonstrate a new mechanism for controlled electron-enhanced silicon etching based on H_2 DEA from secondary electrons and H^- attraction to the positive sample voltage on the silicon sample.

11:30am **ALE2-TuM-15 Suppressing Surface Roughness in Tungsten Wet Atomic Layer Etching using Halogenation***, **Tulashi Dahal**, Kate Abel,* Tokyo Electron America Inc.,*; Karthik Pillai,* TEL Technology Center, America, LLC*; Trace Hurd, Antonio Rotondaro,* Tokyo Electron America Inc.,

As the interconnect schemes of leading-edge devices become increasingly complex, there is continued pressure to minimize the via resistance. One path is to minimize post-etch tungsten (W) surface roughness by replacing the current W etch processes with a less damaging approach. Wet Atomic Layer Etching (ALE) offers materials removal in atomic scale in two sequential, self-limiting steps at or near room temperature under ambient pressure without roughening the post-etch morphology. Here we present and compare our results on wet ALE of metallic tungsten (W) using either an oxidizer or a halogenating agent as surface modifying species.

Tungsten surface modification was studied using either an oxidizer or a halogenating agent in appropriate solvents. We expect the hydrolysis of tungsten halides based on their water reactivity so the halogenated surface will be only a reactive intermediate with the passivation layer ultimately composed of hydrolysis product. Solubilization of surface product can be suppressed and self-limiting surface modification of W can be achieved in non-aqueous solutions of oxidizer and halogenating species. Cyclic etch experiments were carried out to estimate the W etch amount per cycle by exposing W coupon in both oxidizing and halogenating solution followed by a rinse step and selective removal of modified layer in second chemistry different than the solvent used in the first step. W ER of ~0.33 nm/cycle (Fig. 1) in halogenating solution is about 2.5 times higher than W ER of ~0.13 nm/cycle achieved from oxidizing solution which may be attributed to the formation of thicker metal halide as surface passivation. The measured RMS roughness (Fig. 2) and the SEM images (Fig. 3) show that surface smoothness [RMS roughness of post-etch coupon ~ (1.109±0.081) nm is lower than as the RMS roughness ~ (1.275±0.130) nm of as deposited W coupon] is improved in post-etch halogenated W coupon up to about 8 nm. We attribute the improved morphology in halogenated post-etch W coupon to the formation of conformal metal halide as surface passivation. The evolution of surface roughness in post-etch W following oxidation route suggest that self-limiting surface modification is the necessary but not the sufficient condition to preserve or improve the surface morphology.

11:45am **ALE2-TuM-16 Plasma-Enhanced Isotropic Atomic Layer Etching of Molybdenum with Fluorocarbon Layer Formation Followed by Plasma Oxidation***, **Heeju Ha**, Hyeongwu Lee, Heeyeop Chae,* Sungkyunkwan University (SKKU), Republic of Korea

In this work, plasma-enhanced atomic layer etching (ALE) processes were characterized for molybdenum (Mo) with fluorocarbon deposition in the modification step and oxidation in the removal step. The Mo surface was fluorinated with C_4F_8 or CHF_3 plasma and C_4F_8 shows higher fluorine-contents at the same fluorocarbon layer thickness of 1 nm. The deposition rate of fluorocarbon layer on the Mo surface decreased with increasing temperature and C_4F_8 plasma shows a higher fluorocarbon deposition rate than CHF_3 plasma. The fluorinated surface was removed by oxidation reaction with O_2 plasma. The etch per cycle (EPC) of Mo was observed 0.96 ~ 16 nm/cycle for C_4F_8 plasma and 0.43 ~ 11.2 nm/cycle for CHF_3 plasma in the temperature range of 25 ~ 200 ℃ possibly due to higher fluorine concentration in the fluorocarbon layers. The activation energy for Mo etching obtained from the slope of the Arrhenius plot is 0.18 eV for C_4F_8 plasma and 0.22 eV for CHF_3 plasma. Fluorine residue after ALE was as low as 6%, which is attributed to the Mo_2CF_x peak.

Emerging Materials
Room Tamna Hall B - Session EM-TuM

Molecular Layer Deposition & Hybrid Materials I

Moderators: Jin-Seong Park, Hanyang University, **Henrik Pedersen**, Linköping University, Sweden

10:45am **EM-TuM-12 Zeolite-Like Frameworks Created by ALD/MLD as an All-Dry Resist Technology***, **Howard Fairbrother**,* Department of Chemistry, Johns Hopkins University*; Peter Corkery, Kayley Waltz,* Department of Chemical and Biomolecular Engineering, Johns Hopkins University*; Patrick Eckhert,* Department of Chemistry, Johns Hopkins University*; Michael Tsapatsis,* Department of Chemical and Biomolecular Engineering, Johns Hopkins University **INVITED**

The drive to further decrease microelectronic device dimensions has led to the expansion of extreme ultraviolet lithography (EUVL) and EBL processes which require next generation resist materials to maximize feature resolution and improve product throughput. Conventional solvent-based resist processes use organic resists which typically requiring time consuming baking steps and generate of organic solvent waste. Furthermore, mechanical stress induced by solution-based development can lead to pattern collapse, limiting the maximum possible density of patterned features. The process described herein avoids the use of, and some issues associated with, organic solvents by depositing films using ALD/MLD to produce amorphous films from 2-methylimidazole and diethylzinc that are chemically similar to zeolitic imidazolate framework-8 with sub-nanometer roughness. Following electron irradiation, areas of the film which were exposed to the electrons maintain the C:N:Zn ratio of the original film and are rendered resistant to etching by vapor phase 1,1,1,5,5,5-hexafluoroacetylacetone (hfacH). In contrast, unexposed areas can be readily removed by exposure to hfacH vapor at 120 °C, demonstrating the efficacy of aZnMIm films as a negative tone resist. The low temperature thermal etching conditions are notable, as the typical requirement of high temperatures in other dry etching processes can be difficult to implement in nanofabrication processes. The use of a molecular etchant (hfacH) also avoids limitations of plasma-based processes. aZnMIm films deposited by atomic/molecular layer deposition (ALD/MLD), patterned with electron beam lithography (EBL), and developed with hfacH achieved well-resolved 22 nm thick, 30 nm pitch lines. Sensitivity, contrast, and critical dimensions of the patterns created on silicon substrates and patterned at 30 keV are determined to be 37 mC cm−2, 0.87, and 29 nm, respectively. This work introduces a new direction for solvent-free resist processing, offering the prospect of scalable, high-resolution patterning techniques. Future work will explore substitution of the zinc metal centers for more EUV absorptive metals and the introduction of more reactive groups onto the organic linkers to increase resist sensitivity.

11:15am **EM-TuM-14 Atomic Layer Regulation of MIL-53 Metal-Organic Framework as Interconnect Low-k Dielectrics*, Fan Yang,*** Luoyu Road 1037, Wuhan, China*; Jisheng Song, Rong Chen,* Huazhong University of Science and Technology, China

Metal-organic frameworks stand out as one of the promising low-k dielectrics candidate to alleviate the delay caused by interconnect resistance of metal wire and capacitance of interlayer dielectrics (RC delay) in the context of the ever-denser and miniaturized integrated circuits. However, achieving nanoscale control over thickness of the fabrication of MOF thin-films is a critical requirement for subsequent lithography and metallization steps as well as of adequate mechanical strength. Therefore, precision preparation and modification of MOF-based dielectric film becomes an urgent need.

In this work, we report a synthetic strategy of ultra-low k (1.93 at 1 MHz) MIL-53 dielectrics by converting atomic layer deposited Al_2O_3 seed layer via microwave-assisted solvothermal method, where nanometer-scale regulated MIL-53 film can be obtained due to the linear dependence of the thickness of MIL-53 film on the Al_2O_3 seed layer. The synthesized the MIL-53 film also exhibits excellent hydrophobic properties and stability, with the dielectric constant remaining stable even after 12 days of aging, reflecting its potential as a dielectric insulating material. In addition, additional Al-O bond enhanced structures were formed in the MIL-53 framework by gas phase atomic layer infiltration (ALI) modification. After ALI treatment, the Young's modulus of MIL 53 increased by 27.7% (from 19.5 GPa to 24.9 GPa), hardness increased by 64.7% (from 0.17 GPa to 0.28 GPa), while only slightly increased on dielectric constant (from 1.93 to 2.32). The MOF film fabrication ALI modification strategy holds great promise for MOF based film synthesis and modification for interconnect dielectrics and various applications.

References

1. Atomic Regulation of Metal–Organic Framework Thin Film for Low-k Dielectric. Meng Cao, Jisheng Song, Haonan Ren, Fan Yang, Rong Chen,*Chem. Mater. 2024, 36, 22, 11160–11169*.

11:30am **EM-TuM-15 Nanolaminated Films with Negative Capacitance Fabriacted by ALD*, Xiang Yang Kong,*** School of Materials Science Engineering Shanghai Jiao Tong University, Shanghai 200240, China

The relization of negative capacitance (NC) behavior has long attracted the interests of electrical engineers. Some evidences have been demonstrated by examining the NC response resulting from adding a ferroelectric layer in series with a dielectric. In this talk, we fabricate a series of multilayered films with negative capacitance by ALD. The NC behavior occurs at the hetero-interfaces between the ferroelectric and paraelectric nanolayers.Regarding NC in hafnia-based materials, the oxygen-deficiency is accounted for unstable features as well as their ferroelectric and dielectric properties. We proposed the mobile ions at interfaces could enhance the stability of NC effects with the induced polarization.Moreover, we also lay out the way for scaling the NC FET nanoelectronics down to 2.5–5nm ferroelectric gate as well as giant density of energy storage.

11:45am **EM-TuM-16 Thermal Annealing of Molecular Layer-Deposited Tincone : Unveiling Sulfur's Structural Impacts in Graphitic Carbon Formation***, Jin-Seong Park, **Gi-Beom Park**, Hyolim Jung, Hae Lin Yang, Ji-Min Kim,* Hanyang University, Korea

As the scaling down of semiconductors based on Moore’s Law continues, efforts to introduce 2D graphitic carbon is being considered for use as a Cu diffusion layer and as top/bottom capping electrodes for Storage Class Memory (SCM), leveraging its high electrical conductivity and small geometric pore size to prevent diffusion between layers.[1,2] Additionally, it has the advantage of low chemical reactivity, making it suitable as an inhibitor in Area-Selective Deposition (ASD).[3] Both Chemical Vapor Deposition (CVD) and Atomic Layer Deposition (ALD) have been studied as methods for depositing graphitic carbon. However, the direct deposition of graphitic carbon on dielectric layers using CVD is limited, requiring a transfer process after deposition on substrates like Cu or Ni.[4] On the other hand, using ALD to deposit on dielectrics increases the sp^3 bonds, which compromises the benefits of sp^2 bond-based carbon.[5] Therefore, research is needed on deposition methods that can directly deposit graphitic carbon on dielectrics, regardless of the substrate. Using Molecular Layer Deposition (MLD) to deposit metalcone thin films followed by thermal annealing has confirmed the formation of graphitic carbon as metal atoms are eliminated.[3] Additionally, metalcone thin films can be effectively deposited on dielectric layers, providing the advantage of forming graphitic carbon regardless of the substrate. However, research on the formation of graphitic carbon through the thermal annealing of metalcone thin films has been limited to organic precursors with hydroxyl groups, such as hydroquinone (HQ). Therefore, it is necessary to study the graphitization behaviors influenced by the composition variations depending on different organic precursors.

In this study, tetrakis(dimethylamido)tin (TDMASn) and 4-mercaptophenol (4MP) were used to deposit tincone, followed by thermal treatment to explore the effect of sulfur within the metalcone thin film on the formation of graphitic carbon after thermal annealing. The MLD tincone films were deposited at 100 °C without impurities, then vacuum post-annealed in a tube furnace to induce graphitization. Spectriscopic Ellipsometry (SE), X-ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy were employed to investigate the effect of thermal annealing on the tincone thin film. As a results, atomic concentration of Sn decreased as increasing annealing temperature but Sulfur deteriorate graphite structure above annealing temperature of 500℃. Threrefore, it is important to find appropriate annealing condition by composition of metalcone thin film.

ALD Applications
Room Tamna Hall A - Session AA-TuA
3D Semiconductor Devices

Moderators: Dennis Hausmann, Lam Research, **Jonas Sundqvist**, BALD Engineering AB

1:30pm **AA-TuA-1 Characteristics of ALD IGZO for the application in Stackable DRAM Cell***, **Seung Wook Ryu**,* R&D Process, R&D division SK hynix Inc, Republic of Korea **INVITED**

This study aims to address the availability of Atomic Layer Deposited InGaZnO (ALD IGZO) as the stackable channel for the application in DRAM (Dynaic Ramdom Access Memory) cell.

The memory industry has grown significantly in response to the changes in the computing environment following the personal computer to artificial inteligence

(AI) era. The need for data creation, storage and processing will increase exponentially with the expansion of AI computing, much more rapidly than the traditional amount of data increase. As DRAM physically arrives at sub ten nanometer scale, the issues been more serious in many aspects, such as patterning for high aspect ratio structure, high-k material innovation as capacitor dielectric, resistance of gate material and so on.

The conversion to new platform is one of promising candidates to overcome current physical limits of DRAM and new channel material is a key component to realize new DRAM platform. IGZO is one of promising candidates as new channel material for DRAM cell transistors.

After physical properties of PVD IGZO related to electrical properties are investigated as the reference, those of ALD IGZO will be compared and then, hydrogen effect from precursor and integration will be presented.

Finally, we are going to check out the properties of ALD IGZO as compared with that of PVD IGZO and discuss the possibility as new form factor.

2:00pm **AA-TuA-3 5 nm Thick Indium Nitride Channel Layers Fabricated by PEALD for 3D Transistor Architectures***, **Doo San Kim**, Minjong Lee, Min Gyeong Jo, Thi Thu Huong Chu, Dushyant Narayan, Dan Le,* The University of Texas at Dallas*; Youngbae Ahn, Ja-Yong Kim, Seung Wook Ryu,* SK hynix, Republic of Korea*; Jiyoung Kim,* The University of Texas at Dallas

As Si channel scaling continues, highly complex 3D transistor architectures, such as complementary FETs (CFETs) and vertical FETs, are emerging. Alternative channel materials, such as two-dimensional transition metal dichalcogenides (2D TMDs) and indium gallium zinc oxide (IGZO) semiconductors, have garnered significant attention as potential replacements for conventional Si channel layers.However, these alternative materials must meet extremely challenging requirements, including high effective field mobility, high drive current, and a large on/off current ratio, while enabling 3D structure Si device compatible process and ensuring channel thickness scalability down to sub-5 nm. Among the promising candidates, indium nitride (InN) stands out due to its high electron mobility (~3,600 $cm^2/V{\cdot}s$), peak electron velocity exceeding 2×10^8 cm/s, and an appropriate bandgap greater than 0.75 eV [1,2].

Despite its potential, there are limited reports on InN-based transistors fabricated by atomic layer deposition (ALD), likely due to the challenges associated with growing sub-10 nm thick films with reliable electrical characteristics at low deposition temperatures. These difficulties stem from the low reactivity of In precursors with NH_3, relatively weak In-N binding energy, contamination from carbon and hydrogen, and challenges in achieving conformal deposition. Additionally, while InN films thicker than 10 nm typically exhibit metallic behavior due to high electron concentration, ultra-thin InN layers are expected to exhibit semiconductor properties.

In this presentation, we report the deposition of sub-5 nm conformal InN films using Hollow-Cathode Plasma (HCP)-enhanced ALD and evaluate their performance in back-gated thin-film transistor (TFT) devices. We examine the impact of process conditions—including plasma power, working pressure, and deposition temperature—on film characteristics. InN layers were deposited at 280°C on a 15 nm–100 nm SiO_2 back-gate dielectric atop a Si substrate. After defining the TFT channel, source/drain contacts were patterned.We presented InN TFT results, including transfer and output characteristics, temperature dependence, and channel length scaling. Our findings demonstrate that InN-based TFTs with a 4 μm channel length achieve an on-current of ~50 μA/μm, an I_{on}/I_{off} ratio exceeding 10^6, and a field-effect mobility of ~10 $cm^2/V{\cdot}s$ at V_D = 5 V.

This work was supported by SK hynix Inc. M. G. Jo. acknowledges IITP-(2025)-RS-2023-00253914 grant funded by the Korea government (MSIT).

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[2] Oseki, M., et al, *Sci. Rep.* **4**, 3951 (2014).

2:15pm **AA-TuA-4 Bottom-Up Mo Fill for Metal Interconnect Applications: Selective and Superconformal Approaches***, **Matthew Griffiths**, Arya Shafiefarhood, David Mandia, Justin Kim, Aleksandr Plokhikh, Youness Alvandi, Nick De Marco, Ben Natinsky, Andrew Melton, Jennifer O'Loughlin,* Lam Research Corporation

As devices continue to scale down to <2nm node, chip suppliers recently started replacing current metals (e.g., copper) with alternative metals due to reduction in current-carrying cross-section, increase in electron scattering, and integration challenges in narrow features. While cobalt (Co) and ruthenium (Ru) are attractive options for resistivity scaling and as middle-of-the-line (MOL) interconnect materials, they require the use of liners and are not amenable to downstream CMP processing. Selective (i.e., bottom-up) molybdenum (Mo) deposition represents a transformative approach to addressing the challenges of void-free filling in high-aspect-ratio structures for semiconductor manufacturing. Mo is a promising alternative to tungsten (W) in MoL applications where the CD of the via is below 15nm. However, achieving large grain Mo growth in complex geometries requires precise control over the deposition process and the use of a well-suited precursor.

This work focuses on $MoO_aX_b(L)$, a family of key precursors due to their unique ability to modulate between etching properties, selective deposition, or conformal deposition, depending on process design & substrate. Because some substrates do not lend themselves well to selective Mo deposition, we developed superconformal Mo deposition strategies so that we could achieve large-grain growth on any substrates and structures.

The proposed void-free Mo fill approaches take two different paths to achieve the same goal:

1. Selective Mo Deposition: Where the Mo inherits its selectivity from the substrate. Highly selective for certain applications but limited by substrate architectures.

2. Superconformal Mo Deposition: Where the bottom-up growth is controlled by the deposition kinetics and is derived from a conformal process. This can be tuned to fill any via or trench over a wide range of aspect ratios and is independent of the material at the bottom of the feature.

Extensive characterization using advanced microscopy techniques, including PED, TEM and EDX, confirms the deposited Mo films' superior quality, showcasing excellent conformality and absence of seam voids, even in features with reentrant profiles. These findings address many of the grand challenges for low resistance interconnects. The insights presented provide critical guidance for future material innovations and process optimization in semiconductor manufacturing.

Keywords: Bottom-up Mo fill, $MoO_aX_b(L)$, selective deposition, ALD, semiconductor manufacturing

2:30pm **AA-TuA-5 Thermal Atomic Layer Deposition of Sn-incorporated MoO_2 Electrode Films for High-performance TiO_2-based DRAM Capacitors***, **Jae Hyeon Lee**, Jeong Hwan Han,* Seoul National University of Science and Technology, Republic of Korea

As dynamic random access memory (DRAM) capacitors continue to downscale, the demand for new electrode materials to improve device performance has increased. Titanium nitride (TiN), a conventional electrode for DRAM capacitors, is approaching its limits due to its low work function and chemical instability at the interface. To overcome these limitations, molybdenum dioxide (MoO_2) has emerged as a promising alternative, as it offers a high work function (>5 eV) that helps suppress leakage current and exhibits excellent stability at the interface with high-k dielectric materials. Notably, its structural similarity to rutile TiO_2 enables the low-temperature crystallization of high-k rutile TiO_2. However, the formation of monoclinic MoO_2 presents challenges, as it is a metastable phase with a higher formation energy than the stable MoO_3 phase. Although numerous studies have explored the fabrication of monoclinic MoO_2 films using a range of deposition methods, including pulsed laser deposition, reactive sputtering, and chemical vapor deposition, these techniques are unsuitable for DRAM capacitor fabrication due to the requirement for conformal growth on a three-dimensional substrate with an exceptionally high aspect ratio.

In this study, a simple thermal atomic layer deposition (ALD) process was developed to grow monoclinic MoO$_2$ films. It was found that the metastable MoO$_2$ phase was stabilized by SnO$_x$ incorporation in MoO$_x$ due to the template effect between SnO$_2$ and MoO$_2$. The electrical conductivity, surface morphology, and thermal stability of ALD SnO$_x$-incorporated MoO$_x$ (TMO) films, as well as their interfacial properties with TiO$_2$ dielectrics, were evaluated to assess their potential as electrodes in TiO$_2$-based metal−insulator−metal (MIM) capacitors. ALD TiO$_2$ films grown on TMO exhibited remarkably suppressed leakage current and enhanced dielectric constants (>100), indicating that monoclinic ALD TMO facilitates the in situ crystallization of rutile TiO$_2$. These findings suggest that ALD TMO films are promising electrode materials for TiO$_2$-based MIM capacitors in advanced DRAM devices.

2:45pm **AA-TuA-6 Highly Ordered Crystalline ALD-InGaO Thin Films with High Mobility and Thermal Stability for Next-Generation 3D Memory Devices***, **Seong-Hwan Ryu**, Hye-Mi Kim, Dong-Gyu Kim, Jin-Seong Park,* Hanyang University, Korea

Recently, interest in atomic layer deposition(ALD)-derived oxide semiconductors (OSs) as a new channel of memory devices has increased dramatically to overcome scaled-down limitations. However, conventional amorphous OSs such as In-Ga-Zn-O are constrained by limitations such as degradation of field-effect mobility and low-phase stability during subsequent high-temperature processes, which are inevitable in memory devices. In this regard, thermally stable OSs with high mobility are required, and highly ordered crystalline OSs are emerging as leading examples. The representative material is In-Ga-O (IGO), doped with Ga to lower the oxygen vacancies in In2O3 with excellent crystallinity and low effective mass. However, in most cases, trimethylgallium is the only Ga source adopted for ALD, and the close distribution of dopants resulting from its small molecular size ultimately leads to a deterioration in crystallinity. This study presents a process to obtain highly ordered and thermally stable crystalline IGO thin films by ALD with bulkier gallium precursor. Through this, we suggest the optimal cation composition (In:Ga=4:1) with extremely high field-effect mobility (128.2 cm2/Vs) using IGO as the channel material in a thin film transistor and the impact of crystal structural changes on various film properties. An in-depth study of the IGO crystal structure suggests that the alignment degree of the cubic (222) planes is directly related to electrical performance and thermal stability. Also, process-wise, its excellent step coverage (side: 96%, bottom: 100%), compositional uniformity in a 40:1 aspect ratio structure, and superior crystal growth in vertical structures make it a promising candidate for application as a channel in next-generation 3D memory devices

3:00pm **AA-TuA-7 Amino Acid-Based BiomimeticOrganic-Inorganic Hybrid Memristors by Molecular Layer Deposition for Neuromorphic Applications***, Lin Zhu, **Ai-Dong Li**, Song Sun,* Nanjing University, China*; Yan-Qiang Cao,* Nanjing University of Science and Technology, China

With the rapid development of artificial intelligence, the need to mimic biological functions has become increasingly important so as to perform complex tasks under complicated external environments. Memristors have emerged as an extremely competitive candidate for neuromorphic artificial electronic devices owing to their biological-like capabilities. It is urgent to develop new memristive materials and architecture to meet diverse demands in artificial intelligence and neuron network systems.

In this study, drew inspiration from neurotransmitters in the human brain, we selected essential amino acids cysteine (Cys) as organic precursor to construct biomimetic titanium-based cysteine hybrid films via molecular layer deposition (MLD). The stability of the hybrid films was extensively examined, demonstrating excellent durability in both water and air. A vertically integrated single-layer Pt/Ti-Cys/TiN device exhibits reproducible volatile switching behavior, with gradual changes observed during the set/reset process. Notably, the device successfully emulates bio-pain sensation and synapse functions, indicating that these biomimetic hybrid films hold great potential for the development of artificial sensory systems.

The organic-inorganic hybrid materials possess abundant physical/chemical properties and unique merits from combination of both components, enabling great potential in flexible devices due to tunability and versatility in tailoring material structures and properties. To further optimize and regulate its performance, the bilayer-structured ultrathin memristor Pt/Al-Cys/Ti-Cys/TiN was prepared. The introduction of Al-Cys improves the device's resistive switching and retention characteristics, showing repeatable nonvolatile bipolar switching with an on/off ratio greater than 10^2. Some crucial bio-synaptic functions, such as long-term potentiation, long-term depression, paired-pulse facilitation, spike rate-dependent plasticity and pattern recognition were also realized in this device. Our results indicate the great potentials of MLD derived amino acid-based biomimetic hybrid memristor for flexible robust neuroscience applications.

ALD Fundamentals
Room Halla Hall AB - Session AF1-TuA
Analysis

Moderators: Christophe Detavernier, Ghent University, Belgium, **Adrie Mackus**, Eindhoven University, Netherlands

1:30pm **AF1-TuA-1 Interface Evolution in ALD of HfO$_2$ on TiN: LEIS and XPS in Vacuo Studies***, **Mykhailo Chundak**, Heta-Elisa Nieminen, Marko Vehkamäki, Laura Keränen, Matti Putkonen, Mikko Ritala,* University of Helsinki, Finland

Hafnium dioxide (HfO$_2$) is a high-k dielectric material that was initially introduced as a replacement for SiO$_2$ to overcome the scaling limitations of silicon-based field-effect transistors. HfO$_2$ has therefore been qualified as a material compatible with complementary metal oxide semiconductor (CMOS) technology. It has recently regained attention following the discovery of ferroelectricity in doped hafnium oxide fluorite-structure oxides. This discovery has enabled the development of ferroelectric field-effect transistors (FEFETs) and ferroelectric memories, which offer the potential for further downscaling of CMOS-compatible ferroelectric based devices. However, as the thickness of ferroelectric layers is decreased from the current 5–10 nm to approximately 3 nm or even less, their properties become increasingly influenced by the surrounding environment, making precise interface engineering crucial for device reliability. The choice of the capacitor electrode plays a key role in stabilizing the ferroelectric phase, mitigating interfacial effects, and ensuring long-term performance. Titanium nitride (TiN) is widely employed due to its moderate work function, chemical stability, and compatibility with CMOS technology, yet its interaction with ultrathin HfO$_2$ films, along with potential contamination and deposition conditions, can significantly impact device behavior. A detailed understanding of these effects is therefore essential to optimize material integration and enhance the performance of next-generation semiconductor devices.

To investigate the growth of these films using surface science techniques, we utilized the cluster tool setup in the HelsinkiALD laboratory[1] (Fig. 1a)). This system enables *in vacuo* growth studies, providing direct insights into surface reactions during deposition. We employed a commercial flow-type ALD reactor combined with low-energy ion scattering (LEIS) (Fig. 1b)) and X-ray photoelectron spectroscopy (XPS) (Fig. 1c)) to observe the cycle-by-cycle growth of HfO$_2$ thin films. The films were deposited with CpHf(NMe$_2$)$_4$ (HyALD$^{\text{TM}}$) precursor in combination with ozone (O$_3$) on TiN substrate. This approach provided critical information of the interface formation and film growth mechanisms. We determined that ~30 ALD cycles are required to achieve full coverage of HfO$_2$ on TiN without pinhole defects. This research is offering a valuable information for optimizing thin-film deposition for next-generation semiconductor technologies.

1. Nieminen, H.-E., et al., *In vacuo cluster tool for studying reaction mechanisms in atomic layer deposition and atomic layer etching processes.* Journal of Vacuum Science & Technology A, 2023. **41**(2).

1:45pm **AF1-TuA-2 In Situ Ambient Pressure X-ray Photoelectron Spectroscopy Study of Atomic Layer Deposition of Hafnium Oxide on (Ag,Cu)(In,Ga)Se$_2$ Absorbers Relevant for Thin Film Solar Cells***, **Natalia M. Martin**,* Uppsala University, Angstrom Laboratory, Sweden

Thin film solar cells based on (Ag,Cu)(In,Ga)Se$_2$ (ACIGS) absorbers have reached efficiencies of up to 23.6%, which together with demonstrated long term stability has set the basis for commercial application. To reach closer to the theoretical maximum efficiency (~30%), further reductions of optical and electrical losses are needed. One of the most critical parts in ACIGS-based solar cells is the interface formation between the p-type absorber and n-type (buffer) layer forming the pn-junction. Energy band alignment at this interface is a key parameter, but also absorber surface band gap widening, interlayer formation and distribution of alkali trace elements. In addition, the deposition of ultrathin barriers of HfO$_x$ has previously been investigated in Cu(In,Ga)Se$_2$ (CIGS) thin film solar cells and shown to be an effective passivation layer by reducing interface recombination with an appropriate contacting approach. However, the ALD HfO$_x$ growth on ACIGS has not truly been explored and the surface chemistry and reactions occurring on the ACIGS absorber surface during

HfO_x deposition are unknown. An important step towards achieving superior device performance is to understand the chemical reactions occuring during the first deposition cycles of HfO_x, which could result in better interface quality, and to ultimately design better solar cells.

We employed ambient pressure X-ray photoelectron spectroscopy (AP-XPS) to study how the surface properties of ACIGS and how the reaction between ALD precursors and the ACIGS surface proceed during the deposition of HfO_x. ACIGS thin films of similar bulk composition, with and without a surface treatment were compared. Using *in situ* AP-XPS, we followed in real time the reactions occurring during the initial ALD of HfOx on ACIGS. The results show that the ACIGS surface plays an important role in the initial ALD surface chemistry, with surface hydroxyls, fluorine and alkali elements that may exert significant influence on the surface chemistry during the initial TDMA-Hf half-cycle. Whereas the HfOx growth occurs directly upon a short TDMA-Hf pulse on a non-treated ACIGS surface, an increase in the induction/coalescence time period at the beginning of ALD is observed for a RbF-treated ACIGS, likely due to the presence and diffusion of Rb and F to ACIGS surface, limiting the surface diffusion of O-containing species, i.e. the available sites for TDMA-Hf molecule to adsorb and react on, or even the lower oxide amount present on the surface before the ALD growth. Understanding the ALD reaction mechanism, especially during the initial growth of HfOx on ACIGS is crucial to improving interface properties in ACIGS-based devices.

2:00pm **AF1-TuA-3 Development of a Home-Built Atomic Layer Deposition Reactor for *in-Situ* Synchrotron GISAXS and XAS Characterization***, **Marina Armengol-Profitós**, Jordi Prat, Montserrat Prieto, Zbigniew Reszela, Cristián Huck-Iriart, Massimo Tallarida, Eduardo Solano, Carlos Escudero,* ALBA synchrotron light source, Spain

The high photon flux and energy tunability of synchrotron facilities provide a clear advantage for the characterization of Atomic Layer Deposition (ALD) processes. At the ALBA synchrotron, a mobile custom-built reactor has been developed to enable in-situ monitoring of film growth and characterization using up to now two X-ray-based techniques: Grazing-Incidence Small-Angle X-ray Scattering (GISAXS) and X-ray Absorption Spectroscopy (XAS). The ALD reactor has been designed to be compatible with both techniques, and it can currently operate at two different ALBA beamlines (NCD-SWEET for GISAXS measurements and NOTOS for XAS) to provide complementary insights into film morphology and chemical composition.

The setup consists of a high-vacuum, pump-type reactor compatible with multiple deposition processes. It achieves a base pressure of at least 10^{-6} mbar and is equipped with a sample heater capable of reaching 1000°C, allowing in-situ annealing under different atmospheres without exposing the sample. To accommodate the specific geometries required for each X-ray technique, the mobile reactor features two different configurations: for GISAXS, two CF40 flanges with mica windows allow the passage of incident and reflected X-rays, while for XAS, two perpendicularly oriented flanges with 50 µm-thick Kapton windows enable measurements covering all the beamline energy range (4.7 - 30 keV), with the fluorescence detector used (SDD with 13 channels) at 90° relative to the X-ray beam and the sample at around 30° with respect to the incident beam. Fig. 1 A shows the reactor in the GISAXS configuration at the NCD-SWEET beamline.

To validate the reactor's performance, TiO_2 thin films were deposited using titanium isopropoxide (TTIP) as a precursor in combination with water on SiO_2/Si substrates. The process exhibited a growth rate of 0.15 Å/cycle, allowing the study by GISAXS and XAS in the sub-nanometer range during the initial growth cycles. Fig. 1 B presents XANES measurements at the Ti K-edge over 1000 ALD cycles at 200°C, revealing an increase in the XANES-edge jump intensity within the first five cycles. Since the edge jump magnitude is proportional to the TiO_2 thickness, these results indicate different growth regimes: a first stage significantly slower for 325 cycles, followed by a stage where the growth rate becomes linear. After 325 cycles, XAS measurements confirmed the formation of TiO_2 with features consistent with anatase-like coordination. The XANES features during the first 325 cycles are consistent with previously studied electronic effects in ultra-thin TiO_2 films[1]. Additionally, XAS mapping over a 20 mm x 20 mm area validated the film's uniformity.

2:15pm **AF1-TuA-4 Evaluation of Initial Nucleation of Co-ALD by CCTBA Using in-Situ Reflectance Monitoring and Atomistic Simulator Based on Neural Network Potential***, **Naoki Tamaoki**,* The University of Tokyo, Japan*; Yubin Deng,* The University of Tokyo, China*; Jun Yamaguchi, Noboru Sato, Atsuhiro Tsukune, Yukihiro Shimogaki,* The University of Tokyo, Japan

Area-selective atomic layer deposition (AS-ALD) technology, which enables atomic-level control of the film thickness and inherently prevents misalignment in self-aligned patterning, is gaining attention in ULSI device manufacturing. AS-ALD utilizes the difference in the adsorption energies of the precursor molecules to deposit a film only on the growth surface. It is crucial to explore the surface pretreatment and process conditions that maximize the incubation time to improve selectivity. In-situ differential reflectance spectroscopy (DRS) is a simple and effective method that assists in this exploration by monitoring the nucleation density and film growth evolution during the initial deposition stages. To better understand the mechanism of AS-ALD, in-situ DRS and an atomistic-level simulator (Matlantis™) based on neural network potentials were used to study Cobalt ALD.

In this study, the initial growth process of Co thin films on SiO_2 insulating films using CCTBA (Cobalt Carbonyl Tertiary-Butyl Acetylene) precursors via ALD was evaluated. Co AS-ALD is expected to be a promising method for forming cap layers that suppress Cu diffusion and electromigration (EM) in ULSI-Cu interconnects. After APM cleaning, Co-ALD was performed for 500 cycles at different substrate temperatures (140, 150, and 160°C), and the reflectance changes at a wavelength of 740 nm were measured (Figure 1). The reflectivity gradually decreased as the island-like growth of Co began, reaching a minimum value before increasing again. By analyzing the timing of the minimum reflectivity, it is possible to determine when the initial nuclei form and evolve into a continuous film [1]. Figure 2 shows the growth per cycle (GPC) measured after film formation as an Arrhenius plot. Figure 3 shows the Arrhenius plot of the initial nucleation density calculated from the minimum reflectance point and GPC data. While GPC exhibited a mild temperature dependence with an activation energy of 14.6 kJ/mol, the initial nucleation density showed a relatively high activation energy of 100.5 kJ/mol. Although lowering the film-formation temperature may increase the concentration of carbon impurities in the film, it is expected to suppress the initial nucleation density and improve the selectivity. We will also report the results of the reaction analysis using an atomistic-level simulator (Matlantis™).

[1] N. Tamaoki et al., DPS 2024

2:30pm **AF1-TuA-5 Low Energy Ion Scattering Analysis of GC/IrOX /SiO_2 Layer Structure***, **Philipp Brüner**, Thomas Grehl,* IONTOF GmbH, Germany*; Rens Kamphorst, Katherine S. Encalada Flores, Ruud Kortlever, Ruud van Ommen,* TU Delft, Netherlands

While ALD with its self-limiting properties and sub-nm precision provides an ideal method for growing ultra-thin coatings, 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 SiO_2 films grown by ALD on an electrodeposited IrO_x catalyst layer on glassy carbon (GC). In LEIS, the energy spectrum of noble gas ions (He, Ne, Ar) scattered from the sample surface is recorded. The elemental peaks in the resulting spectra represent the elemental composition of the first atomic layer, which can be analyzed quantitatively [1]. 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, depending on the sample composition.

We show how combining the top atomic layer sensitivity with layer thickness information allows us to quantify the surface coverage of the deposited SiO_2 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 [2], 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.

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2:45pm **AF1-TuA-6 Tailoring Interface and Bulk Properties: An Oxidant Co-Dosing Approach to ALD Growth of Hafnia Thin Films***, **Dushyant Narayan**, Dan Le, Soham Shirodkar, Soubhik De, Geon Park, Minjong Lee, Thi Thu Huong Chu, Jin-Hyun Kim,* The University of Texas at Dallas*; Walter Hernandez, Adrian Alvarez, Josh Garretson, Jeffrey Spiegelman,* RASIRC*; Jiyoung Kim,* The University of Texas at Dallas

As semiconductor devices continue to scale down and integrate into complex 3D architectures, precise control over interfacial properties becomes increasingly critical to device performance and reliability. Hafnia-based thin films have been widely adopted in industry, as they exhibit superior equivalent oxide thickness (EOT), high dielectric constant and superior leakage current properties as compared to traditional dielectrics like SiO_2. These attributes make HfO_2-based materials essential for applications such as high-k gate dielectrics, DRAM capacitors, and ferroelectric memory devices.

In our prior studies investigating the impacts of various oxidant sources on HfO_2-based films, we found that the conventional ozone (O_3)-based ALD process led to extensive oxidation of the titanium nitride (TiN) bottom electrode (BE) during metal-insulator-metal (MIM) capacitor fabrication. In contrast, the use of hydrogen peroxide (H_2O_2) in HfO_2-based ALD was not only shown to produce films with superior growth characteristics and material properties, but also effectively suppressed unwanted interface formation.[1] Building upon these findings, we have developed a unique ALD approach, where oxidants (H_2O_2, O_3, and H_2O) are strategically co-dosed/sequentially-dosed to achieve a greater control of film properties.Through this process, customizable ALD growth conditions can provide tailored properties at the interface and in the bulk. Furthermore, results of an *in-situ* Reflection Absorption Infra-Red Spectroscopy (RAIRS) experiment will be presented, investigating the underlying mechanisms at the surface and in the bulk when mixing oxidants during the deposition of hafnia. For instance, While H_2O_2 on its own produces film with superior properties, it is not known if mixing O_3 and H_2O_2 would further enhance material properties. Additional combinations including H_2O, O_3 and H_2O_2 will also be shown. Beyond IR analysis, we will also present the effect of this approach on electrical properties of hafnia thin films, with particular attention paid to dielectric constant, leakage current, and time dependent dielectric breakdown (TDDB). This study thus represents an additional process variable that can be utilized to further optimize the use of HfO_2-based materials in next-generation device applications. Detailed experimental procedure and results will be discussed.

This work is supported by RASIRC. The BRUTE® Peroxide and RASIRC Peroxidizer® are provided by RASIRC Inc. The O_3 used in this work was provided by a TMEIC Ozone Generator (OP-250H).

[1] J. Kim et. al., Applied Surface Science**, 686**, 162197 (2025)

3:00pm **AF1-TuA-7 Mechanical Properties and Wear Resistance of Atomic Layer Deposited Ternary Cr-Hf-O Films: A Comparative Study with Binary Chromium Oxide and Hafnium Oxide Films***, **Mahtab Salari Mehr**, Lauri Aarik, Taivo Jõgiaas, Hugo Mändar,* University of Tartu, Estonia

The complex materials including doped and ternary compounds have received considerable attention in the last decades due to the exhibition of superior mechanical, optical, and electrical properties compared to their binary counterparts. [1,2]. Chromium oxide is technologically an important engineering material due to its corrosion, wear resistance, and high mechanical hardness [3,4].This study presents the characterization results of ternary chromium-hafnium oxide films ((Cr1-xHfx)2O3) in thickness range from 40 to 80 nm that were deposited at 275 °C on Si substrate by atomic layer deposition (ALD) using the cycle formula of [*m* ($Cr(thd)_3$-O_3) + ($HfCl_4$-O_3), *m*=0 to 500]. The X-ray fluorescence showed the change in atomic ratio of Hf/(Hf+Cr) (*x*) in the films from 0.05 to 1 by changing *m* in the ALD cycle. Grazing incidence X-ray diffraction analysis of pure hafnium oxide film showed reflections of the monoclinic phase, whereas for pure chromium oxide film the observed reflections confirmed the presence of the eskolaite phase. For the $(Cr_{1-x}Hf_x)_2O_3$ films when $0.05 \leq x \leq 0.40$, the eskolaite phase was present, however, the films containing $x \geq 0.68$ showed semi-amorphous structure. The density of the films (from X-ray reflectivity analysis) showed a linear increase from 5.57 g/cm³ to 10 g/cm³ when the amount of *x* changed from 0.05 to 1. The hardness, elastic modulus, and wear resistance of the films were measured using nanoindentation on Hysitron Triboindenter by Berkovich-type diamond tip. The results at indent displacement of 8 nm showed an increase in hardness mean values of ternary films compared with binary chromium oxide (14±1.5 GPa) and hafnium oxide (12±1.2 GPa). The highest hardness of 19±0.9 GPa was achieved when *x*=0.40. The study of wear resistance of the films under different loads in the range of 90 to 180 µN, using different wear cycles of 2 to 10 cycles showed an improvement of about ~70% of wear resistance of the ternary compound films compared to binary oxides (Fig. 2). Our findings showed that the deposition of multicomponent films paves the way for tailored thin film materials with enhanced mechanical properties and wear durability for various industrial applications.

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3:15pm **AF1-TuA-8 In-situ X-ray photoelectron spectroscopy for determining oxidation state, composition, and morphology of ALD-based CeO_x, SnO_x, and $Ce_xSn_{1-x}O_y$ deposits***, **Rudi Tschammer**, Dominic Guttmann,* BTU Cottbus, Germany*; Marcel Schmickler, Anjana Devi,* Leibniz Institute for Solid State and Materials Research, Germany*; Karsten Henkel, Carlos Morales, Jan Ingo Flege,* BTU Cottbus, Germany

The controllability of the physical and chemical properties of ultrathin (< 20 nm) films grown by atomic layer deposition (ALD) requires a thorough understanding of the surface cross-interactions established between substrates, grown thin films of variable thickness, and the exposed reactants. In most ALD works focused on applications, samples are grown in dedicated ALD reactors on wafer-scale substrates and characterized through various *ex-situ* techniques to obtain information on film thickness, sample composition, and cation valency. However, *ex-situ* characterization bears the risk of unintentional changes due to layer contact with the atmosphere, ranging from surface contamination to changes in the surface cation oxidation state. The latter issue is especially pronounced for reducible oxides intended to switch between different oxidation states depending on factors such as gas environment or film-substrate interaction (e.g., CeO_x, widely used in catalysis and sensing). Thus, a surface science methodology supported by *in-situ* characterization becomes highly desirable to minimize changes imparted during sample transfer in the atmosphere and unravel the true structure and chemical state of the pristine active layer.

In this contribution, we examine the material composition, cation valency, and film morphology through *in-situ* X-ray photoelectron spectroscopy (XPS) and inelastic peak shape analysis (IPSA) combined with operando spectroscopic ellipsometry. By investigating the ALD deposition of CeO_x using $Ce(dpdmg)_3$ and different oxidants (H_2O, O_2, O_3), we observe a distinct dependence of the cerium valency on the film thickness and the used oxidant, in all cases accompanied by changes in film morphologies and precursor residues. Similarly, a detailed XPS analysis of the early stages of SnO_2 deposition via TDMASn/O_3 reveals hitherto unreported changes that could be correlated with residual nitrogen impurities, significantly influencing the electrical resistivity of these films. Following a bottom-up approach, the results from both investigations are combined to tailor the growth of ultrathin SnO_x/CeO_x heterostructures and mixed $Ce_xSn_{1-x}O_2$ oxides for gas sensing applications.

ALD Fundamentals
Room Halla Hall AB - Session AF2-TuA
Plasma ALD

Moderators: Ruud van Ommen, Delft University of Technology, **Seung-Yeul Yang**, Samsung

4:00pm **AF2-TuA-11 Controlling the Crystalline Nature of PEALD Thin Films Through Tuning of Plasma Characteristics***, **Peter Litwin,*** Naval Research Laboratory, USA*; Marc Currie, Neeraj Nepal, Maria Sales, David Boris,* US Naval Research Laboratory*; Michael Johnson,* Naval Research Laboratory, USA*; Scott Walton, Virginia Wheeler,* US Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) utilizes a plasma-based reactant step increasing the complexity of the deposition process compared to thermal ALD. The plasma-based reactant step introduces a flux of energetic particles (ions, fast neutrals, electrons, photons, etc.) directed towards the surface of the growing thin film, which helps reduce the energetic barriers to high growth rates or crystallinity at low temperatures. Understanding the role that these energetic species play in the deposition process potentially enables better tunability of the growth conditions for a given application. For example, during the plasma step, careful control of the power, pressure, gas flow mixture, and substrate bias all enable control over the magnitude of the ion energy flux density delivered to the sample surface. The consequence of this is a greater level of control over the properties of the deposited material. This has been experimentally observed in previous studies, namely in the control of the crystalline phase of various compounds. For example, through alteration of the gas chemistry, flow rate, and pressure used during the reactant half-step it has been shown that the rutile and anatase phases of TiO_2 and the α- and β-phases of Ga_2O_3 could be selectively deposited [1, 2].

In this work, we investigate methods to vary the properties of the plasma in our PEALD system. We use a suite of characterization techniques, including optical emission spectroscopy (OES) and Langmuir probe measurements, to examine how various plasma conditions (power, pressure, and gas flow ratio) impact the ion flux, plasma potential, and atomic O concentrations produced in our Kurt J. Lesker 150 LX PEALD system. As a testbed, we deposit vanadium oxide and report on how the changing properties of the plasma impact the properties of the deposited thin films. We find that through alteration of the pressure in the system during the plasma process, the films can be selectively deposited in an amorphous or crystalline manner. We correlate this change in crystallinity with the change in the energy flux density delivered to the material surface during deposition. From this, we estimate the critical energy flux density necessary for crystallization of vanadium oxide films deposited in our PEALD system. Lastly, we discuss these results more broadly and consider the applicability of these findings to other material systems.

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4:15pm **AF2-TuA-12 Comparative Study of CeO_2 Thin Films Prepared by Plasma-Enhanced and Thermal Atomic Layer Deposition Using a New Liquid Ce Precursor***, **Yewon Seo**, Sang Bok Kim, Soo-Hyun Kim,* Graduate School of Semiconductor Materials and Devices Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan, Republic of Korea

Cerium oxide (CeO_2) has been widely studied for applications such as optical waveguides, solid oxide fuel cells (SOFCs), and gas sensors. In particular, it is considered a promising gate dielectric material for complementary metal-oxide-semiconductor (CMOS) devices due to its high dielectric constant (23–52), high refractive index (2.2–2.8), excellent dielectric strength (25 MV/cm), moderate bandgap (3.0–3.6 eV), and thermodynamic stability in contact with silicon [1]. So far, research on ALD CeO_2 films, especially plasma-enhanced ALD (PEALD) of CeO_2, has been very limited, mainly due to the lack of suitable precursor-reactant combinations; thus, more detailed investigations are required. In this study, CeO_2 thin films were deposited by ALD using a new liquid Ce precursor with O_2 molecule or O_2 plasma as reactants. The deposition process was conducted at temperatures ranging from 150 to 350 °C, and both thermal ALD (Th-ALD) and PEALD exhibited self-limiting surface reactions at 250 °C.In addition, increases in peak intensities for PEALD CeO_2 film as compared to that of Th-ALD one were confirmed through XRD analysis (figure 1), indicating the improvement of the film crystallinity by using plasma as a reactant. Film properties varied with deposition conditions such as growth temperature, plasma power, reactant pulsing time, etc..and were characterized by SEM (thickness), TEM (step coverage, microstructure), XRR (density, thickness, roughness), XRD (crystallinity), and XPS (composition and impurity) etc. Electrical properties were evaluated via Metal–Oxide–Semiconductor capacitors, focusing on dielectric constant and leakage current. The detailed results will be presented at the conference.

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4:30pm **AF2-TuA-13 Tuning Crystallinity of Plasma-Enhanced Atomic Layer Deposited Aluminum Nitride Thin Films using an Electron Cyclotron Resonance Microwave Source***, **Julian Pilz**, Tai Nguyen,* Silicon Austria Labs, Austria*; Paul Dreher,* Evatec AG, Switzerland*; Marco Deluca,* Silicon Austria Labs, Austria

Aluminum nitride (AlN) thin films are widely utilized in microelectronic devices as high thermal conductance heat spreaders, piezoelectric actuators and sensors or high-k dielectrics.[1,2] In most applications, (0002)-textured wurtzite films are required to achieve the desired device performance.[3] While deposition techniques such as metalorganic chemical vapor deposition[4] and reactive magnetron sputtering[5] have demonstrated to produce highly textured/epitaxial films with low mosaic spread, these deposition techniques faces severe issues such as CMOS-incompatibility due to high temperature growth and poor conformality. Atomic layer deposition (ALD) is renowned for precise control of atomic arrangement and excellent conformality. However, achieving AlN with comparable crystal quality by ALD on Si substrates remains challenging and is under investigation [6,7,8], with factors such as oxygen and carbon contaminations shown to decrease the crystal quality.[9,10]

In this work, AlN thin films are deposited on 200mm Si(111) wafers by plasma-enhanced atomic layer deposition (PE-ALD) utilizing trimethylaluminum (TMA) and NH_3-plasma as reactants. A novel ALD module is used for the deposition of the films (Evatec PEALD), which utilizes an electron cyclotron resonance microwave source and is *in-vacuo* connected in a cluster tool to etch and sputtering modules, with the potential to overgrow and surface pretreat wafers without vacuum break, respectively. The focus of this work is to investigate how NH_3 plasma parameters (pressure, power, duration) produced by the microwave source influence the plasma/chemical species during deposition and resulting thin film properties in terms of thickness uniformity, crystallinity, roughness, and chemical composition. For example, while films grown with 2 s NH_3-plasma duration showed similar growth per cycle values as films grown with 5 s plasma duration, they appear amorphous and structurally unstable in atmosphere. Increase of plasma duration up to 20 s significantly improves the crystalline quality of films showing a preferential 0002 orientation even at a substrate temperature of 200 °C. This points to the importance of considering the kinetic effects of plasma-film interactions and their relevance for crystallite formation as well as influence on the composition of the films.

In a nutshell, this work presents effective mechanisms for producing PE-ALD AlN thin films with preferential c-axis orientation on 200 mm wafers, highlighting the importance of plasma source and parameter choice, as well as showing application potentials for growing layer stacks of ALD and sputtered layers without vacuum break in-between deposition.

4:45pm **AF2-TuA-14 Plasma-Enhanced Atomic Layer Deposition of High-Quality InN Thin Films Using a Novel In Precursor and NH_3 Plasma***, **Yejun Kim**, Chaehyun Park, Minjeong Kweon, Soo-Hyun Kim,* Ulsan National Institute of Science & Technology, Republic of Korea

Indium nitride (InN), a III-V nitride semiconductor, has a narrow bandgap (0.7 eV), high electron saturation velocity (4.2×10^7 cm/s), low electron effective mass ($0.07\ m_0$), and high electron mobility (4400 $cm^2/V\cdot s$). These properties make InN ideal for sensors, optoelectronics, and high-electron-mobility transistors (HEMTs). However, MOVPE and MBE face challenges due to InN’s low thermal stability (~ 500 °C decomposition into In and N_2), making them unsuitable for high-aspect-ratio microelectronics. Plasma-enhanced ALD (PE-ALD) enables precise thickness control and low-temperature processing, offering an alternative, though ALD-grown InN research is still in early stages. This study explores InN ALD using a novel ethanimidamidinate-based indium precursor and NH_3 plasma in a showerhead-type PE-ALD reactor (IOV dX1 PEALD, ISAC Research, Korea). The optimal deposition temperature was 275 °C, confirming self-limiting growth with a saturated rate of ~ 0.57 Å/cycle. A linear relationship between thickness and ALD cycles was observed. Film properties were analyzed using a 4-point probe (resistivity), SEM/TEM (thickness, step coverage), XRR (density, roughness), XRD (crystallinity), RBS (In/N ratio, impurities), UV-Vis (optical bandgap), and Hall measurement (carrier density, mobility). Detailed results will be presented at the conference.

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5:00pm **AF2-TuA-15 Insights Into Tuning TiO_2 Film Property Distribution in 3D Structures During Peald Process***, **Takashi Hamano**, Nobuyuki Kuboi, Hiroyasu Matsugai, Shoji Kobayashi, Yoshiya Hagimoto, Hayato Iwamoto,* Sony Semiconductor Solutions Corporation, Japan

Plasma-based deposition techniques are widely employed to fabricate cutting-edge electronic devices with vertical and complicated 3D structures. In addition, owing to the increasing demand for various advanced devices with organic films, low temperature deposition processes are required. During deposition processes, precise control of feature profile, i.e., coverage, and film properties is significant. In general, it is difficult to directly measure the film properties in a local area of 3D structures. Therefore, simulation techniques are effective tools to understand the deposition mechanisms in complicated 3D structures. Recently, we have developed a new simulation model based on the statistical ensemble method to predict both coverage and film properties and analyzed the PECVD and PEALD processes [1][2]. In this paper, we improved the simulation model and investigated the TiO_2 film properties in 3D structures during PEALD process.

In the simulation model, gas transportation and surface reactions, such as adhesion/desorption, migration, and binding are expressed by the movement of voxels using a stochastic algorithm. The voxel status indicating the bonding states and crystallinity is determined depending on the total energy flux of ions at each surface voxel solving the ion transportation in 3D structures. The variation in film thickness by ion bombardment is also modeled. The difference in the bonding states and crystallinity of TiO_2 between the planar region and sidewall of the hole structure was predicted. Especially, at lower process temperature, the film property distribution inside the hole structures becomes remarkable reflecting the distribution of incident ions.

To confirm the simulation results, we evaluated TiO_2 film properties inside the hole structures with an aspect ratio of 5 focusing on the wet etching rate (WER) of TiO_2. WER at the sidewall and bottom regions is several times higher than that at the planar region. In addition, the distribution of WER inside the hole structure notably changes depending on the process temperature.

Present results indicate that the process optimization considering both process temperature and ion irradiation (i.e., flux, energy and angular distribution of ions) is key to obtain the desirable film property distribution in 3D structures.

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[2] T. Hamano et al., Proc. Symp. Dry Process, 2024, p. 19.

5:15pm **AF2-TuA-16 The Application of Diiodosilane to Deposit SiN Film as Insulation Layer***, **YUN-CHIH Chiang**, Yong-Jay Lee,* Industrial Technology Research Institute, Taiwan

As chip miniaturization advances, the demand for thinner and more uniform films has increased. SiO_2 oxide films tend to emerge leakage current issues under this trend, whereas SiN films offer lower leakage current characteristics, gradually replacing SiO_2 as the insulating layer in MOSFETs. Traditional silicon-based precursors, such as silane or HCDS, perform well in mature process nodes like 20 nm. However, at smaller process nodes, these precursors lead to poor film quality. Switching to a precursor with higher reactivity, such as Diiodosilane (DIS), can improve film characteristics. Due to the lower bond energy of the Si–I bond, DIS enables film deposition at lower process temperatures, resulting in higher-quality SiN films while minimizing unreacted halogen residues. Additionally, DIS contains no carbon and can prevent carbon contamination in the deposited film, while releases less CO_2 during ALD process. These advantages make DIS a promising candidate for the usage of next-generation semiconductor processes below 3 nm.

In this study, DIS was used as an ALD precursor to deposit SiN films via plasma-enhanced atomic layer deposition (PEALD). In addition to demonstrate the advantages of DIS, we verified the SiN film which deposit by ALD process through ellipsometry, TEM, XPS, and electrical measurements. Furthermore, optimized process conditions were explored to achieve high-quality films, making this approach highly promising for advanced semiconductor devices in sub-3 nm processes.

Atomic Layer Etching
Room Samda Hall AB - Session ALE1-TuA

ALE Tools & ALE Modeling

Moderators: Satoshi Hamaguchi, Osaka University, Japan, **Dmitry Suyatin**, AlixLabs A.B.

1:30pm **ALE1-TuA-1 Isotropic and Anisotropic ALE: Tool Aspects, Processes, and Applications***, **Harm Knoops**,* Oxford Instruments Plasma Technology, UK **INVITED**

Applications' demands on control of etch depth, surface state, damage, and etching in 3D structures have caused atomic layer etching (ALE) to receive strong interest in recent years. One can distinguish ALE processes into two categories, isotropic and anisotropic processes. In this contribution, tool aspects, exemplary processes, and key applications for both isotropic and anisotropic ALE will be highlighted and, when appropriate, foundations and links between ALD and ALE will be addressed. Historically, tool designs for anisotropic ALE are built on those for reactive ion etching focusing on ion-energy control. Isotropic ALE processes are generally developed on ALD or ALD-like systems focusing on careful delivery and purging of precursor vapor at raised temperatures. To bring ALE to the next level, a closer look needs to be had at both the tool and process requirements. Among the general aspects important in the different steps in the ALE process are: control of plasma radical and ion fluxes and energies, delivery and removal of reactants and products from the chamber, process pressure and temperature (from ~350 ˚C down to cryogenic). For processes the discussion will range from BCl_3/Cl_2-Ar anisotropic chemistries to SF_6-$AlMe_3$ isotropic chemistries. Regarding applications, besides the well-known CMOS logic and 3D memory ones, power electronics, photonics, and quantum will be discussed. The aim being to highlight that control of interfaces and surfaces at the atomic scale is important even if the feature scale of the device is above ~100 nm. It is important to consider the different application spaces for ALE as this will also shape the requirements on tools and processes.

2:00pm **ALE1-TuA-3 Study on Plasma Induced Damaged Layer Formation Using Molecular Dynamics***, **Junghwan Um**, Sung-Il Cho,* Samsung Electronics Co., Republic of Korea

Plasma etching is a key technology in semiconductor fabrication, enabling precise patterning at the nanoscale. However, plasma-surface interactions often lead to the formation of a damage layer, which can negatively impact material properties and device performance. Understanding the mechanisms of damage layer formation at the atomic scale is crucial for optimizing plasma etching conditions and minimizing unwanted effects.

In this study, we employ molecular dynamics (MD) simulations to investigate the fundamental processes involved in plasma-induced damage layer formation. The simulations focus on the effects of ion energy, ion species and surface chemistry on the evolution of the damage layer. By simulating energetic ion bombardment and its interactions with the substrate, we analyze structural modifications. Our results show that higher ion energy leads to deeper penetration of ions into the substrate, increasing the damage layer thickness. Low-energy ions, on the other hand, primarily cause surface modifications without significant subsurface damage. The choice of ion species also plays a critical role, with heavier ions inducing more structural disorder compared to lighter ions due to their higher momentum transfer. Furthermore, we examine the role of reactive species in plasma etching, such as fluorine (F) or chlorine (Cl), which contribute to both material removal and chemical modification of the substrate. The competition between physical sputtering and chemical etching is analyzed to determine the optimal conditions for achieving a damage-free etching process. By comparing MD simulation results with experimental findings, we establish a comprehensive understanding of plasma-induced damage mechanisms. Our study provides valuable insights into designing advanced plasma etching processes with minimized damage, which is essential for next-generation semiconductor devices. These findings can guide the development of new plasma processing strategies, including low-damage etching techniques and optimized plasma parameters for emerging nanofabrication applications.

2:15pm **ALE1-TuA-4 Theoretical Analysis on Crystalline Phase-Dependent Surface Fluorination of HfO_2 for Atomic Layer Etching***, **Sujin Kwon**, Bonggeun Shong,* Hongik University, Republic of Korea

Hafnium oxide (HfO_2) thin films have garnered significant attention in microelectronics industry due to its high dielectric constant, and more recently, the ferroelectric (FE) properties of hafnium zirconium oxide (HZO). For applications of HfO_2 thin films, precise control of the thickness is necessary, and thus atomic layer deposition (ALD) and atomic layer etching (ALE) processes of HfO_2 can be crucial. Several ALE chemistry of HfO_2 are known, and most of them include fluorination of the surface using HF. While ALE is often believed to reduce roughness, some previous experimental reports indicate that the surface roughness of HZO thin films can increase after ALE [1]; additionally, the etch rates in ALE of HfO_2 and ZrO_2 are dependent on their crystallinity [2], which can be related to the propensity toward surface fluorination [3]. In this study, we investigate the variation of surface fluorination of HfO_2 according to its crystalline phases. The HF-based surface fluorination of four representative phases of HfO_2 – monoclinic, tetragonal, orthorhombic, and cubic – is explored. Using machine-learning interatomic potential (MLIP) calculations, Natarajan-Elliott (N-E) analyses on spontaneous etch (SE) versus self-limiting (SL) conditions of surface fluorination are performed [4]. Based on current results, it can be inferred that the variation in fluorination behaviors across different crystallinity and phases of the polycrystalline HfO_2 thin films may lead to increased surface roughness after ALE due to differences in etch rates.

Acknowledgments. This work was supported by Samsung Electronics.

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2:30pm **ALE1-TuA-5 Removal Reaction Mechanisms During Thermal Atomic Layer Etching of Aluminum Oxide: A First-Principles Study***, **Khabib Khumaini**, Gyejun Cho, Hye-Lee Kim, Won-Jun Lee,* Sejong University, Republic of Korea

Understanding the mechanism of atomic layer etching (ALE) is essential for process design and optimization. Thermal ALE of metal oxides typically involves surface fluorination followed by ligand exchange reactions to remove the fluorinated layer. In the removal step, surface fluorine groups are usually replaced by methyl groups or chlorine atoms to increase the volatility of the modified substrate using metal precursors. Surface reactions during the removal step of ALE aluminum oxide (Al_2O_3) using various metal precursors have been reported using *in situ* characterizations [1]. However, the investigation of the atomic-scale mechanism remains limited. Therefore, we performed density functional theory (DFT) calculations to study the removal reaction during ALE of Al_2O_3. Since the fluorination step produces an amorphous aluminum fluoride (a-AlF_3) layer, we constructed an amorphous substrate model by the melt-quench method and optimized the surface group density. Removal reactions with $Al(CH_3)_3$, $AlCl_3$, $AlCl(CH_3)_2$, $SiCl_4$, and $TiCl_4$ were then simulated. At 250°C, the removal of a-AlF_3 by $Al(CH_3)_3$ and $AlCl_3$, releasing $Al_2F_2(CH_3)_4$ and $Al_2F_2Cl_4$, occurs spontaneously with low activation energies of 1.08 and 0.85 eV, respectively. $AlCl(CH_3)_2$ preferentially removes a-AlF_3 with activation energies of 0.54–0.74 eV, which is lower than $Al(CH_3)_3$ and $AlCl_3$. Conversely, reactions with $SiCl_4$ or $TiCl_4$ release only $SiFCl_3$ or $TiFCl_3$ molecules with no release of aluminum-containing species, indicating that a-AlF_3 etching does not occur at 250°C. These results are in agreement with the experimental observations. Our DFT calculation results indicate that the substitution of a methyl group with a chlorine atom in the precursor increases the reactivity, while the substitution of aluminum with silicon and titanium significantly decreases both reactivity and spontaneity. These results will contribute to the rational design of precursors for thermal ALE processes.

[1] J.W. Clancey et al., J. Phys. Chem. C **124** (2020) 287–299.

2:45pm **ALE1-TuA-6 Multiscale Modeling of Gallium Nitride Atomic Layer Etching in Chlorinated Plasmas: A Combined Dynamic Global Model, Ab-initio and Kinetic Monte Carlo Approaches***, **Tojo Rasoanarivo**, Cédric Mannequin, Isabelle Braems,* Institut des Matériaux de Nantes Jean Rouxel, France*; Fabrice Roqueta, Mohamed Boufnichel,* STMicroelectronics, France*; Ahmed Rhallabi,* Institut des Matériaux de Nantes Jean Rouxel, France

Plasma Atomic Layer Etching (ALE) is a cyclic etching process for which one cycle relies on two self-limited half-reactions, separated by purges. An ideal ALE cycle comprises an adsorption step to modify the outermost surface layer, followed by an activation step to selectively remove the aforementioned modified layer without etching the underlying non-modified layers, thereby achieving atomic-scale resolution. The ALE of GaN using alternating Cl_2 and Ar plasma for the adsorption and activation steps, respectively, has been the subject of extensive research [1]. These studies suggest that the adsorption step relies on surface modification by chlorine radicals, while the activation step is achieved by selectively controlling the energy of ionic bombardment. However, the majority of ALE research has been conducted through experimental approaches, with some modeling studies employing molecular dynamics for common materials such as silica-based substrates [2].

In this study, we propose a multiscale kinetic model of GaN ALE in chlorinated plasmas. The temporal evolution of precursors fluxes during ALE cycles is provided by a dynamic global model of chlorinated plasmas [3]. The interactions between chlorine species and the GaN surface are investigated through the use of Density Functional Theory (DFT), while ion bombardments are consequently calculated using the Stopping and Range of Ions in Matter software (SRIM) considering the ion energy and angular distributions induced by the sheath at the interface between the plasma and the surface. Thereafter, those results are implemented in our new kinetic Monte-Carlo etching model with an atomic scale description. The simulation results demonstrate the effects of machine parameters (pulse lengths, flow rates, pressure, RF power) on the plasma composition, the etched depth and the etched GaN surface morphology at each ALE cycle.

Our approach is less time-consuming than molecular dynamics or DFT-only methods for atomic layer etching processes while following entire processes. Its suitability to a wide range of ALE recipes, for instance purge-free processes, could offer insights for process optimization.

References
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3:00pm **ALE1-TuA-7 Utilization of Molecular Dynamics Simulations and a Reduced Order Model to Analyze the Atomic Layer Etching Window of the Si-Cl2-Ar+ System***, **Joseph Vella**,* TEL Technology Center, America, LLC, USA*; David Graves,* Department of Chemical and Biological Engineering, Princeton University

Atomic-layer etching (ALE) processes are often characterized by the ALE window. The ALE window is a range of ion energies where the amount of substrate stays constant as a function of the ion energy. The Si-Cl_2-Ar^+ system is often used as an example to illustrate concepts of ALE, including the ALE window.[1] Despite this, when examining the literature, properties of the ALE window for this system remain obscure. For example, Kim et al.[2] studied Si-Cl_2-Ar^+ ALE and report that the ALE window should be below 40 eV. On the other hand, Park et al.[3] report the ALE window as being from 70 to 90 eV. Still others report an Ar^+ ion energy of 50 eV as being within the ALE window.[4] In this work, we aim to resolve these contradictory reports by studying the Si-Cl_2-Ar^+ ALE with classical molecular dynamics (MD) simulations and a reduced order model (ROM), also known as a transient site balance model.[5] The MD results show that the range of Ar^+ ion energies where the amount of Si etched per cycle (EPC) does not change is from 15eV to 20 eV, which is very narrow. The EPC in this region is also less than one atomic layer, because atomic Cl sputtering is significant. Despite this, it is believed this is where the ALE window is located. The MD simulations also show that a large ion fluence (roughly 4.2 10^{16} ions/cm^2 for 15 eV ions) is required to remove all Cl from the near surface region. Using the ROM, parameters can be varied to observe their effect on properties of the ALE window. For example, by increasing the threshold sputtering energy of Si, the width of ALE window can be increased. While this study focuses on the relatively simple Si-Cl_2-Ar^+ system, it is clear learnings from this study can be extended to general ALE processes.

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[5] J. R. Vella, Q. Hao, M. A. I. Elgarhy, V. M. Donnelly, and D. B. Graves, “A Transient Site Balance Model for Atomic Layer Etching”, Plasma Sources Sci. Technol., 2024, 33, 075009.

3:15pm **ALE1-TuA-8 Characteristics of the Power Delivery System of Transformer-Coupled Plasma Source for Remote Plasma Process in Semiconductor Manufacturing**, *Tae S. Cho, **Hakmin Kim**, Giwon Shin, Jaehoon Choi, Sooyoung Hwang, Jihyun Kim,* Wonik IPS, Republic of Korea

As the semiconductor industry progresses with sub-10 nm features, 3D stacked architectures, and intricate gate-all-around structures, the demand for remote plasma technologies has grown significantly. The requirements for the remote plasma are to generate a high density of radicals at low power and deliver them to the wafer processing region with minimal loss during transport, while preventing damage to the wafer from ion bombardment. "We have conducted an analysis of the power delivery system of the transformer-coupled plasma (TCP), which is one of the most commonly used plasma sources that meets these requirements. Since the power efficiency of the TCP directly influences the plasma properties, understanding the power transfer characteristics is crucial for improving process stability and uniformity."

The model was expressed as a function of the number of ferrite cores and dielectric breaks, that are the primary components of the TCP. The model was experimentally validated by varying the number of ferrites and breaks in the TCP, and it was confirmed that the experimental results were in good agreement with the values predicted by the model. Therefore, the proposed model was able to effectively predict the characteristics of the power delivery system of the TCP source. In future work, we aim to derive a more accurate equivalent model and a generalized equation by incorporating variables related to the plasma properties

Atomic Layer Etching
Room Samda Hall AB - Session ALE2-TuA

ALE Applications II

Moderators: Harm C.M. Knoops, Oxford Instruments Plasma Technology, Netherlands, **Jaewon Lee**, SK Hynix

4:00pm **ALE2-TuA-11 Development of an Atomic Layer Etching Process Dedicated to Diamond Material**, ***Marine Régnier,*** Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel; Institute of Applied Physics, University of Tsukuba; Japanese-French Laboratory for Semiconductor Physics and Technology J-FAST, CNRS, Univ. Grenoble Alpes, University of Tsukuba, France*; Aboulaye Traoré,* LSPM, CNRS, Université Sorbonne Paris Nord, France*; Marceline Bonvalot,* Univ. Grenoble Alpes, CNRS, Grenoble INP, LTM; Japanese-French Laboratory for Semiconductor Physics and Technology J-FAST, CNRS, Univ. Grenoble Alpes, University of Tsukuba, France*; Etienne Gheeraert,* Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel; Institute of Applied Physics, University of Tsukuba; Japanese-French Laboratory for Semiconductor Physics and Technology J-FAST, CNRS, Univ. Grenoble Alpes, University of Tsukuba, France

Diamond power devices, such as Schottky diodes and MOSFETs are currently being intensively investigated for possible application in power electronics and require dedicated fabrication processes to achieve adequate operating performances. Conventional etching techniques often lead to defects, surface roughness and sub-surface damages, which can significantly degrade carrier mobility and breakdown voltage of power devices. Thus, it becomes essential to develop diamond etching processes minimizing induced defects. Atomic layer etching (ALE) is then the perfect candidate allowing a very soft etching leading to defect-free etched surfaces and sub-surfaces. The first report of ALE of diamond dates back to 1988 with a patent describing a sequential process involving a surface modification upon NO_2 exposure, followed by a sputtering with a mixture of noble and hydrogen gasses [1]. However, since then, no further studies have been reported.

In this work, the ALE process optimization of (100) diamond is presented. The ALE process is achieved by first modifying the surface and then using a soft plasma to induce the selective removal of this modified surface. Experiments have been performed in a standard inductively coupled plasma reactive ion etching equipment with in-situ plasma monitoring by optical emission spectroscopy. They have been characterized as a function of the etching rate per cycle (EPC) estimated from diamond etched depth after 100 ALE cycles. The impact of the incident ionic bombardment kinetic energy during the 2nd ALE reaction has been evaluated from the dc self-bias voltage (V_{DC}). Results show a clear plateau of approximatively 5 V (Fig. 1), called ALE window, demonstrating the self-limiting effect of the etching process within one ALE cycle. The etching is of 6.7 Å per cycle, corresponding to the removal of two diamond (100) monolayers per cycle. Finally, synergy factor has been calculated. Synergy measures the effect of combining the two ALE steps. Separately, 100 cycles of step 1 then 100 cycles of step 2 leads to an etching rate of 3.8 Å per cycle. But 100 cycles of (1+2) steps lead to 6.7 Å per cycle, *i.e.* a synergy of 43%. This again demonstrate the effectiveness of the ALE process.

Reference

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4:15pm **ALE2-TuA-12 Atomic Layer Etching of MgO-doped Lithium Niobate Using Sequential Plasma Exposures**, ***Austin Minnich,*** *Ivy Chen, Jennifer Solgaard, Ryoto Sekine, Azmain Hossain, Anthony Ardizzi, David Catherall, Alireza Marandi,* Caltech*; James Renzas,* University of Nevada, Reno*; Frank Greer,* Jet Propulsion Laboratory (NASA/JPL)

Lithium niobate (LiNbO3, LN) is a ferroelectric crystal of interest for integrated photonics owing to its large second-order optical nonlinearity and the ability to impart periodic poling via an external electric field. However, on-chip device performance based on thin-film lithium niobate (TFLN) is presently limited by propagation losses arising from surface roughness and corrugations. Atomic layer etching (ALE) could potentially smooth these features and thereby increase photonic performance. Here, we report an isotropic ALE process for x-cut MgO-doped LN using sequential exposures of H2 and SF6/Ar plasmas. We observe an etch rate of 1.59 ± 0.02 nm/cycle with a synergy of 96.9%. The process is found to decrease the sidewall surface roughness of TFLN waveguides etched by physical Ar+ milling by 30% without additional wet processing. We also discuss alternate ALE chemistries using chlorine or bromine, as well as results for a directional etch. Our ALE process could be used to smooth sidewall surfaces of TFLN waveguides as a post-processing treatment, thereby increasing the performance of TFLN nanophotonic devices and enabling new integrated photonic device capabilities.

4:30pm **ALE2-TuA-13 Comparison of Gas-Pulsing Atomic Layer Etching (ALE) Characteristics Between Low-GWP Alternative Gases C_4F_6, $C_4H_2F_6$ and a Conventional Gas C_4F_8**, *Shinjae You,* Department of Physics, Chungnam National University and Institute of Quantum Systems (IQS), Chungnam National University, Republic of Korea*; **Dongki Lee**, Inho Seong,* Department of Physics, Chungnam National University, Republic of Korea*; Young-seok Lee,* Tokyo Electron Korea Ltd., Republic of Korea*; Sijun Kim,* Laboratoire de Physique des Plasmas (LPP), CNRS, Sorbonne Université, École Polytechnique, Institut Polytechnique de Paris, Republic of Korea*; Chul_Hee Cho, Wonnyoung Jeong,* Department of Physics, Chungnam National University, Republic of Korea*; Ehsanul Haque Jami,* Department of Physics, Chungnam National University, Bangladesh*; Min-su Choi, Byeongyeop Choi, Seonghyun Seo, Isak Lee, Woobeen Lee, Won-gyun Park, Jinhyeok Jang,* Department of Physics, Chungnam National University, Republic of Korea

The conventional gases used in the semiconductor industry, such as C_4F_8, have a high Global Warming Potential (GWP), driving research efforts to find environmentally sustainable alternatives. Additionally, in 3D NAND structures, Self-Aligned Contact (SAC) etching is required, and Atomic Layer Etching (ALE) can be effectively utilized, particularly when uniformity and selectivity are critical. This study evaluates the performance of low-GWP alternative gases in ALE processes. In-situ ellipsometry was employed to monitor the self-limiting behavior of these processes in real time. Furthermore, diagnostic tools were used to analyze the key mechanisms that determine the etching characteristics of different materials. By measuring the gas species generated during the process and analyzing the surface composition after etching, this study aims to identify the key factors influencing the differences in the etch rates of SiO_2 and Si_3N_4 for each gas. Through this analysis, the impact of variations in chemical reactivity, Plasma-surface interaction, and byproduct formation on etch rates will be investigated.

4:45pm **ALE2-TuA-14 The Influence of Laminate Doping of Atomic Layer Etching of Zinc Oxide*, Sabir Hussain*,** *Emily Duggan, Lynette Keeney, Jun Lin, Ian Povey,* Advanced Materials and Surfaces Group, Tyndall National Institute, University College Cork, Lee Maltings Complex, Dyke Parade, Ireland*; Mark Sowa, Laurent Lecordier,* Veeco Instruments

The challenging feat of both uniformly depositing and then conformally etching thin film materials can be overcome by the methods of both atomic layer deposition (ALD) and atomic layer etching (ALE) with Ångström-level control. This study examines the etching of ALD Zinc oxide (ZnO) and doped variants incorporating Hf and Al, (19:1 - Zn: metal ratio) at the full 200 mm wafer scale. Thin films were grown at 180 °C by using diethyl zinc and H_2O as precursors in a VEECO Fiji ALD system. All growth was performed on 200 mm silicon wafers with a 85 nm SiO_2 insulation layer to enable electrical characterization. The subsequent etching sequence was also performed in the same VEECO Fiji system, employing alternating acetylacetone (acac) and O_2 plasma pulses [1].

ZnO ALD produced polycrystalline Wurtzite material with a (100) preferred orientation. The growth rate was measured to be 1.86 Å per cycle, with a uniformity (after 500 cycles) of ~ 2% over a full 200 mm wafer. The measured resistivity (~8.5 X 10^{-3} Ω cm), mobility (~30 $cm^2 \cdot V^{-1} \cdot s^{-1}$) and carrier concentration (~2 x 10^{19} cm^3) are typical of ALD grown nominally undoped ZnO. The ALE of nominally undoped ZnO proceeds at a linear etch rate (~0.29 Å) for 400 cycles albeit at a lower etch rate as compared to Mameli et al. [1]. Etch uniformity is shown to be ~ 5 % across the full 200 mm wafer. The electrical properties were unchanged by the etching process beyond a small degradation of resistivity (8.5 x10^{-3} to 1.5 x 10^{-2} Ω cm) after 400 cycles.

The laminate doping of ZnO at a 19:1 ratio introduce complexity in doping process, Under the same etching conditions Al doped ZnO did not appear to etch even after 400 cycles, whereas the Hf doped ZnO appeared to undergo etching that terminated after an initial number of cycles due to the formation of an etch barrier or poisoned layer. Here we present physical (XRD, XPS, AFM, SKPFM) and electrical data to elucidate the mechanism of etch retardation

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5:00pm **ALE2-TuA-15 Ale of Tin Using Sf_6:H_2 Plasma: The Role of H, F, and Hf in Defining the Ale Window*, Guillaume Krieger*,** *Silke Peeters, Erwin Kessels,* Eindhoven University of Technology, The Netherlands*; Harm Knoops,* Oxford Instruments Plasma Technology, UK, Eindhoven University of Technology, Netherlands

Recently, etching processes relying on in-situ HF formation in plasmas have proven to tackle several challenges in the semiconductor industry such as etching high aspect ratio (HAR), enabling atomic scale control, and achieving high selectivity.[1] The selectivity between a nitride and its oxide counterparts is an important research field in the development of HF-based atomic layer etching (ALE) processes, with a strong focus on the selective etching between SiN and SiO_2.[2] Beyond Si-based materials, good selectivity between metal oxides and metal nitrides is also of interest. SF_6:H_2 mixtures have been used to selectively etch the oxidized top-layer of TiN over the bulk of the film, enabling an ALE process of TiN by alternating the oxidation and plasma etch step.[3] This selectivity is suggested to be driven by the formation of HF in the plasma. However, the roles of the various plasma species in defining the SF_6:H_2 upper and lower boundaries of the ALE window remains unclear.

In our work, we experimentally confirm that the formation of HF is driving the aforementioned ALE processes. Additionally, we demonstrate that the presence of HF cannot, by itself, explain the ALE window as a function of the $SF_6/(SF_6 + H_2)$ gas ratio of the etch step. We have correlated this window with various species measured in the plasma including H and F atoms by optical emission spectroscopy (OES) and HF, H_2S, and SF_6 by quadrupole mass spectroscopy (QMS). These measurements demonstrate that the upper bound, in terms of the $SF_6/(SF_6 + H_2)$ ratio, is determined by the presence of F atoms in the plasma leading to spontaneous TiN etching. For establishing the lower bound, an ABC-type recipe with an H_2 plasma between the oxidation step and the SF_6:H_2 plasma has been used to highlight the role of the H radicals in the ALE process. The H_2 plasma quenches the etching of the SF_6:H_2 plasma, suggesting prominent role of H in reducing TiO_2 top-surface, which prevents the etching by HF. These results suggest a strong interplay between H, F, and HF in the selective etching mechanism. This understanding can act as a stepping stone to expand this ALE process to other conductive nitrides.

References:

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5:15pm **ALE2-TuA-16 Atomic Layer Etching of Ruthenium Using Surface Oxidation with O_2 Plasma and Chelation with Formic Acid*, Hojin Kang*,** *Eunsu Lee, Minsung Jeon, Heeyeop Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Atomic layer etching (ALE) was developed via oxidizing the Ru surface with O_2 plasma, followed by removing the oxidized surface with a chelation reaction using formic acid (HCOOH). Surface oxidation reactions were performed up to 300 °C, and the RuO_2 layer after oxidation was identified using X-ray photoelectron spectroscopy (XPS). The Ru^{2+} oxidation state and Ru to O atomic ratio of 1:2 suggest that the oxidation layer formed is RuO_2. In the removal step, the RuO_2 layer is removed via a chelation reaction with HCOOH at process temperatures above 150 °C. The etch per cycle (EPC) of Ru is about 3 Å/cycle at a process temperature of 150 ~ 200 °C, and the EPC gradually decreases at temperatures above 200 °C, possibly due to the decomposition reaction of HCOOH. The EPC of Ru increases with increasing O_2 plasma exposure time without any saturation. The EPC of Ru was saturated at 3 Å/cycle with an HCOOH injection time of 100 sec. The surface roughness increases from 0.57 to 1.68 nm after ALE cycles, which can be attributed to etch rate differences according to facets. Ru has a hexagonal polycrystalline structure of (1,0,0), (0,0,-2), (1,0,1), (1,0,2), (1,1,0), (1,0,3), (1,1,2), and (2,0,1), which was confirmed by X-ray diffraction (XRD). No crystal structure changes after 100 cycles of ALE, and the maximum strength decreases by 97, 66, 74, 68, 89, 63, 52, and 75%, respectively. The surface oxide residue is less than 4% after ALE, which is similar to the pristine Ru. The Ru to SiO_2, HfO_2, and Si_3N_4 selectivity is infinity, and 56 for TiN and 77 for TaN.

Area Selective ALD
Room Tamna Hall A - Session AS-TuA

Area Selective Deposition I

Moderators: Il-Kwon Oh, Ajou University, **Mikko Ritala**, University of Helsinki

4:00pm **AS-TuA-11 Surface Chemistry Characterization for Area-Selective Atomic Layer Deposition of Ruthenium*, Eun-Hyoung Cho,*** 2D Device TU(SAIT)/Samsung Electronics, Republic of Korea **INVITED**

Achieving atomic-scale precise control over material layering is critical for the development of future semiconductor technology. Area-selective deposition (ASD) has emerged as an indispensable tool for crafting semiconductor components and structures via bottom-up pattern transfer. The most widely used approach for ASD relies on self-assembled monolayers (SAMs) to deactivate specific surfaces. However, alternative strategies are being explored to better align with the requirements of high-volume device manufacturing and address the limitations of the SAM method. One promising alternative involves the application of small molecule inhibitors (SMIs). However, limited research has been conducted to elucidate the mechanisms governing their adsorption and inhibition of deposition. Additionally, research on elucidating the ASD mechanism, in which precursors are blocked rather than chemically adsorbed on SMIs, has predominantly relied on simulations such as density functional theory (DFT) calculations or Monte Carlo (MC) simulations. By closely investigating these interfacial phenomena using precise surface analysis techniques, a deeper understanding of the role that SMI composition and structure play in adsorption and inhibition can be achieved, ultimately contributing to the design of SMIs for future ASD systems. Recently, it was confirmed that by controlling the crystal orientation of metal grains, atomic layer deposited ruthenium (Ru) thin films on amorphous dielectric substrates exhibit electrical resistivity comparable to that of single crystal Ru. However, the oxidative counter-reactants such as O2 often used for atomic layer deposition (ALD) of metallic Ru films result in a considerable increase in contact resistance because of substrate oxidation, limiting the applications of both ALD and ASD of Ru. In this study, Ru ASD is demonstrated using two-step ALD with the sequential use of H2 and O2 as counter-reactants and dimethylamino-trimethylsilane (DMATMS) as a precursor inhibitor. Both theoretical and experimental results demonstrate that in the two-step Ru ALD, the oxide layer can be eliminated via the reduction of the oxidized substrate metal surface by the H2 counter-reactant. This mechanism simultaneously facilitates the adsorption of the Ru precursor (tricarbonyl-(trimethylenemethane)-ruthenium) and removal of the surface oxide layer. Consequently, Ru growth is suppressed on the DMATMS-inhibited SiO2 surface during ASD, enabling exclusive deposition of Ru on the Mo surface. The currently proposed Ru ASD scheme using two-step ALD is highly promising for driving advancements in interconnect technology for commercial applications.

4:30pm **AS-TuA-13 Dopant-Selective Atomic Layer Deposition (DS-ALD) for Fabrication of Electronic Devices***, **Daniel Aziz**, Nishant Deshmukh,* Georgia Institute of Technology, USA*; Ryugo Shimamura,* University of Tokyo, Japan*; Amy Brummer,* Georgia Institute of Technology, USA*; Kaifan Yue,* University of Michigan, Ann Arbor*; Siddharth Kurup,* Georgia Institute of Technology, USA*; Kira Barton,* University of Michigan, Ann Arbor*; Eric Vogel,* Georgia Institute of Technology*; Michael Filler,* Georgia Institute of Technology, USA

Area-selective atomic layer deposition (AS-ALD) methods promise bottom-up approaches for device fabrication, yet it remains difficult to achieve high selectivity with subtle surface chemical differences. In this work, we demonstrate dopant-selective ALD (DS-ALD) for the patterning of differently doped silicon surfaces. Our approach enables orthogonal patterning which can direct ALD to either heavily or lightly doped silicon. As a result, we can fabricate a metal oxide semiconductor field effect transistor (MOSFET) gate [1] on lightly doped silicon and a semiconductor-metal contact [2] on heavily doped silicon. In each of these patterning approaches, an organic surface-initiated mask is grafted from the surfaces of dopant modulated silicon structures. An etchant (aqueous KOH) then diffuses through the mask and selectively attacks the underlying silicon surface, thus degrafting the mask only in targeted regions. This process yields features to which ALD chemistries can deposit compatible metal or dielectric thin films. We characterize the process through a combination of X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and Current-voltage (IV) measurements.

To direct ALD of gate dielectric and metal to the lightly doped silicon typically in the channel of a MOSFET, a hydrosilylation and subsequent polymerization results in the appropriate pattern after applying the selective etchant. We characterize the doping contrast required to enable this approach as well as the minimum achievable feature sizes. Notably, we observe an increase in etching selectivity as etching progresses which mimics the mechanism of aqueous KOH etching of bare silicon. ALD of the gate dielectric and metal results in working field effect devices.

To direct ALD of contact metal towards heavily doped silicon, as might be needed for the source/drain regions of a MOSFET, we leverage undecylenic acid's bifunctional nature which results in different attachment chemistry on differently doped silicon surfaces. Treatment with KOH removes the mask from the heavily doped silicon surface allowing the deposition of Pt metal via ALD on that same region. Current-voltage measurements demonstrate a metal semiconductor silicide contact.

In summary, by combining different organic mask materials with differently doped semiconductor surfaces, we can direct patterning and the subsequent AS-ALD. Our findings establish guidelines for novel approaches to nanoscale patterning and set the stage for fabricating a variety of high-performance electronic devices.

4:45pm **AS-TuA-14 ALD Outstanding Presentation Award Finalist: High Temperature Area Selective ALD SiN by in-Situ Selective Surface Fluorination***, **Haonan Liu**, Ken Okoshi, Hiroki Murakami, Yamato Tonegawa,* Tokyo Electron Technology Solutions Ltd., Japan

Presently, research on area selective atomic layer deposition (AS-ALD) is attracting strong interest. AS-ALD simplifies the process of deposition on patterned substrates and high aspect ratio (AR>70) structures, holding promise for various applications in semiconductor manufacturing. Inhibitors such as self-assembled monolayers (SAMs) and (dimethylamino)trimethylsilane (DMA-TMS) are typically used to passivate non-growth areas.[1] However, the deterioration of selectivity at temperatures exceeding 500℃ limits their applications in high temperature deposition processes. Fluorination is regarded as a candidate for overcoming these problems.[2] In this study, we present a novel approach to achieve high selectivity in high temperature AS-ALD on SiN versus SiO_2 through effective surface-selective fluorination without damage to the substrates.

Experiments were conducted with a batch furnace capable of treating over one hundred 300 mm wafers simultaneously. A wide range of substrates were utilized including 300mm wafers with blanket SiN and SiO_2 films and various nanostructured samples. Prior to inhibition, samples were precleaned by dilute HF to remove native oxides. An HF gas passivation was employed at 630℃ for 10 minutes to selectively inhibit the SiO_2 surface. ALD SiN was deposited with dichlorosilane (SiH_2Cl_2) as the precursor and NH_3 as the co-reactant at 630 ℃.

The initial AS-ALD sequence involved performing ALD cycles following HF passivation, resulting in AS-ALD of up to 6 nm SiN on SiN while maintaining good within-wafer non-uniformity (Win Unif.) of <3%. We then developed the area-selective-deposition-Loop (ASD-Loop) technique, consisting of alternating 10-minute HF passivation with ALD cycles, as shown in Figure 1. We achieved an AS-ALD of 28 nm on SiN blanket wafers with high selectivity while keeping excellent Win Unif. of <2% and high film quality, as confirmed by the wet etching rate. The ASD-Loop has also been successfully applied to SiN/SiO stripe-patterned substrates (Figure 2), resulting in a maximum ASD thickness of 21 nm; and to high-AR holes on SiO_2/SiN stacks (Figure 3), resulting in AS-ALD with high conformality of >90%. Thus, we have demonstrated high-temperature AS-ALD on 300 mm wafers and complex nanostructures with high selectivity, superior uniformity, and reliable quality. This offers a new pathway for the integration of AS-ALD into nanofabrication schemes, showing significant potential for advancing high-performance semiconductor applications including DRAM and 3D NAND manufacturing.

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5:00pm **AS-TuA-15 Mutifunctional Ru/ZnO Bilayer for Sustainable Cu Interconnects using Area-Selective Atomic Layer Deposition of barrier with Small Molecule Inhibitor***, **Minwoo Kim**, Yeseul Son, Sang Bok Kim, Soo-Hyun Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

With the scaling of semiconductor devices, the increase in via resistance, which constitutes a significant portion of the Cu interconnect resistance, has emerged as a critical issue. To reduce via resistance, studies [1, 2] have been conducted on forming bottomless barriers using area selective deposition (ASD), where a high-resistivity barrier layer is selectively deposited only on the via/trench sidewalls, SiO_2-based dielectrics without being deposited on the via bottom, Cu. In these studies, self-assembled monolayers (SAMs) with long alkyl chains were used as inhibitors for preventing the adsorption of the precursor on metallic surfaces. However, SAMs are typically adsorbed onto surfaces through solution-based processes, which pose compatibility issues with semiconductor processes and, due to their relatively long molecular structure, cannot form a uniform inhibitor layer within 3D nanostructures. To prevent these issues, this study used a small molecule inhibitor (SMI) to form a bottomless barrier. Additionally, based on previously reported studies [1], the Ru/ZnO bilayer, with ZnO for the bottomless barrier and Ru for the liner and seed layer, was applied for the sustainable Cu interconnects [Figure 1]. The ZnO ASD process is carried out using an amine-based SMI that selectively absorbs on Cu, with diethylzinc and H_2O used for the ZnO ALD process. After the ZnO ASD process and the removal of the inhibitor, the Ru film was deposited using an ALD process with tricarbonyl(trimethylenemethane)ruthenium and O_2. By controlling the conditions of the ZnO ASD process, we confirmed and analyzed the selective deposition of ZnO on the SiO_2-based dielectric substrate not on Cu one using TEM, XPS, and XRD etc. The detailed results will be presented in the conference.

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Acknowledgements

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TiN interconnects via high-temperature atomic layer deposition (ALD) and development on new interconnect materials based on ALD) funded by the Ministry of Trade, Industry & Energy (MOTIE, Korea) (1415187401). This work was also supported by SK hynix semiconductor through the cluster research between UNIST and SK hynix semiconductor.

5:15pm **AS-TuA-16 Technological Promise of a Frustratingly Elusive Ni(^{tbu2}DAD)$_2$—Yet the Challenge is Part of the Breakthrough***, Gabriele* ***Botta,*** Nanogune, Italy

Over the past decade, research into the area-selective behavior of M-(^{tbu_2}DAD)$_2$ compounds has highlighted the significant potential of these precursors. [1,2] The low-temperature AS-ALD deposition of metallic nickel and cobalt films on various metallic surfaces has demonstrated its technological relevance. However, while Co(^{tbu_2}DAD)$_2$ continues to be the focus of many studies, [3][4] Ni(^{tbu_2}DAD)$_2$ has seemingly received less attention. Despite their similar thermodynamic properties, handling Ni(^{tbu_2}DAD)$_2$ has proven more challenging than its cobalt counterpart.

In this study, we further investigate the delivery characteristics of Ni(^{tbu_2}DAD)$_2$ and expand the range of growth and non-growth materials for its selective deposition. We also examine the loss of selectivity on silicon-based surfaces, which are typical non-growth areas. This undesirable material nucleation can arise from several factors, but in the case of Ni(^{tbu_2}DAD)$_2$, it is especially pronounced on hydroxyl groups of silicon oxide substrates. After identifying the nature of these nucleation sites, we developed a method to deliberately create growth regions using focused ion beam (FIB) irradiation. This approach enables direct patterning of growth areas on non-growth substrates, such as SiO_2. Our findings demonstrate that both induced selectivity (achieved through FIB area activation) and the inherent selectivity of Ni(^{tbu_2}DAD)$_2$ for metallic surfaces can coexist, offering new potential strategies for advanced nanofabrication.

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Emerging Materials
Room Tamna Hall B - Session EM-TuA
Molecular Layer Deposition & Hybrid Materials II

Moderators: Jolien Dendooven, Ghent University, Belgium, **Chang-Yong Nam**, Brookhaven National Laboratory

1:30pm **EM-TuA-1 Vapor Phase Infiltration for Membrane Modification***,* ***David Bergsman,*** University of Washington **INVITED**

Membrane filtration is a promising tool for reducing energy consumption and carbon emissions in areas like industrial manufacturing, food and beverage, municipal water treatment, and pharmaceuticals. However, improvements to membrane permeability, selectivity, thermal stability, chemical stability, and fouling resistance will be required before they are cost-effective enough to handle the acidic, alkaline, organic, and otherwise complex feed streams present in many applications. Of the commercial membranes commonly available, polymeric membranes are relatively low cost but often suffer from low thermal and chemical stability, while other membrane materials can be difficult or expensive to manufacture. Vapor phase infiltration (VPI), also known as sequential infiltration synthesis or atomic layer infiltration, is one potential cost-effective strategy for making higher-performance membranes. In VPI, a polymer is exposed to vapor phase metal-organic reactants which absorb, diffuse, and react in the polymer to form a composite material. This approach could be used to upgrade existing membranes through post-synthetic modification to improve their performance. However, more work is needed to understand the impact of this process on polymer properties and to discover new materials that best enable the wider implementation of membrane separations. This presentation will highlight our work to apply the VPI process to membrane separations. We will review examples of how we have used VPI to improve the conductivity of membranes through the formation of laser induced graphene, our work to understand the trade-off between infiltration and polymer toughness, and our exploration of organic reactants that could expand the library of infiltration processes. In doing so, this presentation will showcase the potential of VPI to create next-generation membranes for diverse and challenging separation applications.

2:00pm **EM-TuA-3 Dry Developing Process of Molecular Layer Deposited Hf-Based Hybrid Thin Films for EUV Lithography***,* ***Minki Choe,*** *Dan Le, Thi Thu Huong Chu, Hyunah Sung,* University of Texas at Dallas*; Nikhil Tiwale,* Brookhaven National Laboratory*; In-Hwan Baek, Rino Choi,* Inha University, Republic of Korea*; Chang-Yong Nam,* Brookhaven National Laboratory*; Jiyoung Kim,* University of Texas at Dallas

EUVL plays a critical role in device down-scaling and thereby extending the life of Moore's law to beyond sub-7nm node. However, the current EUV photoresists based on spin-on processing and followed by wet development, which faces challenges such as high processing costs of organic solvents, pattern collapse due to capillary forces during wet development, and undercut. [1,2] These problems increase overall process costs and limit the patterning performance. In this context, fully dry lithography process has the potential to overcome the drawbacks of wet lithography and accelerate the advancement of EUV lithography.

Herein, we report a Hf-based hybrid resist thin film system that synthesized via molecular layer deposition (MLD) using Tetrakis(dimethylamido)hafnium (TDMA-Hf) and 2,3-Dimercapto-1-propanol (DMP). In our other study, we found that the Hf-based resist thin film system exhibited negative-tone behavior and excellent sensitivity, with pattern formation observed at a remarkably low dose of ~96 μC/cm^2 under 100 eV e-beam exposure. In this study, we specifically focus on investigating the dry development process using inductively coupled plasma reactive ion etching (ICP RIE) that suitable for the deposited Hf-based resist thin films. To mitigate the contribution of fluorinated greenhouse gases (F-gases) to global warming, we employed fluorine-free gases. During the etching process with fluorine-free gas, we conducted parameter optimization by varying crucial factors such as bias power, substrate temperature, and working pressure. This optimization aimed to find optimal conditions that maximize the etch rate difference between exposed and non-exposed regions. This research focuses on developing a fully dry lithography approach by combining MLD-deposited organic-inorganic hybrid photoresists with a dry development process using fluorine-free gas in ICP RIE. The goal is to establish a cost-effective and environmentally friendly lithography technique that can facilitate the realization of high-resolution patterns in EUV lithography while overcoming the limitations associated with conventional wet processes.

This work is supported by the U.S. DOE Office of Science Accelerate Initiative Award 2023-BNL-NC033-Fund. Minki Choe supported by KIAT/MOTIE (RS-2024-00435406).

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2:15pm **EM-TuA-4 Inverted Living Molecular Layer Deposition: Rapid Conformal Polymer Coatings through Vapor-Phase Living Polymerization***,* ***Karina Ashurbekova,*** *Mato Knez,* CIC nanoGUNE, Spain

This study presents an inverted living MLD technique that enables precise polymer growth with tailored architectures, functional groups, and customizable properties. We present the first vapor-phase synthesis of polyoxazolines (POx) via a living cationic ring-opening polymerization (CROP) mechanism.

The two-step process involves a pulsed delivery of vaporized initiator (P-Toluenesulfonyl chloride) into a reactor, where it adsorbs onto the substrate as a molecular layer, functionalizing it. This is followed by chain propagation, where the monomer is introduced and reacts with the chemisorbed initiator layer.

We utilized three substituted oxazolines as monomers: 2-methyl-2-oxazoline, 2-phenyl-2-oxazoline, and 2-isopropenyl-2-oxazoline. The substrate was exposed to the monomer vapors for several seconds, after which the chamber was purged, and another dose of vaporized monomer was introduced. With each pulse of monomer, the polymer layer thickness gradually increased until the monomer was consumed. This allows precise control over the final coating thickness through the monomer dose and the number of feeding cycles, while still maintaining conformality of the coating. The growth process is terminated by introducing water vapor into the reactor.

The living nature of the polymerization has been confirmed by in situ QCM studies. We observed fascinating surface effects, while the composition and morphology of the POxs were examined using ATR-FTIR, XPS, SEM/TEM, and AFM. In this presentation, we focus solely on the growth of POx homopolymers, though copolymerization through sequential monomer addition is also achievable.

The key advantages of this approach include the elimination of multicomponent solution-based impurities, precise thickness control, conformality, and strong adhesion of the polymer films to a wide range of substrates.

Our approach opens the door for customization of materials for plentiful applications. As such, this development marks the beginning of a novel approach to rapid surface functionalization with highly conformal coatings with functional polymeric materials.

2:30pm **EM-TuA-5 ALD Outstanding Presentation Award Finalist: Recent Advancement of Inorganic-Organic Hybrid Resist Thin Films Deposited via Molecular Atomic Layer Deposition for Dry EUV Resist Platforms***, Dan N. Le, Thi Thu Huong Chu, Hyunah Daniela Sung, Minki Choe, Minjong Lee,* University of Texas at Dallas*; Won-Il Lee,* Stony Brook University*; Nikhil Tiwale,* Brookhaven National Laboratory*; Jean-Francois Veyan, Doo San Kim,* University of Texas at Dallas*; Chang-Yong Nam,* Brookhaven National Laboratory*;* ***Jiyoung Kim,*** University of Texas at Dallas

In order to sustain the device down scaling below the sub-1nm node, the implementation of high/hyper numerical aperture (NA) extreme ultraviolet (EUV) lithography is essential. This advancement drives the need for innovative resist platforms that meet rigorous performance criteria, including ultra-thin film (<15 nm), uniformity, mechanical and chemical robustness, and superior etch resistance. Conventional polymer-based spin-coated resists struggle to meet these stringent requirements. In contrast, ALD-based synthesized inorganic-organic hybrid dry resist thin films offer significant advantages, providing precise atomic-scale thickness control, enhanced material uniformity, and strategic incorporation of metal elements to improve sensitivity, mechanical strength, and etch resistance.

Herein, we report various molecular-atomic layer deposited hybrid resist thin film systems, contributing to the advancement of the dry EUV resist platform. We explore different combinations of metal ALD precursors, such as TMA, DEZ, TDMA-Hf with organic sources like hydroquinone (HQ), 4-mercaptophenol (4MP), and 2,3-Dimercapto-1-propanol (DMP). By using various combinations of these inorganic and organic sources, we achieve hybrid thin film systems consisting of Al-HQ, Zn-HQ, Al-4MP, Zn-4MP, Hf-4MP, Hf-DMP, and Zn-DMP. The growth characteristics of these hybrid resist thin films were thoroughly evaluated, along with detailed material characterization. The electron sensitivity of various hybrid resist thin films was investigated using electron beam lithography (EBL) at 100 V acceleration voltage, mimicking EUV exposure conditions. Upon electron irradiation, all these hybrid resist thin film systems exhibited negative tone resist characteristics when evaluated in different developer solutions. Among these resist thin films, the Hf-DMP system demonstrated the highest sensitivity when subjected to 100 eV electron energy irradiation, requiring the lowest exposure dose to maintain most of their thickness. The chemical transformations in these hybrid resists are also investigated using *in-situ* IR spectroscopy equipped with an electron gun and a residual gas analyzer (RGA). The IR absorbance and operando RGA spectra suggested that aromatic and chain organic moieties exhibited different crosslinking pathways. Detailed experimental procedures and results will be discussed including actual EUV sensitivity of hybrid dry PRs.

This work is supported by the U.S. DOE (2023-BNL-NC033-Fund), and NRT/MSIT (2022M3H4A3052556) in Korea. We acknowledge Drs. Sangsul Lee, Geonhwa Kim, Jiho Kim at Pohang Accelerator Lab (PAL) for EUV exposure test.

2:45pm **EM-TuA-6 Rethinking Thermoelectrics: The „Power" of Hybrids Engineered by Vapor Phase Infiltration***,* ***Kristina Ashurbekova,*** CIC nanoGUNE, Spain*; Maksim Naumochkin, Heiko Reith, Kornelius Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany*; Mato Knez,* CIC nanoGUNE, Spain **INVITED**

Hybrid thermoelectric (TE) materials aim to outperform traditional TEs by creating synergies between organic and inorganic materials. The simultaneous exploitation of the low thermal conductivity (λ) of organics and the high Seebeck coefficient (S) and electrical conductivity (σ) of inorganics is particularly attractive. To achieve this, we developed a new family of hybrid TE materials by applying vapor phase infiltration (VPI) of Sb_2Te_3, Bi_2Te_3, Sb_2Se_3, or Bi_2Se_3 into polymeric matrices. The resulting hybrid materials feature a unique structure, with chalcogenide nanocrystals grown within the bulk of the conducting polymers.To fully understand the complexity of these hybrid materials, we extensively characterized the infiltrated chalcogenides. We observed a clear correlation between the polymer thickness and the precursor exposure time with the evolving chalcogenide crystals size within the final hybrid material. Thinner polymers resulted in smaller crystals, likely related to the faster out-diffusion of unbound precursors from the polymer during the process. TEM was used to investigate the structural organization of the nano clusters in the hybrids and to study the nucleation processes of chalcogenide nanocrystals, distinguishing between those chemically bound to the polymer chains and those physically entrapped within the polymer. SEM tomography was used to evaluate a network of chalcogenide nanocrystals inside the polymer matrix and the degree of their three-dimensional connectivity. The TE properties of the hybrids were characterized between 293–433 *K* using a lab-on-chip ZT test platform, which allowed simultaneous characterization of all in-plane parameters of the films, including the σ, S, λ, Hall coefficient R_H, and the derived Power Factor (PF) and ZT. Interestingly, all the measured parameters (σ, S, Hall coefficient R_H, λ) changed considerably within the first several heating-cooling cycles. For example, in the case of Sb_2Te_3-infiltrated PEDOT:PSS, the difference in σ between successive measurements increased to values of exceeding 80 S cm^{-1}, while the change in λ decreased. This decoupling of σ from λ is attributed to suppression of the lattice λ by enhanced boundary-scattering of heat-carrying phonons. Simultaneously, the chemical bonds between the inorganic and organic phases promote direct electronic interaction, facilitating electron transport. Finally, remarkable PF and ZT values of were obtained. This presentation will provide an overview over the conceptualization, fabrication, and evaluation of this new hybrid TE materials system, highlighting its advantage over traditional TE material concepts.

Nanostructure Synthesis and Fabrication
Room Tamna Hall B - Session NS-TuA

2D Materials and Devices

Moderators: Nathanaelle Schneider, CNRS-IPVF, **Tamar Segal-Peretz**, Israel Institute of Technology

4:00pm **NS-TuA-11 Towards Low-Resistance P-Type Contacts to 2D Transition Metal Dichalcogenides Using Plasma-Enhanced Atomic Layer Deposition***,* ***Ageeth Bol,*** University of Michigan, Ann Arbor **INVITED**

One major limitation of 2D transition metal dichalcogenide (TMD) based FETs is the high contact resistance between metallic electrodes and semiconducting channels, particularly for p-type contacts. In this presentation I will address how PEALD of p-type TMDs can be used to improve this contact resistance. First, I will go over controlled doping strategies to form p-type 2D TMD contact materials using PEALD, with an emphasis on Al doped MoS_2 [1] and Nb Doped WS_2 [2]. Our recent results show contact resistancevalues as low as 0.30 ± 0.26 kΩ·μm between Pd and PEALD $Nb_xW_{1-x}S_2$ [3], demonstrating that low resistance contacts between metal and p-type TMDs are possible. Then, I will discuss reducing unintentional p-doping introduced during PEALD of TMDs. PEALD TMDs typically contain some level of hydrogen impurities that leads to unintentional p-doping. We have shown that these impurities can be reduced by introducing an Ar plasma C step in the standard PEALD TMD process [4]. Finally, the use of remote plasmas in PEALD for contact deposition can lead to the creation of undesired impurities and defects in the 2D TMD channel, possibly impacting electronic behavior. I will present how adjustments to the PEALD process of WS_2 can reduce the impact of the plasma and maintains the integrity of the underlying TMD channels.

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4:30pm **NS-TuA-13 Selective Passivation of 2D TMD Surface Defects by Atomic Layer Deposition for Enhancing Recovery Rate of Gas Sensor***, **Minji Kim**, Inkyu Sohn, Dain Shin, Sangyoon Lee, Hwi Yoon, Jisang Yoo, Seung-min Jung, Hyungjun Kim,* Yonsei University, Korea

Two-dimensional transition metal dichalcogenides (2D TMDs) have gained significant interest as promising materials for gas sensors due to their high surface-to-volume ratio, high electron mobility, tunable band gap, and efficient sensing capabilities at room temperature.[1] However, commercialization of TMD gas sensors is currently limited by low recovery rates due to strong chemisorption of gas molecules on surface defects. Unfavorable desorption of gas molecule from defects hinders reliability and long-term stability of TMD gas sensor.[2] In this study, atomic layer deposition (ALD) is used to selectively passivate surface defects of MoS_2 and WS_2 gas sensors with Al_2O_3. SEM analysis confirms that Al_2O_3 are deposited only at defective sites such as grain boundaries and vacancies of MoS_2 and WS_2. As a result, Al_2O_3 passivated TMD gas sensor shows nearly complete recovery rate of 96% even at room temperature, which improved from 74% recovery rate of pristine TMD gas sensor. Also, passivated gas sensor shows higher response toward NO_2 gas compared to pristine gas sensor due to n-type doping effect of Al_2O_3 on TMD. This result shows that defect-selective passivation is a promising strategy to overcome low recovery rate of TMD gas sensor and enhance its sensing properties.

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4:45pm **NS-TuA-14 Beyond the conventional AB process: Advanced ALD approaches for controlling the properties and growth of MoS_2 and WS_2 2D Materials***, **Cindy Lam**, Eryk Gruszecki, Erwin Kessels, Bart Macco,* Eindhoven University of Technology, The Netherlands

As the semiconductor industry is advancing towards the Ångstrom era of transistor scaling, the ultrathin 2D transition metal dichalcogenides (TMDs) serve as potential candidates in replacing the current Si-based channel material for next-generation field-effect transistors (FETs) in integrated circuits (ICs). Atomic layer deposition (ALD) holds great promise as a deposition technique to grow 2D materials directly on the device (i.e. transfer-less) with good conformality in 3D structures and back-end-of-line (BEOL) compatible temperatures. However, several challenges remain in attaining high-quality, large crystals of semiconducting 2D TMDCs like MoS_2, WS_2, and WSe_2 in comparison to other techniques such as chemical vapor deposition (CVD). In addition to that, the development of doping strategies is of great interest to control their conductivity type.

In this presentation, we showcase advanced ALD approaches to address these challenges, through the use of plasma treatments with controlled ion energies, supercycles for incorporating dopants, and surface pretreatments to control the nucleation. We showcase that the morphology and electrical characteristics of ALD WS_2 can be improved upon using an Ar plasma treatment (ICP, RF: 13.56 MHz) in an ABC-type PEALD process along with varying the plasma process parameters such as the exposure time t_p(ranging from 0 to 180 s) and ion energy E_i (from 16 to 41 eV). Sulfur vacancy formation V_s within the film likely induces *p*-type conductivity and enhancement of Hall effect properties with the mobility $\mu_H$ranging between 0.1 and 1.1 $cm^2/(V·s)$ and a carrier density $p$in the order of 10^{19} - 10^{20} cm^{-3} (See Supplementary Information). In the case for MoS_2, substitutional transition metal doping by tantalum (Ta) utilizing a supercycle method, leads to MoS_2 with a similar carrier type and $\mu_H$ranging from 0.04 to 0.16 $cm^2/(V·s)$ and with carrier density p values around ~10^{21} cm^{-3} upon tuning the cycle ratio n MoS_2 : m TaS_2 . These results demonstrates a facile method to create degenerate TMDs by PEALD, interesting for potential applications in areas including contact engineering to enhance device performance. Further customizing and refining the design of the ABC process offers a wide range to tune the electrical properties, optimizing them and achieve desired target values.

5:00pm **NS-TuA-15 Deposition and Characterization of Transition Metal Oxide/2d Transition Metal Dichalcogenide Quantum Wells***, **Shih-Hao Tseng**, Yu-Chuan Lin,* Department of Materials Science and Engineering, National Yang Ming Chiao Tung University, Hsinchu, Taiwan

Quantum well heterostructures made of oxide dielectrics and 2D semiconductors provide exciting optoelectronic applications. As this heterostructure is emerging, it is necessary to combine different vapor phase techniques to integrate them in a bottom-up fashion and find ways to characterize them rapidly and non-invasively. We utilize atomic layer deposition (ALD) to deposit aluminum oxide (AlO_x) on a large area 2D WS_2 film grown by metalorganic chemical vapor deposition (MOCVD) to fabricate quantum well superlattices and explore a variety of characterization techniques to study their structures and properties. First, we tested a range of ALD temperature for effective nucleation and growth of continuous 5 and 10 nm AlO_x on WS_2 inert surface. Subsequently, we grow another 2D WS_2 film on top of the 1st stack of AlO_x/WS_2 by MOCVD at low temperatures and encapsulate it with another ALD AlO_x. The single and double AlO_x/WS_2 quantum wells were characterized with Raman and photoluminescence spectroscopy and scanning probe microscopy to understand their optical properties. Next, we used hard X-ray photoelectron spectroscopy (HXPES) to analyze the WS_2 layers sandwiched between AlO_x with varied thicknesses (5-20 nm). To obtain the thickness, roughness, and density of the AlO_x and WS_2 in the quantum wells, X-ray reflectivity (XRR) measurement was performed on the quantum wells. Finally, we examined the impact of AlO_x thicknesses on the effectiveness of HXPES and XRR and the optical and electrical properties of the AlO_x/WS_2 quantum wells.

5:15pm **NS-TuA-16 Engineering Al_2O_3 Interlayer via Atomic Layer Deposition for Enhancing Contact Properties of MoS_2-Based FET***, **Minu Cho**, Hwi Yoon, Sanghun Lee, Seongyeong Park, Inkyu Sohn, Hyungjun Kim,* Yonsei University, Korea

As transistors have advanced and continued to downscale, 2D transition metal dichalcogenides (TMDCs) have gained attention as a promising channel material. However, high contact resistance(R_c) has emerged as a major issue in 2D TMDC field-effect transistors (FETs). This problem is primarily caused by Fermi level pinning, which hinders control over the Schottky barrier height, even when the metal’s work function (WF) is altered, leading to increased contact resistance. Various approaches have been explored to address this issue, among them placing an insulating layer between the metal and the channelhas been proposed as a potential solution to mitigate Fermi level pinning. However, a key challenge in implementing this method is achieving optimal thickness for insulating layer and ensuring uniform deposition of the insulating interlayer on the inert surface of the 2D material.

In this study, we aimed to suppress Fermi level pinning by depositing Al_2O_3 via atomic layer deposition (ALD) as an interlayer for the metal-insulator-semiconductor (MIS) contact of bottom-gated MoS_2 FETs. ALD was utilized to optimize the thickness, leveraging its precise thickness control, and to enhance the uniformity of the Al_2O_3 interlayer on the inert MoS_2 surface. We optimized the coverage of ALD-grown Al_2O_3 by controlling precursor injection pressures on MoS_2 and discovered that improved film uniformity significantly reduces R_c. Additionally, tunneling resistance across the MIS contact was lowered through n-type doping of MoS_2, induced by isopropyl alcohol (IPA) used as a mild oxidant in the ALD process. As a result, with the uniform Al_2O_3 interlayer which induces n-type doping effect we were able to reduce contact resistance by more than two orders of magnitude compared to other MoS_2 FETs fabricated in this study.

ALD Applications
Room Event Hall - Session AA-TuP
ALD Applications Poster Session

AA-TuP-1 The Role of Al2O3 ALD Coating on Sn-Based Intermetallic Anodes for Rate Capability and Long-Term Cycling in Lithium-Ion Batteries*, **Niloofar Soltani**, Amin Bahrami, Daria Mikhailova, Kornelius Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany

The electrochemical performances of CoSn2 and Ni3Sn4 as potential anode materials in lithium-ion batteries (LIBs) are investigated using varying thicknesses of an alumina layer deposited by the atomic layer deposition (ALD) technique. Rate capability results showed that at high current densities, Al2O3-coated CoSn2 and Ni3Sn4 electrodes after 10-ALD cycles outperformed uncoated materials. The charge capacities of coated CoSn2 and Ni3Sn4 electrodes are 571 and 134 mAh g−1, respectively, at a high current density of 5 A g−1, while the capacities of uncoated electrodes are 363 and 11 mAh g−1. When the current density is reduced to 1 A g−1, however, the cycling performances of Al2O3-coated CoSn2 and Ni3Sn4 electrodes fade faster after almost 40 cycles than uncoated electrodes. The explanation is found in the composition of the solid-electrolyte interface (SEI), which strongly depends on the current rate. Thus, X-ray photoelectron spectroscopy analysis of SEI layers on coated samples cycles at a low current density of 0.1 Ag−1, revealed organic carbonates as major products, which probably have a low ionic conductivity. In contrast, the SEI of coated materials cycled at 5 Ag−1 consists mostly of mixed inorganic/organic fluorine-rich Al-F and C-F species facilitating a higher ionic transport, which improves electrochemical performance.

AA-TuP-2 ALD on Particulate Materials: A Data-Driven Review of Technologies, Materials and Applications from the Bottom Up*, **Peter M. Piechulla**, Mingliang Chen,* Delft University of Technology, Netherlands*; Riikka L. Puurunen,* Aalto University, Finland*; J. Ruud van Ommen, Aris Goulas,* Delft University of Technology, Netherlands

The most prominent application of ALD today is semiconductor manufacturing using wafer-based processes, although some of the earliest fundamental ALD studies were carried out on particles. However, ALD on particulate materials (ALDpm) remained a comparably small research area over several decades, and only gained momentum recently, when researchers recognized its ability to tailor nanomaterials (thin films, nanoparticles) with atomic-level control as a valuable trait for a number of particle-based applications. While thermocatalysis was the initial driver of research, and still is important today, drastic innovations to the respective industrial processes are difficult to introduce. New drivers of ALDpm research are highly innovative application fields such as energy conversion (i.e. electrocatalysis) and storage (batteries), where the disruptive potential of ALDpm technology has been recognized in previous application-centered review articles[1].

Here, we cast a broader view on the field. First, we identified approximately 800 original research articles on ALDpm[2], with the key qualification that particles remain in dispersible form after the process. Previous review work[3] had shown the following main categories as defining for ALDpm: reactors, precursor chemistry, support materials, process conditions and properties of coated material. In a second step, we aggregated key qualitative and quantitative data from every article for each of these categories into a single dataset (reduced version online)[2]. Third, we perform a bottom-up analysis of the field of ALDpm by systematic categorization and statistical analysis of the dataset. This includes, e.g., the different reactor engineering approaches to address the challenges of processing particulate substrates, substrate materials, coated materials, and processing conditions. While being agnostic about applications during article screening, we also provide an overview of recent and popular applications. In summary, this review provides both new inspiration for potentially high-volume, high-value applications, and an overview of technologies available to perform ALDpm.

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AA-TuP-3 Atomic Layer Deposition of Silver Catalysts for Hydroxide Exchange Membrane Fuel Cells*, **Gwon Deok Han**,* Sookmyung Women's University, Republic of Korea*; Beum Geun Seo,* Korea University, Republic of Korea*; Hyung Jong Choi,* Stanford University*; Junmo Koo,* Korea Maritime & Ocean University, Republic of Korea*; Fritz Prinz,* Stanford University*; Joon Hyung Shim,* Korea University, Republic of Korea

Hydroxide exchange membrane fuel cells (HEMFCs) are an emerging class of low-temperature fuel cells. A key advantage of HEMFC technology is its operation under alkaline conditions, which enables the use of non-platinum group metals (non-PGMs) as catalysts for fuel cell reactions. In contrast, proton exchange membrane fuel cells (PEMFCs), widely used in fuel cell electric vehicles (FCEVs), require the use of expensive platinum group metals (PGMs). Thus, the development of HEMFCs plays a crucial role in accelerating the growth of the FCEV market.

Silver has been investigated as a promising catalyst for HEMFCs due to its catalytic activity and durability in alkaline environments. Moreover, given its cost-effectiveness compared to platinum, silver catalysts offer a viable solution for significantly reducing the high production costs of FCEVs. Recent studies have proposed various methods for preparing silver catalysts as HEMFC cathode materials. However, there remains ample room for enhancing the electrochemical performance of HEMFCs through the rational design of silver catalysts.

Here, we demonstrate for the first time that an atomic layer deposition (ALD)-based silver catalyst applied to the HEMFC cathode can achieve high fuel cell performance. We successfully coated silver nanoparticles uniformly onto porous carbon nanotubes using plasma-enhanced ALD. The ultralow loading of silver catalysts enabled by ALD contributes to achieving power density exceeding 2 kW/mg_{Ag} in an alkaline environment. This study highlights the potential of ALD as an effective approach for fabricating fuel cell catalysts.

AA-TuP-4 A Study on the Development of a New Ga Precursor for IGZO Thin Films and the Characteristics of Thin Films Using the Same*, **kyung-eun Lee**, Min-hyuk Nim, Taek Seung Yang,* lakematerials, Republic of Korea

New Ga precursors containing -F and -Cl were synthesized, and their reactivity was confirmed. The physical properties of two of these precursors were confirmed. ALD deposition evaluation was performed using these precursors, and the ALD window was confirmed at 160-220 ° C. The deposition result was analyzed using XPS, and step coverage was confirmed through deposition using Trench wafer.

AA-TuP-5 A Study on the Characteristics of Thin-Film Using New in Producers for IGZO Thin-Film*, **HAN-BOM KIM**, MIN-HYUK NIM, Taek Seung Yang,* lakematerials, Republic of Korea

The characteristics of ALD thin films were investigated using a newly developed liquid indium (In) precursor. The ALD window was identified within the temperature range of 160–200℃, and the film composition was analyzed using X-ray photoelectron spectroscopy (XPS). Additionally, step coverage was evaluated through deposition on a trench wafer.

AA-TuP-6 A Study on the Characteristics of IGZO Thin Films Using New Ga and In Precursors*, **Yeon-Soo Kim**, Kyung-Eun Lee, Min-Hyuk Nim, Taek Seung Yang, Chang Ho Song,* LAKE MATERIALS CO., LTD., Republic of Korea*; Nam Eun Kim, Ki-Seok An,* KRICT, Republic of Korea

In this study, we investigated the properties of IGZO thin films using novel Ga and In precursors for the development of next-generation IGZO materials. During the deposition process, DADI and DATI (L2i-8) were used as In precursors, Ga-009 and Ga-026 as Ga precursors, and DEZ as the Zn precursor. These precursors were deposited via atomic layer deposition (ALD) with an In:Ga:Zn composition ratio of 1:1:1. The composition of the deposited IGZO films was analyzed using X-ray photoelectron spectroscopy (XPS), and their mobility characteristics were measured. Based on these results, we identified the optimal precursor combination for IGZO thin films and evaluated their potential application in next-generation high-performance thin-film transistors (TFTs). This study is expected to contribute to the enhancement of IGZO thin-film performance and their application in advanced electronic devices.

AA-TuP-7 Effect of Al_2O_3 Passivation Layer on Atomic Layer Deposited ZnSnO and Al-doped ZnSnO Thin-Film Transistors with Remarkable Bias-Stress Stability*, **Jinheon Choi**, Sahngik Mun, Juneseong Choi, Jaewon Ham, Hyungjeung Kim, Shihyun Kim, Subin Moon, Cheol Seong Hwang,* Seoul National University, Korea (Democratic People's Republic of)

Dynamic random-access memory (DRAM) has followed the direction of increasing integration density, and the cell structure may change from a planar configuration to a three-dimensional (3D) configuration. The stacked cell structure of 3D DRAM requires channel materials for each layer, rendering silicon substrates impractical. Therefore, amorphous oxide semiconductors (AOSs) are feasible candidates due to their excellent uniformity, low leakage current, reasonable mobility (~10 cm^2/Vs), and ability to be deposited by atomic layer deposition (ALD). For 3D DRAM structure, a passivation layer is essential to isolate cells and prevent chemical reactions between AOSs and the ambient environment. Still, AOS properties are significantly influenced by subsequent processing steps, particularly the diffusion of ubiquitous mobile hydrogen. Diffused hydrogen can induce a negative shift of threshold voltage (V_{th}) of thin-film transistors (TFTs), leading to increased power consumption and degrading negative/positive gate bias stress (NBS/PBS) stability. Thus, detailed mechanisms of adopting passivation layers and their optimization are critical for designing effective TFTs in 3D DRAM applications.

This study investigates a new mechanism for the impact of passivation layers on amorphous zinc tin oxide (*a*-ZTO) and Al-doped *a*-ZTO (*a*-AZTO) thin films and their corresponding TFTs and demonstrates optimized properties. Unoptimized passivation layers increased the hydrogen content in *a*-ZTO, leading to a significant V_{th} in the negative voltage direction. Conversely, optimized passivation mitigated hydrogen penetration but caused oxygen deprivation of *a*-ZTO, which still led to a large negative V_{th}. In contrast, for *a*-AZTO TFTs, the pre-existing Al-O bonds in the channel minimized oxygen deprivation, leading to negligible V_{th} variations. Nevertheless, hydrogen diffusion through a HfO_2 gate insulator persisted even under optimized passivation conditions, causing an abnormal hump during PBS tests. Replacing the gate insulator with Al_2O_3 effectively eliminated this anomaly. Finally, using a 10-nm-thick Al_2O_3 gate insulator and indium-tin-oxide source/drain electrodes demonstrated optimized TFT characteristics for 3D DRAM: V_{th} of -0.12 V, field-effect mobility of 10.12 cm^2/Vs, subthreshold swing (SS) of 135 mV/decade, and minimal V_{th} shifts of -15 mV, 1 mV during 1000 s of NBS, PBS tests, respectively.

AA-TuP-8 Ferroelectric-Like Tunnel Switch Behavior of an Antiferroelectric/Dielectric $Hf_{1-x}Zr_xO_2/Al_2O_3$ Bilayer Structure*, **Seungheon Choi**, Seungyong Byun, Han Sol Park, Cheol Seong Hwang,* Seoul National University, Republic of Korea

Ferroic heterostructures have recently emerged as a key methodology for developing advanced ferroic devices. Among them, ferroelectric (FE) and antiferroelectric (AFE) nanolaminate structures have demonstrated improved ferroelectric properties, such as higher remanent polarization (P_r) and lower coercive field (E_c).[1] Furthermore, scaling these structures has shown promise for capacitance-boosting effects due to ferroelectric negative capacitance in direct integration with semiconductor channel structures.[2]

The devices with integrated (anti)ferroelectric complex heterostructures require a systematic understanding of the behaviors of the individual layers and the electrostatic interactions between them. As a preliminary step, this study investigates the unique electrical behavior of AFE/dielectric (DE) bilayer systems, which is crucial for understanding the complex behavior of FE-AFE heterostructures because AFE and FE materials inherently possess dielectric properties.

Specifically, $Hf_{1-x}Zr_xO_2$ thin film exhibiting strong AFE characteristics was deposited using thermal atomic layer deposition, and this film demonstrates ferroelectric-like switching behavior when in direct contact with Al_2O_3 thin film. This bilayer structure shows tunnel-switch behavior similar to that observed in the FE/DE bilayer.[3]

Ferroelectric polarization switching in FE/DE bilayers induces a large internal field, making the dielectric layer susceptible to tunneling. Consequently, charges are trapped at the FE/DE interface, compensating the ferroelectric bound charge. Similarly, in AFE/DE bilayers, interface-trapped charges compensate for spontaneous polarization induced by external bias. Unlike a typical AFE single-layer capacitor, where metal electrode charges are free to move, the trapped charges in the AFE/DE structure are less mobile when the bias is removed. This behavior prevents the AFE layer from back-switching to a non-polar state, and only when a reverse bias is applied can the trapped charge tunnel out, enabling switching. This results in a macroscopic tunnel-switch behavior, distinct from conventional AFE pinched loop hysteresis.

These findings challenge the conventional understanding of antiferroelectricity and emphasize the importance of AFE/DE bilayer as a step toward more complex heterostructures and AFE-based devices. By building a stepwise understanding of these interactions, this work lays the groundwork for advancing next-generation ferroic devices and optimizing their performance.

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AA-TuP-9 Demonstration of Amorphous Oxide Semiconductor Thin Film Transistors with Mold Structure via Channel-Last Process*, Cheol Seong Hwang, **Subin Moon**, Sukin Kang, Jinheon Choi, Sahngik Aaron Mun, Juneseong Choi, Jaewon Ham, Hyungjeung Kim, Shihyun Kim,* Seoul National University, South Korea

Three-dimensional dynamic random-access memory (3D DRAM) offers significant potential to enhance memory density and performance through vertically integrated cell architectures. Among various channel materials, amorphous oxide semiconductors (AOSs) have emerged as promising candidates due to their compatibility with atomic layer deposition (ALD), which enables precise and conformal deposition even on 3D structures. Also, AOS materials exhibit feasible electron mobility (~10 $cm^2V^{-1}s^{-1}$), high uniformity, and low leakage current. However, the electrical characteristics of AOS thin-film transistors (TFTs) can be degraded when adopted to 3D DRAM. When the channel is deposited at the early stages of fabrication, hydrogen incorporation[1] and plasma-induced damage[2] during multi-layer stacking deteriorate TFTs' electrical stability and switching characteristics. Even though several strategies have been proposed to address these issues, an optimal solution for reliably integrating AOS into stacked-layer designs remains challenging.

This study introduces a novel strategy using mold structures that deposit channel materials as a late step to prevent the degradation of AOS characteristics. To define the mold structure, a tungsten sacrificial layer was utilized to define the channel volume, followed by selective tungsten recess to form a SiO_2 mold. Subsequently, an amorphous ZnSnO (a-ZTO) channel was deposited within the predefined empty region of the mold. This approach allows the AOS channel to be deposited after constructing structures, effectively preventing hydrogen incorporation, plasma-induced damage and high-temperature treatments known to degrade material properties. TFTs fabricated within the mold structure demonstrated threshold voltage, saturation mobility and subthreshold swing of -0.13 V, 5.37 $cm^2V^{-1}s^{-1}$, and 230 mV/decade, respectively. These results, comparable to those measured in conventional a-ZTO TFTs[3], confirmed that this approach preserves the intrinsic characteristics of AOS, achieving stable switching performance and reliable device operation.

AA-TuP-10 Utilizing Ethanol as a Pre-reducing Agent for Atomic Layer Deposition MoO_2/TiO_2-Based Metal-Insulator-Metal Capacitors to Enhance Electrical Properties*, **Soomin Yoo**,* Kyunghee University, Republic of Korea*; Seungwoo Lee,* Kyunghee Univerity, Republic of Korea*; Chaeyeong Hwang, Woojin Jeon,* Kyunghee University, Republic of Korea

Metal-insulator-metal (MIM) structures, such as capacitors in DRAM devices, play a critical role in determining the operating characteristics of various memory semiconductors. [1] To enhance the performance of such devices, it is essential to achieve high capacitance in MIM capacitors. Among the various high dielectric constant (*k-value*) materials, TiO_2 is the most promising dielectric because it has a very high dielectric constant of 170 when in a rutile crystalline structure.[2] To obtain rutile TiO_2, an electrode with crystallographic similarity used such as MoO_2 or Ru. In the case of employing MoO_2 as the electrode, MoO_2 is initially deposited in the form of higher oxidation state of MoO_x ($2<x<3$)on a TiN electrode and followed by a thermal annealing process to induce the reduction of MoO_x to MoO_2 through the oxygen scavenging effect of TiN. During this reduction process, a severe morphology degradation of MoO_2 is observed which is induced by simultaneous reduction and crystallization process occur.[3] This morphology degradation of MoO_2 would induce degradation in crystallinity and morphology of TiO_2 thin film deposited on the MoO_2. To prevent morphology degradation during the reduction from of $MoO_x$to MoO_2 and TiO_2 of dielectric layer, a reducing agent was introduced into the MoO_2 ALD process to pre-reduction MoO_x before to crystallization.

In this study, ethanol was introduced after the Mo precursor feeding step, allowing the pre-reduction of MoO_x before the subsequent oxidation step. This approach effectively modulates the oxidation state of MoO_x. First, we compared the oxidation states of Mo ion in the as-deposited thin films using X-ray photoelectron spectroscopy analysis. As a result, the Mo^{6+} ratio in EtOH-treated MoO_x decreased, indicating that the MoO_x thin film was pre-reduced through ethanol treatment. This result well coincides with the X-ray diffraction result of the as-deposited state, indicating that the proportion of the intermediate phase Mo_4O_{11} increased due to the pre-reduction effect after ethanol treatment. Furthermore, atomic force microscopy analysis confirmed the improvement in the morphology of TiO_2 deposited on ethanol-treated MoO_2.

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AA-TuP-11 Nontemplate *in-Situ* Crystallization of Atomic Layer Deposited Molybdenum Dioxide *via* Substitutional Doping of Ruthenium, ***Chaeyeong Hwang,*** Kyunghee university, Republic of Korea; *Myeong Ho Kim, Yoon-A Park, Jin-Sik Kim,* R&D Team 1, UP Chemical Co., Ltd., Republic of Korea; *Woojin Jeon,* Kyunghee University, Republic of Korea

Rutile-phased TiO_2, with its high dielectric constant (~170), is a promising insulator for next-generation metal-insulator-metal (MIM) capacitors [1]. However, due to its thermodynamically high-temperature stable phase, thermal annealing within the actual devices process temperature limits is insufficient for crystallization. Consequently, extensive research has focused on utilizing the template effect, through structural similarity with bottom electrodes to facilitate crystallization. Among various candidates, MoO_2 has emerged as a promising material due to its high work function (~5.8 eV), and superior redox stability [2,3]. A previous study showed that MoO_2 crystallization can be achieved by ALD MoO_x ($2 < x < 3$) on TiN, the utilizing TiN's oxygen scavenging to form rutile TiO_2 and induce the template effect [3].

While promising for mass production, MoO_2 requires a TiN/MoO_2 stacked electrode, increasing the proportion of the bottom electrode within the capacitor thickness limits. This, reduces the thickness of the TiO_2 insulator, exacerbating leakage current concerns due to the small bandgap of TiO_2.

To address this limitation, crystallization technique of MoO_2 on SiO_2 substrates is required. However, in the absence of the oxygen scavenging and template effect, the crystallization temperature of MoO_2 is inevitably higher on SiO_2. This presents a significant challenge as MoO_3, a component of MoO_x ($2 < x < 3$), undergoes sublimation at 550℃ [4]. Consequently, crystallization leads to severe mass loss, resulting in a discontinuous MoO_2 thin film with exposed SiO_2, which interferes with MIM capacitor formation.

In this study, we adopted Ru doping to facilitate MoO_2 crystallization on SiO_2 while maintaining its applicability as a MIM capacitor film. Increasing Ru concentration reduced the crystallization temperature of MoO_2, ultimately enabling as-deposited crystallization. Comprehensive analyses confirmed that Ru-doped MoO_2 successfully induced rutile TiO_2 formation, verifying its suitability as an electrode.

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AA-TuP-12 Comprehensive Study on ALD HfO_2-based RRAM with Next-Generation Ru Electrodes for High-Performance Memory Technology, ***Yunsur Kim,*** *Jiyong Woo,* Kyungpook National University, Republic of Korea

Emerging memory technologies are gaining significant attention as researchers seek to revolutionize the existing memory hierarchy. These technologies, which rely on resistance-based data storage, include phase change memory (PCM), magnetoresistive random access memory (MRAM), ferroelectric random access memory (FeRAM), and resistive random access memory (RRAM). Among them, RRAM stands out due to its fast switching speed, low power consumption, sub-10 nm scalability, long endurance, and potential for non-volatile storage and neuromorphic computing.

RRAM operates by modulating resistance through the formation and rupture of a conductive filament (CF) within a metal oxide layer. When the applied voltage exceeds a threshold, oxygen vacancies (V_0) migrate and form a CF, resulting in a low resistance state (LRS). Reversing the voltage disperses the V_0, rupturing the CF and restoring a high resistance state (HRS). This resistive switching behavior has been extensively studied in binary metal oxides such as hafnium oxide (HfO_x), titanium oxide (TiO_x), tantalum oxide (TaO_x), and aluminum oxide (AlO_x) due to their compatibility with the CMOS back-end-of-line (BEOL) process.

The deposition method for the switching layer significantly impacts RRAM performance. Common techniques include pulsed laser deposition (PLD), atomic layer deposition (ALD), and reactive sputtering. ALD is favored for its precise thickness and uniformity control, ensuring reliable device characteristics.

Electrode selection also plays a crucial role, affecting switching speed, endurance, and retention. Conventional electrodes include Al, Ti, Cu, and W, but noble metals such as Ru, Ir, and Pt are being explored for improved performance. Among them, Ru is of particular interest due to its high work function (~4.7 eV), low resistivity (7 μΩ·cm), and strong chemical stability, enhancing RRAM reliability.

In this study, we investigated the resistive switching properties of HfO_x-based RRAM with different stack configurations. We compared RRAMs with a stoichiometric HfO_2 layer deposited via ALD and a sub-stoichiometric HfO_x layer formed by sputtering. Additionally, we examined the impact of various electrode materials, including W, Ti, Ta, and Ru. The ALD-HfO_2-based RRAM with a Ru bottom electrode exhibited superior endurance, excellent cycle-to-cycle uniformity, and high device-to-device uniformity. These findings highlight the importance of optimizing both the switching layer and electrode material for high-performance RRAM applications in next-generation memory and neuromorphic computing.

AA-TuP-13 Effect of the Number and Distribution of Al_2O_3 Atomic Layer Deposition Cycles Within Hfo_2 Layer on Ferroelectric Characteristics, ***Hyoungjin Park,*** *Jiyong Woo,* School of Electronic and Electrical Engineering, Kyungpook National University, Republic of Korea

Since the 1990s, extensive research has been conducted on ferroelectric devices, which are considered emerging candidates that can replace the conventional charge-based memory devices. The spontaneous polarization of these materials, commonly observed in ternary perovskite compounds such as $BaTiO_3$, $PbZr_xTi_{1-x}O_3$, and $Sr_2Bi_2TaO_9$, results from the rapid reorientation of dipoles, enabling fast switching speeds and excellent endurance characteristics. However, the practical application of these materials is hindered by their complex chemical composition, which lacks compatibility with standard semiconductor fabrication processes, as well as the requirement for relatively thick films (>100 nm) to achieve stable polarization. Recently, thin HfO_2 films have garnered significant attention due to their remarkable ferroelectric properties. These properties originate from the formation of a specific orthorhombic (o) crystalline phase, induced by high-temperature annealing. However, because the o-phase is thermodynamically unstable, strategies such as dopant incorporation and post-metallization annealing, which introduce global strain, have been employed to enhance its stability. Studies have demonstrated that ferroelectricity in HfO_2 can be realized through doping with elements such as Si, Zr, and Al, followed by high-temperature annealing. Among these, Al-doped HfO_2 (Al:HfO_2) has been widely investigated due to its excellent thermal stability and reduced leakage current, attributed to its wide energy bandgap. The fabrication of Al:HfO_2-based ferroelectric devices commonly involves atomic layer deposition (ALD), where Al_2O_3 layers are periodically introduced into HfO_2 films to incorporate Al dopants. Prior research has focused on optimizing ALD process parameters for HfO_2 and Al_2O_3 to enhance ferroelectric properties from a fabrication standpoint. In addition, advanced annealing techniques have been explored to promote crystallization at lower temperatures and stabilize the o-phase by controlling the cooling process. Beyond annealing optimization, interfacial engineering strategies have been developed to sustain the o-phase, such as integrating an additional dielectric layer within doped HfO_2 films or modifying the ferroelectric/electrode interface. Despite these advancements, most studies assume a uniform dopant distribution throughout the HfO_2 layer. In this work, we systematically investigate the impact of Al_2O_3 distribution within the HfO_2 matrix on ferroelectric performance. Furthermore, we demonstrate that asymmetric doping, wherein Al dopants are concentrated primarily in the bottom region of the HfO_2 layer, leads to enhanced polarization characteristics.

AA-TuP-14 Atomic Layer Deposited Single-Atom Catalysts of Pt/Co3O4 for Improved Electrocatalytic Hydrogen Evolution Reaction Performance, *Yue Huang,* ***Ying-Jie Ma,*** *Ai-Dong Li,* Nanjing University, China

Atomic layer deposition (ALD) technique enables precise control over material synthesis at the atomic scale, which has been successfully employed to design and fabricate single-atom catalysts. In contrast to traditional catalyst synthesis methods, the self-limiting nature of ALD ensures the production of catalysts with monodisperse sizes and uniform distribution on the support, leading to enhanced catalytic activity, selectivity, and stability. Furthermore, the ALD process results in minimal contamination from residual salts, therefore it is urgent to develop ALD-derived single-atom catalysts and their catalytic properties.

In this study, ALD was explored to regulate the pulse time of the platinum precursor in the chamber, thereby controlling the uniform dispersion of Pt atomic catalysts on Co_3O_4 support. Isolated metallic Pt atoms directly bonded to the support. The metal atom-support interaction generated charge transfer between them, which greatly modulated its electronic and catalytic properties. We evaluated the performance of single-atom Pt/Co3O4 catalysts.Interestingly, the catalyst demonstrated strong hydrogen evolution reaction (HER) activity under alkaline conditions, exhibiting a remarkably low overpotential of only 34 mV at 10 mA cm^{-2} (Figure 1). Furthermore, the interaction between the Pt single atoms and the Pt-O-Co bond interface enhances the stability of the catalyst surface, preventing aggregation or cluster formation, which contributes to an extended catalyst lifespan. Our results provide a new way to develop efficient and stable single-atom electrocatalytic materials using ALD.

AA-TuP-15 Atomic Layer Deposited Amorphous High-entropy Oxide Protective Layer for Stable Zinc Metal Anode*, Li-Ling Fu, **Ai-Dong Li**,* Nanjing University, China

Aqueous zinc ion batteries (ZIBs) have attracted much attention in the field of future large-scale energy storage, with the advantages of high theoretical capacity (820 mAh/g and 5855 mAh/cm^3), low reduction potential (-0.76 V), high safety and low cost. However, dendrites and side reactions on the surface of the zinc metal anode greatly limit the cycling stability of zinc ion batteries. To address this problem, an effective method is to construct an artificial protective coating on the surface of the zinc anode.The preparation of conventional single metal oxide coating materials using atomic layer deposition (ALD) processes can inhibit zinc dendrite generation to some extent. However, unitary, binary or ternary oxides are many times insufficient to address the various challenges in zinc ion batteries.

In this work, inspired by the concept of high entropy, we constructed $TiYZrAlSnO_x$ amorphous high-entropy oxides (HEOs) coatings on the surface of zinc anode by atomic layer deposition (ALD) as shown in Fig. 1. This high-entropy oxide electrode has abundant zinc-friendly sites due to the cocktail effect generated by mixing various zinc-friendly elements with corrosion-resistant elements, which promotes uniform zinc deposition and suppresses zinc dendrites and by-products on the zinc anode surface. Moreover, this high-entropy oxide enhances the migration kinetics of Zn^{2+}, facilitates the desolvation process of Zn^{2+}, and reduces the zinc deposition energy barrier.

In addition, this amorphous high-entropy oxide coating can effectively inhibit the hydrogen precipitation reaction and reduce the generation of by-products. As a result, this Zn@HEOs anode exhibits excellent cycling stability more than 4000 h at 5 mA cm^{-2} and 1 mAh cm^{-2}. Compared with the conventional high-entropy oxide preparation process, this work combined with ALD technology to realize an amorphous high-entropy oxide protective layer on the surface of zinc anode at low temperature, which provides an alternative strategy to achieve a stable zinc metal anode.

AA-TuP-16 Transforming Waste Textiles into VC/V_2O_{3-x}-Decorated Porous Carbon for Flexible Battery Hosts*, **Viet Phuong Nguyen**, Seung Mo Lee,* Korea Institute of Machinery & Materials (KIMM), Republic of Korea

In this study, we present a sequential synthesis approach combining V_2O_5 atomic layer deposition with subsequent carbothermic reduction to transform waste textiles into porous, flexible carbon textiles uniformly decorated with VC/V_2O_{3-x} hybrid nanoparticles. This innovative material serves as a robust and flexible host for both sulfur cathodes and lithium metal anodes in flexible Li–S batteries. The defective V_2O_{3-x} component effectively traps polysulfides, while the conductive VC phase catalytically promotes their fragmentation. Additionally, the well-dispersed VC/V_2O_{3-x} nanoparticles act as lithiophilic sites, facilitating uniform lithium nucleation and suppressing dendrite growth. As a result, the full cell exhibits outstanding rate performance (882 mAh g^{-1} at 5 C) and an exceptionally low capacity decay rate of 0.02% per cycle over 1000 cycles at 1 C. Even at a high sulfur loading of 7.0 mg cm^{-2}, the battery achieves a remarkable areal capacity of 6.29 mAh cm^{-2} at 0.2 C. This work offers an effective strategy to simultaneously mitigate the polysulfide shuttle effect and lithium dendrite formation, paving the way for high-performance, flexible Li–S full batteries.

AA-TuP-17 Dual Ferroelectric Stack by ALD with Tunable Coercive Voltage for High-Density 3D Memory Applications*, Jiyong Woo, **Jiae Jeong**,* Kyungpook National University, Republic of Korea

Doped HfO_2-based thin films have been regarded as promising material for non-volatile memories due to their scalability and complementary metal-oxide-semiconductor compatibility. To induce the ferroelectricity in HfO_2 film, a specific dopant needs to be incorporated into the HfO_2 layer, followed by a high-temperature annealing process, which enables the formation of an orthorhombic phase. This structural transformation facilitates the generation of permanent dipoles, allowing the HfO_2 dielectric layer (DL) to transform into a ferroelectric layer (FL). Among various dopant candidates, Zr-doped HfO_2 (HZO) has attracted attention because the orthorhombic phase in HZO can be achieved at a relatively low temperature (400 ℃) while exhibiting a high remnant polarization (P_r).

Due to its low thermal budget, HZO is considered a strong candidate to replace conventional charge-trap approaches in 3D ferroelectric NAND applications. In a ferroelectric field-effect transistor structure, where the HZO FL is positioned between the gate and oxide channel layers, applying a gate voltage aligns the dipoles within the FL either the downward or upward direction. This dipole reorientation modulates the threshold voltage (V_T) by either attracting or repelling electrons at the channel interface, creating a memory window (MW) in transfer characteristics. Consequently, MW is created by the difference between high and low V_T. Fine-tuning multilevel V_T states can be obtained within the MW is crucial for enhancing memory density. The V_T range is primarily determined by the coercive voltage (V_C) of FL. While previous research has confirmed that the HZO FL exhibits a high P_r due to abrupt polarization switching at V_C, it has also been observed that the V_T remains unchanged even at higher voltages. Various approaches have been explored to enhance V_C, including incorporating an Al_2O_3 DL within the HZO FL or constructing dual-layer HZO FL structures with varying thicknesses.

In this study, we focus on investigating ferroelectric properties by examining the relationship between ramping voltage and V_C modulation, P_r control. Furthermore, our findings provide insights into applications where precise adjustments of P_r and V_C in ferroelectric capacitors are required. This adjustability is achieved through the sequential stacking of heterogeneous FLs, where each layer is deposited using atomic layer deposition (ALD). Specifically, Al-doped HfO_2, which exhibits more gradual polarization switching at V_C, was integrated with HZO. Through the synergistic interaction between the heterogeneous FLs, we successfully tuned P_r values from 1 to approximately 20 μC/cm^2 while varying V_C from 1 to 3 V.

AA-TuP-18 Inducing the Tetragonal-Phase HfO_2 in ZrO_2/HfO_2 Stack by Introducing the Controlled Interfacial Layer*, **Woo Young Park**,* WONIKIPS, Republic of Korea

ZrO_2 and HfO_2 have been employed as insulators in dynamic random access memory (DRAM) capacitor and gate dielectric applications. Moreover, HfO_2 was introduced to the ZrO_2/HfO_2 laminated structure for enhancing the dielectric constant (*k*) because it was reported that tetragonal-phased HfO_2 has a *k* value of 46.9. In this regard, various results for achieving a tetragonal-phased HfO_2 thin film deposition process have been reported. However, the formation of a polymorph of the HfO_2 thin film, the monoclinic phase, was inevitable. Furthermore, the crystal composition of HfO_2, a ratio of tetragonal and monoclinic phases, is strongly affected by the film thickness, resulting in a severe k value change in HfO_2 thin film depending on its thickness. This *k* value change of HfO_2 makes it hard to obtain a designated *k* value of ZrO_2/HfO_2 laminated structure by controlling the HfO_2 layer thickness.

In this paper, we introduced a “controlled interfacial layer (CIL)” for suppressing the changing of the *k* value of the HfO_2 layer depending on its layer thickness in the ZrO_2/HfO_2 laminated structure. The newly introduced CIL allows to maintain the Tetragonal phase of HfO2 even if the thickness of the HfO2 layer increases in a given ZrO2/HfO2 stack structure. Consequently, relatively high and constant *k* values of HfO_2 were obtained in the various ZrO_2/HfO_2 laminated structures. Finally, an optimized ZrO_2/HfO_2 laminated structure with the CIL was investigated for the DRAM capacitor dielectric application.

AA-TuP-19 Boosting SERS Performance of Moo_3 Substrates via ALD Surface Modifications*, **Yanqiang Cao**, Wenyue Yin,* Nanjing University of Science and Technology, China

Surface Enhanced Raman Scattering (SERS) has emerged as a highly potent analytical technique, finding extensive applications in chemical and biological sensing, primarily attributed to its remarkable sensitivity and distinct molecular fingerprinting capabilities. Among a diverse array of SERS substrates, MoO_3 based materials have garnered substantial attention owing to their unique semiconductor characteristics and great potential for high performance SERS applications. Nevertheless, the inherent SERS performance of MoO_3 substrates frequently requires enhancement to satisfy the demands of practical applications.

In this research, the surface of MoO_3 was treated using Atomic Layer Deposition (ALD) technology, leading to a notable improvement in the SERS performance of the MoO_3 substrate. By depositing a thin and uniform layer of Al_2O_3 along with hydroxyl functional groups on the surface of MoO_3, the charge separation efficiency within the $MoO_3@Al_2O_3$ composite was significantly enhanced, approximately doubling the SERS performance of orthorhombic MoO_3. Subsequently, the $MoO_3@Al_2(MoO_4)_3$ heterojunction was fabricated through a calcination process, further augmenting the SERS performance of the MoO_3 substrate. Ultimately, a SERS substrate with high sensitivity, excellent uniformity, and remarkable stability was successfully developed.

During the exploration of the SERS performance enhancement mechanism, it was discovered that the SERS performance of the $MoO_3@Al_2O_3$ substrate, both before and after calcination, exhibited a strong correlation with the thickness of the ALD deposited Al_2O_3 coating. The modified MoO_3 substrate and the $MoO_3@Al_2(MoO_4)_3$ heterojunction substrate demonstrated a detection limit of 10^{-8} M for methylene blue (MB) molecules and retained excellent SERS performance even after 90 days. Through precise control of the ALD cycle number of Al_2O_3, we systematically investigated the impact of the Al_2O_3 thickness on the SERS performance of the substrate, thereby deepening our understanding of the strategies for enhancing the performance of semiconductor based SERS substrates.

AA-TuP-20 ZrO_2 Seed-layer Induced Crystallization of $Hf_{1-x}Zr_xO_2$ with Energy Barrier Lowering Effect of the Ferroelectric Orthorhombic Phase Transition

Kyongjae Kim*, Eunseo Jo, Myeonggeun Yoo, Youseung Rim,* Sejong University, Republic of Korea

Ferroelectric $Hf_{1-x}Zr_xO_2$ has garnered significant for the next generation of non-volatile memory material, architecture and logic circuits.For materials to integrate to devices, research of ferroelectric $Hf_{1-x}Zr_xO_2$ has been studied terms of the controllability of dopants, strain, surface energy, and oxygen deficient to meet criteria beyond high remnant polarization, including low leakage current levels, high stability and durability. However, the challenge of achieving ferroelectricity enhancement with reliability at back-end-of-line compatibility, which requires less than 400°C remains. [1], [2] Here, we demonstrate a ZrO_2-seed layer embedded ferroelectric $Hf_{1-x}Zr_xO_2$ films to control the phase ratios of tetragonal, orthorhombic, and monoclinic at low temperatures (<400°C). The ZrO_2-seed layer affects the initial growth with small grain nuclei of $Hf_{1-x}Zr_xO_2$ films which can manifest the ferroelectric transition. As a result, the ZrO_2-seed layer not only reduces the post-metallization annealing temperature but also achieves high remnant polarization with endurance exceeding 10^9 cycles. We also present that the different thickness of ZrO_2-seed layer affects ferroelectric properties. Specifically, ZrO_2-seed layer (5 cycles) embedded $Hf_{1-x}Zr_xO_2$ exhibits 30.3 $\mu C/cm^2$ of the remnant polarization value at 350 °C, respectively. These values showed better than those of $Hf_{1-x}Zr_xO_2$ films without (12.1 $\mu C/cm^2$) and with 7 cycles of ZrO_2-seed layer (13.0 $\mu C/cm^2$). It could be attributed to the different ratios between the non-ferroelectric tetragonal phase and the ferroelectric orthorhombic phase related to the ZrO_2-seed layer induced phase transition during the post-metallization annealing. Our finding suggests that atomic-level control of the ZSL is crucial for enhancing ferroelectricity while lowering the post-metallization annealing temperature. This indicates that optimizing the ZrO_2-seed layer is essential for high-performance ferroelectric $Hf_{1-x}Zr_xO_2$, enabling it to be compatible with back-end-of-line integration for future non-volatile memory architecture.

Acknowledgments

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AA-TuP-21 Highly Conductive Transparent Hybrid Superlattices with Excellent Gas-Barrier Properties and Flexibility

Myung Mo Sung, Hanyang University, Korea*;* ***Quang Khanh Nguyen,*** Hanyang University, Korea, Viet Nam

Transparent electrodes and passivation layers find extensive application in optoelectronic devices such as light-emitting diodes, solar cell. Integrating transparent conductive and gas diffusion barrier layers into a unified component holds promise for enhancing device performance and cost-effectiveness. In this study, we present a novel transparent conductive gas diffusion barrier achieved through a cutting-edge hybrid superlattice structure, combining ZnO with self-assembled monolayers. Fabricated using low-temperature atomic layer deposition and molecular layer deposition techniques, the superlattice demonstrated exceptional electric conductivity, attributed to the precisely designed phase-composite ZnO nanolayers. We systematically optimized the ZnO nanolayer thickness to attain a well-defined amorphous/crystalline phase-composite structure. The resulting superlattice, with a thickness of 100 nm, exhibited a low sheet resistance of 65 $\Omega\ sq^{-1}$ and maintained over 90% transmittance at a wavelength of 550 nm. The organic layers within the superlattice structure contribute to resilience against environmental degradation and mechanical deformation, achieved through the formation of a multilayered structure that effectively decoupled defects in the underlying layers. The hybrid superlattice exhibited robust electric conductivity, surpassing 1400 $S\ cm^{-1}$ even after 15 days in damp heat conditions and exceptional moisture barrier characteristics (water vapor transmission rate $< 4 \times 10^{-7}\ g\ m^{-2}\ day^{-1}$) alongside remarkable flexibility that retained the performance after 10,000 bending cycles. These compelling features position the hybrid superlattice as a promising candidate for transparent conductive gas diffusion barriers, with diverse applications in emerging optoelectronics.

AA-TuP-22 Enhanced Growth Stability of ZrO_2, HfO_2, and In_2O_3 Deposited by Liquid Injection Atomic Layer Deposition

Il-Kwon Oh, ***Soon-Kyeong Park****, Ji-Won Jang,* Ajou University, Republic of Korea

In conventional thermal atomic layer deposition (ALD), when a high number of ALD cycles is conducted, the vapor pressure of the precursor consumed often exceeds that generated, leading to a critical issue where the thickness of the deposited film decreases. This issue negatively impacts targeting the desired thickness of the thin film at high ALD cycles. Liquid injection atomic layer depositionvia a liquid deliverysystem (LDS) is an ideal thin-film deposition method for addressing this issue. Utilizing LDS ensures a consistent vapor pressure ratio of precursor during the process [1]. The LDS can handle most solid and liquid compounds including low vapor pressure, thermally labile, and viscous ones for the synthesis by ALD of thin films [2]. The LDS employment for the synthesis by metal-organic chemical vapor deposition (MOCVD) and ALD has been reported for vanadium oxide, and titanium oxide thin films [3-4]. Despite these advantages, research on thin films deposited via liquid injection atomic layer deposition is still few.

In this study, the excellent growth stability of ZrO_2, HfO_2, and In_2O_3, which are commonly used as gate dielectrics and channel materials, was confirmed through liquid injection atomic layer deposition, and the growth characteristics of these materials at high ALD cycles were specifically investigated. Cyclopentadienyl Tris(dimethylamino) Zirconium (Cp-Zr), Cyclopentadienyl Tris (dimethylamino) Hafnium (Cp-Hf), and (3-Dimethylaminopropyl) dimethyl indium (DADI) were used as the precursors, and O_3, H_2O as the oxygen source, to deposit on Si substratesSpectroscopic ellipsometry measurements were conducted to confirm the thickness of thin films deposited at various ALD cycles. X-ray photoelectron spectroscopy (XPS), which allows for the analysis of chemical composition ratios, was used to determine whether stable vapor pressure was maintained to form the thin film even at high ALD cycles. Consequently, this study is expected to provide insights into achieving stable thin film growth and precise thickness control for high ALD cycle applications through liquid injection atomic layer deposition.

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AA-TuP-23 Enhanced Cryogenic Stability and Endurance of CMOS-Compatible ALD $HfZrO_2$ FeCAPs with Optimized WO Interfacial Layer

Eunjin Kim*, Jiyong Woo,* Kyungpook National University, Republic of Korea

$HfZrO_2$-based ferroelectric capacitors (FeCAPs) are gaining attention as promising candidates for non-volatile memory devices due to their CMOS compatibility and ability to achieve low aspect ratios. Despite these advantages, a major challenge arises during the post-metallization annealing (PMA) process, which is crucial for realizing ferroelectricity. These

FeCAPs, typically fabricated on W-plugs, are prone to the unintended formation of a non-stoichiometric WO_x layer at HZO-electrode interface. This unwanted oxide layer induces defect states and increases oxygen vacancy (V_O) concentrations through a scavenging effect. To address this, we introduced sputtered amorphous WO interfacial layer(IL) engineering. The polarization-voltage (P-V) measurements showed remnant polarization (P_r) greater than 20 $\mu C/cm^2$ in the ALD-grown HZO FeCAP. However, the achieved polarization was vulnerable to PMA times, exhibiting leaky P-V curve explained by uncontrollable defects due to interfacial WO_x near the bottom electrode (BE). The introduction of 10 nm WO IL into the HZO FeCAP not only increased $2P_r$ to 52 $\mu C/cm^2$, but also enhanced the thermal stability of achieved P_r. Since a less prominent top interfacial layer was observed in the Transmission Electron Microscopy image, a sandwich-type WO/HZO/WO was also fabricated, but P_r was rather degraded. Next, the impact of WO IL stoichiometry was investigated by varying Ar/O_2 gas ratio during WO IL deposition. Unlike HZO FeCAP, where P_r was degraded noticeably with decreasing temperature, insertion of WO IL made P_r immune to temperature. Note that $2P_r$ greater than 58 (or 40) $\mu C/cm^2$ at 300 (or 123) K was achieved for the HZO/$WO_{2.8}$ FeCAP. The endurance characteristic proportional to the stoichiometry of WO IL. The relatively large amount of V_Os in the $WO_{2.4}$ IL can be easily clustered to form leakage paths, causing breakdown failure after 10^4 cycles. In contrast, leveraging more stoichiometric WO ILs (e.g., $WO_{2.8}$ or WO_3) can alleviate the interfacial or bulk defects that cause dipole pinning in the HZO, thereby improving endurance over 10^8 cycles. However, when stoichiometric WO_3 IL was used, P-V curve with increased coercive voltage began to be measured only at slow frequencies. This means that the applied voltage is less effectively used to rotate the dipoles in the HZO/WO_3 FeCAP. Therefore, introducing $WO_{2.8}$ IL enables an environment, where the intrinsic HZO properties can be robustly resilient to the interface defects by mitigating W BE scavenging effect. This resulted in larger diffraction intensity of the orthorhombic-phase in the HZO/$WO_{2.8}$, allowing most of the formed dipoles in the HZO to participate in switching.

AA-TuP-24 Thermal Atomic Layer Deposition of Ru-incorporated Molybdenum Carbide Thin Films via Inter-ligand Reaction for Advanced Copper Metallization*, Jeong Hwan Han,* ***Ji Sang Ahn,*** Seoul National University of Science and Technology, Republic of Korea

As the width of metallization wire in semiconductor device decreases, there is an increase in the overall resistance of Cu interconnect including diffusion barrier and seed layer. This not only limits the device speed but also hinders further scaling down of the device. Therefore, there has been growing demands for the development of materials that can serve as both the Cu diffusion barrier and seed layer. In this regard, atomic layer deposition (ALD) is an essential technique due to its ability to precisely control thickness down to the sub-nm level and excellent step coverage in complex structure. For decades, transition metal nitride and carbide multi-layer such as Ti/TiN, Ta/TaN, Ta/TaCN are widely introduced as Cu diffusion barrier and liner. Molybdenum-based carbide and nitride materials have recently gained attention as promising options for diffusion barrier and liner due to their high melting point, low resistivity, excellent thermal stability, and low reactivity with Cu.

In this study, Ru-incorporated MoC_x thin films were deposited from metal-organic Mo and Ru precursors by thermal ALD using inter-ligand reaction. Herein, Ru precursor was served as the counter-reactant for the Mo precursor without the use of common ALD reactant gases such as H_2 and O_2. The crystallinity, chemical binding states, impurity, and electrical characteristics of Ru-incorporated MoC_x were investigated. Additionally, atom probe tomography (APT) analysis confirmed the incorporation of Ru into the MoC_x matrix. The Cu diffusion barrier performance of ALD Ru-incorporated MoC_x was evaluated by fabricating Cu/Ru-incorporated MoC_x/Si structure, which was subsequently annealed at the high-temperatures for 15 min. The seed layer performance was also evaluated by carrying out Cu electroplating deposition depending on the thickness of the Ru-incorporated MoC_x films. In conclusion, Ru-incorporated MoC_x deposited by ALD can be considered a promising option for combined Cu diffusion barrier and seed layer applications.

AA-TuP-25 Stabilization of Metastable Rutile TiO_2 Through Engineering of the Upper Layer for Memory Applications*,* ***Jeon Ji Hoon,*** *Kim Seong Keun,* Korea Institute of Science and Technology (KIST), Republic of Korea

The increasing demand for DRAM memory density necessitates continuous scaling down of device size. The reduction in capacitor size compromises charge storage, leading to uncertainties in data read operations. To address this, materials with a higher dielectric constant than the currently used HfO_2 and ZrO_2 (~40) are needed. Rutile TiO_2, with a dielectric constant of 80–170 depending on crystallographic orientation, is a promising alternative. However, its metastable nature and high formation temperature pose challenges for integration.

A common approach to stabilizing rutile TiO_2 in the as-grown state via ALD is to use bottom electrodes such as RuO_2, IrO_2, SnO_2, and MoO_2, which provide lattice matching. However, this approach requires replacing existing bottom electrodes, complicating integration with current DRAM architectures. TiN, the industry-standard bottom electrode, does not have lattice matching with rutile TiO_2, making it difficult to apply these conventional methods.

In this work, we address the challenge of forming rutile TiO_2 in environments without lattice matching. Instead of relying on lattice-matched bottom electrodes, we induce rutile TiO_2 crystallization by introducing an upper layer with a rutile crystal structure. This approach enables the integration of high-k rutile TiO_2 while maintaining the TiN bottom electrode, ensuring compatibility with existing DRAM fabrication processes. Additionally, we discuss potential challenges associated with this method in the context of DRAM capacitors.

AA-TuP-26 Enhancing Plasma Resistance in Semiconductor Equipment with Atomic Layer Deposition Thin Films*, Young Yeon Ji,* ***Bongjun Koo,*** *Changsup Kwon, In-rae Park,* Hansol IONES, Republic of Korea

This study applies ALD coating to enhance plasma resistance and physical properties of semiconductor equipment chamber components in the corrosive environment of semiconductor processes. High-density plasma or corrosive gas can cause surface corrosion and contaminant particles to accumulate in the components, which can adversely affect semiconductor processes. To address this issue, ceramic material coatings are being applied to protect semiconductor equipment chamber components. Ceramic materials with excellent plasma resistance properties can be coated using various coating methods such as PVD (Physical Vapor Deposition), APS (Atmospheric Plasma Spray), AD (Aerosol Deposition), and ALD (Atomic Layer Deposition). Especially, ALD coating offers high resistance to plasma environments, superior step coverage, and conformity compared to other coating methods, enabling high-density uniform deposition even in complex 3D structures, making it a promising next-generation coating technology for semiconductor equipment chamber components. In this study, ALD coating was applied through the chemical reaction of yttrium, aluminum precursors along with oxidants such as water, O2, and O3 to produce yttrium oxide (Y2O3), aluminum oxide (Al2O3), and yttrium aluminum garnet (YAG) thin films with excellent plasma resistance properties. The physical properties and impurities in the deposited coating layer were analyzed using XPS, XRD, nano-indentation and SEM. These coating layers were applied to substrates made from various materials including metal, ceramic, polymer and complex 3D structures. This result is expected to enhance the reliability and performance of the semiconductor equipment chamber components.

AA-TuP-27 Crystallization Annealing-Free Ferroelectric Tunnel Junctions with ZrO_2 Seed-layer and HfO_2-ZrO_2 Superlattice*,* ***Kwang Min Jeong,*** *You Seung Rim,* Department of Semiconductor Systems Engineering and Convergence Engineering for Intelligent Drone, Sejong University, Republic of Korea

Ferroelectric tunnel junction (FTJ) devices have recently been considered promising candidates for non-volatile memory due to their non-destructive readout, low power consumption, and fast operation speed. Additionally, their two-terminal structure enables high-density integration with a compact $4F^2$ cell size. [1] In FTJs, the spontaneous polarization of the ferroelectric layer can be switched by an applied electric field, resulting in electrical resistance modulation depending on the polarization orientation. This phenomenon, known as tunneling electroresistance (TER), arises from changes in the electrostatic potential profile across the ferroelectric layer.[2] In this work, we investigate the switching mechanism of an Al/supercycle engineered ferroelectric HfO_2-ZrO_2/ZrO_2-seed/n++Si FTJ structure under different rapid thermal process (RTP) temperature. The ZrO_2 seed layer influences the initial growth of the HZO films by promoting the formation of small grain nuclei, which are crucial for the ferroelectric phase transition at low temperature.[3] Furthermore, the application of a HfO_2-ZrO_2ferroelectric superlattice enhances ferroelectricity due to tensile stress induced by the mismatch in their coefficient of thermal expansion (CTE) during atomic layer deposition and RTP. [4] Here, we demonstrate an annealing-free FTJ device that exhibits ferroelectricity even without RTP. Our strategies for achieving low-temperature processing, along with a supercycle-engineered ferroelectric layer, lead to an in-depth understanding of their operating mechanism and pave the way for the development of ferroelectric memory switching devices.

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AA-TuP-28 Synthesis and Characterization of $SrTiO_3$ Thin Films by Atomic Layer Deposition with $Sr(dmts)(hfac)_2$ and $(CpMe_5)Ti(OMe)_3$

***Sangyeon Jeong**, Jaejun Lee, Woongkyu Lee,* Department of Materials Science and Engineering, Soongsil University, Republic of Korea

High-capacitance capacitors are essential for achieving the high integration of DRAM. To meet this demand, trench structures with high aspect ratios are employed, and atomic layer deposition (ALD) is utilized to ensure excellent step coverage and uniformity. Traditionally, capacitance has been enhanced by reducing the dielectric thickness, however, this approach leads to increased leakage current, necessitating the use of high-k materials. $SrTiO_3$ (STO) has been extensively studied as a next-generation dielectric material because of its high dielectric constant exceeding 100. However, the low bandgap of $SrTiO_3$ (3.1–3.2 eV) and issues such as crack formation induced by film shrinkage during annealing have led to increased leakage current, presenting significant challenges for its application. From the perspective of precursors, cyclopentadienyl (Cp)-based Sr precursors have been the most extensively studied due to their high thermal stability and sufficient reactivity. However, their excessive interaction with the surface results in the retention of carbon ions from the ligands in the thin film, leading to the formation of strontium carbonate. This poses critical issues in impeding high quality perovskite $SrTiO_3$ phase formation.

In this study, we developed an ALD process for $SrTiO_3$ thin films using a novel Sr precursor, $Sr(dmts)(hfac)_2$, developed by the Korea Research Institute of Chemical Technology. To address the issue of $SrCO_3$ formation during SrO deposition, thermodynamically stable SrF_2 was deposited using $Sr(dmts)(hfac)_2$ and H_2O, while TiO_2 was deposited using $(CpMe_5)Ti(OMe)_3$ and O_3. The subcycle ratio of SrF_2 to TiO_2 was optimized to achieve stoichiometric cation composition of Sr:Ti = 1:1. Finally, post-deposition annealing in an air ambient eliminated fluorine and reduced carbon contamination of SrF_2-TiO_2, enabling the formation of stable $SrTiO_3$ thin films. In this study, we present SEM, XPS, XRD, and other analyses demonstrating the effective removal of fluorine impurities and the successful formation of the perovskite crystalline structure in $SrTiO_3$. The $SrTiO_3$ thin films exhibited a high bulk dielectric constant exceeding 100 in planar-structured metal-insulator-metal capacitors, highlighting their potential as a next-generation dielectric material for DRAM capacitors.

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AA-TuP-29 Ozone Post-Treatment for Highly Stoichiometric TiO_2 Thin Films with Improved Dielectric Performance

***Juan Hong**, Hyeongjun Kim, Woongkyu Lee,* Department of Materials Science and Engineering, Soongsil University, Republic of Korea

In the semiconductor industry, as DRAM and other memory devices continue to shrink, high-k dielectrics are crucial for maintaining capacitance and reducing leakage current. Atomic layer deposition (ALD) processes, which enable precise thickness control, excellent step coverage, and large-area uniformity of thin films, has been essential for the deposition of high-k materials. TiO_2, a high-k material, has gained significant attention as a next-generation dielectric material due to its high permittivity, ranging from 40 to 80 depending on its crystalline phase. However, its narrow bandgap of 3.2–3.35 eV and n-type property due to the oxygen vacancies, lead to high charge mobility and leakage current. The presence of oxygen vacancies also causes deviations in the Ti:O ratio from its stoichiometric composition, resulting in crystalline distortions. A certain portion of other phases such as Ti_2O_3 and Ti_4O_7, in the films decreases the crystallinity of TiO_2 and consequently reduces the dielectric constant of the films.

In this study, ozone post-treatment was applied to TiO_2-based planar capacitor fabrication to improve the stoichiometry and crystallinity of TiO_2 thin films by inducing oxygen diffusion. TiO_2 thin films were deposited via ALD at 250 °C using trimethoxy(pentamethylcyclopentadienyl)titanium as the Ti-precursor and ozone (200 g/m^3) as the reactant. After TiO_2 deposition, ozone post-treatment was performed at 250 °C by injecting ozone (200 g/m^3) for 5, 10, 15 and 20 minutes. The Pt top electrode was deposited via sputtering to fabricate planar capacitors with the structure Pt (60 nm)/TiO_2 (20 nm)/TiN (100 nm). By various surface characterization, it was revealed that ozone post-treatment enhanced the crystallinity of the anatase phase. Regardless of the treatment duration, the refractive index and film density of the TiO_2 thin film approached theoretical values compared to the as-deposited film, which exhibited a refractive index of 2.23 and a density of 3.33 g/cm^3. Additionally, the effect of ozone post-treatment on the electrical properties and polarization mechanisms was investigated. The as-deposited TiO_2 film exhibited a dielectric constant of 42, which increased by 29% after 15 minutes of ozone post-treatment, reaching 54 even in the anatase phase. Concurrently, the impact of ozone treatment on leakage current degradation was negligible.

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AA-TuP-30 Mobility Enhancement in In_2O_3/Al_2O_3 Nanolaminate Structures Grown by Atomic Layer Deposition

***Kyunghun Lyu**, Woongkyu Lee,* Department of Materials Science and Engineering, Soongsil University, Republic of Korea

As device integration advances, capacitors and transistors are becoming smaller, thin films are getting thinner, and device structures are evolving from planar to three-dimensional designs. However, A major limitation of silicon single-crystal substrates, currently used as channel materials, is their difficulty in being applied to 3D structures. In contrast, oxide semiconductors, which can be deposited by physical/chemical vacuum processes, are gaining attention as next-generation channel materials. Among various deposition methods, atomic layer deposition (ALD) is particularly advantageous due to its self-saturating growth behavior, which allows precise control of thickness at the atomic layer level and providing high step coverage even in complex 3D structures. Nevertheless, ALD also faces challenges in achieving compositional uniformity of multi-component materials such as indium gallium zinc oxide which is one of the most promising oxide semiconductors. Therefore, employing the two-dimensional electron gas (2DEG) has gained increasing attention as a method to achieve high mobility through heterostructures.

In this study, a nanolaminate structure was fabricated by alternately stacking semiconducting In_2O_3 (IO) layer and insulating Al_2O_3 (AO) layer. IO and AO thin films were deposited through an ALD process at 300ºC with (3-Dimethylaminopropyl)dimethylindium (DADI) and trimethylaluminum (TMA)as In and Al precursors, respectively. High density (~200 g/m^3) O_3 and H_2O were used as an oxygen source for each ALD process. To investigate the conducting characteristics of the nanolaminate structure, various configurations were fabricated. By Hall effect measurement, no mobility change was observed with varying IO thickness, however mobility obviously increased by 77.5% from 22.2 cm^2/Vs for In_2O_3 single layer to 39.4 cm^2/Vs for a stack of only AO/IO/AO/IO/AO structure. Through variations in AO thickness, it was confirmed that the 2 nm AO/5 nm IO stacked structure exhibited the highest mobility of 48.6 cm^2/Vs which was 117.9% higher than 10 nm IO single layer. For further investigation, ARXPS measurements were conducted at various angles, revealing a significant presence of oxygen vacancies at the interface. Additionally, VBO calculations were performed to evaluate the electronic band alignment and interpret the mobility enhancement observed in the nanolaminate structures.

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AA-TuP-31 Evaluation of Molybdenum Oxidation for the Growth of Rutile TiO_2

*Jin Tae Noh, **Kyong Min Kim**, Byeong Hyeon Kang, Seokjun Han, Seok Nam Koh, Tae Wan Lee,* Wonik IPS, Republic of Korea

Molybdenum dioxide (MoO_2) has attracted attention as a next generation electrode material in DRAM devices. It has been exhibited low leakage current property in MoO_2/TiO_2 based MIM capacitor structure because MoO_2 has a high work function. Also, when TiO_2 deposited on the MoO_2

film, it has been reported that the TiO_2 film tends to form rutile structure. The high capacitance property has been demonstrated in the rutile phase of TiO_2. But, despite these advantages of MoO_2, there are significant challenges in achieving the molybdenum oxide with a proper stoichiometry. In the previous studies, these MoO_x films must be conducted by an additional reduction process for the formation of MoO_2 after the molybdenum oxide (MoOx, 2<x<3) was deposited.

In this study, the oxidation process as a new approach method has been evaluated for the formation of MoO_2 using a molybdenum metal layer. First, the molybdenum metal layer was deposited using MoO_2Cl_2 and H_2 by ALD methods, and then, the oxidation process was carried out at different temperatures using oxygen and ozone as an oxidizer, respectively. In conclusion, MoO2 films were successfully formed through the oxidation of molybdenum using ozone. These films were analyzed using techniques such as X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). Additionally, prior to the oxidation process, the very thin TiO_2 capping layer was deposited on the molybdenum to enhance surface morphology and to improve MoO_2/TiO_2 interface properties. Finally, a TiO_2 layer was deposited as a capacitor layer using ALD method. The above processes carried out in-situ successfully result in rutile TiO_2 crystallinity within the MoO_2/TiO_2 multilayer. This molybdenum oxidation process shows promise for applications of MoO_2/TiO_2 based DRAM devices.

AA-TuP-32 Fast, Remote Plasma ALD of Highly Conductive TiN for Quantum Applications*, **Arpita Saha**, Dmytro Besprozvannyy, Yi Shu, Agnieszka Kurek,* Oxford Instruments Plasma Technology, UK*; Harm Knoops,* Oxford Instruments Plasma Technology, UK, Eindhoven University of Technology, UK

Quantum devices rely on precise control of coatings and material properties at the atomic scale for high performance. Through-Silicon vias are a critical enabler for the next generation of quantum technologies as they provide high-density interconnects, reduced signal loss and improved scalability. Plasma Enhanced ALD (PEALD) is known for its unmatched precision, tuneability and ability to deposit high-quality uniform thin films over large area substrates making it indispensable in production of materials for quantum applications. TiN has gained attention especially for development of superconducting resonators due to its tuneable superconducting properties, chemical stability and compatibility with scalable fabrication methods. Achieving pristine quality superconducting nitrides using ALD can be extremely challenging due to low growth-rates, long cycle times or due to incorporation of background impurities.

In this contribution we will show PEALD results from Oxford Instruments Plasma Technology's recently launched ALD platform, PlasmaPro ASP (PPASP) system aimed towards R&D customers. The remote Capacitively Coupled Plasma (CCP) source and chamber design allows efficient surface reactions for better film quality at a faster rate with low plasma damage. PPASP can deliver different superconducting nitrides along with different variants of TiN using either halide or metal organic chemistry for targeted quantum applications. We have been able to demonstrate deposition of smooth TiN films (roughness below 500 pcm) ranging from 5nm to 200nm using PPASP at high throughput ($\geq$50 nm/h) using metal organic chemistry at low temperatures of 275 ˚C, with room temperature planar resistivity <200 µΩ.cm and good superconducting properties with T_c > 1K. However, these films show slightly larger C (~6 at%) content along with poor via resistivity. To expand the TiN capabilities further, we have developed the halide-based TiN recently using both H_2/N_2 and NH_3 plasma. Tuning the N_2/H_2 ratio in the plasma mix translates direct tuneability of the resistivity and growth per cycle (GPC). NH_3 enhances the GPC, while the H_2/N_2 plasma helps in achieving very low resistivity values of <50 µΩ.cm. The films are polycrystalline and can achieve $\geq$ 85% conformality as confirmed by XRD and SEM. XPS and ToF-SIMS depict minimal O (<3 at%) and negligible C (<0.2 at%) and halide impurity (<0.2 at%) levels while roughness is ~1.5 nm. These films can achieve better via resistivity and stress tuneability for thicker films using recipe parameters. The tuneability of the TiN deposition process using PPASP makes it a promising candidate to tackle material challenges in quantum applications.

AA-TuP-33 Optimized Interface Engineering of ALD SrTiO3 for DRAM Capacitors*, Seong Keun Kim, **Seung Wan Ye**, Hong Keun Chung, Jeon Jihoon,* Korea Institute of Science and Technology (KIST), Republic of Korea

Strontium titanate ($SrTiO_3$, STO) has been extensively studied as a next-generation dielectric material for DRAM capacitors due to its exceptionally high dielectric constant. However, its direct integration with ruthenium (Ru) bottom electrodes presents significant interfacial challenges that hinder its practical application. One of the most critical issues is the compositional inhomogeneity induced by excessive initial SrO growth at the STO/Ru interface. Consequently, STO films grown on Ru remain amorphous or require post-deposition annealing (PDA) at temperatures exceeding 600°C to achieve crystallization, which is incompatible with DRAM manufacturing constraints.

To mitigate interfacial reactions at the STO-Ru interface, we investigated multiple techniques to suppress SrO overgrowth. One effective approach was the insertion of an ultra-thin Pt interlayer (<1 nm) on Ru, which successfully induced in-situ crystallization during ALD. This method facilitated the formation of a high-quality perovskite structure, resulting in a significantly enhanced dielectric constant and an equivalent oxide thickness (EOT).

To further improve STO's electrical performance, we explored perovskite-based bottom electrodes that provide better lattice matching with STO. By evaluating STO growth on these alternative electrodes, we assessed their potential to enhance dielectric properties and ensure scalability for next-generation DRAM capacitors.

AA-TuP-34 Urea Production from Polluted Seawater by Atomic Layer Deposited Catalytic Layers*, **Rens Kamphorst**, Peter M. Piechulla, Ruud J. van Ommen,* Delft University of Technology, Netherlands

Soil and water pollution, in particular driven by agricultural activity, has become a major concern over the last decade. Dissolved nitrates, introduced in water systems by excess fertilizer, disrupt ecosystems and potentially affect marine environments. Effective ways to remove these pollutants from waterways are limited, and expensive.

Within the Horizon Europe project ICONIC, we aim to address this issue by developing systems that electrochemically convert these contaminants, along with dissolved CO_2 into urea, thereby closing the nitrate cycle while providing a sustainable source of fertilizer. A key challenge within the project is the design of catalytic layers to facilitate the simultaneous conversion of nitrates and carbonates into urea. Prior literature identified copper-zinc as a promising candidate material to be used for these layers[1]. Here, ALD stands out as a tool to achieve a unique level of uniformity of the catalyst layer as well as the chemical composition of the copper-zinc compound catalyst. An additional challenge in the context of the application of the layers is maintaining the catalytic performance in the presence of seawater. In this environment, high salinity and dissolved species likely lead to corrosion and fouling of the catalytic layer. To mitigate this, we propose a protective SiO_2 overcoat, demonstrated in a prior study to extend the operational lifetime of electrocatalysts without compromising their activity[2].

Our poster will outline the conceptual framework of our approach, discuss early-stage experimental progress, and highlight the broader potential of this technology for environmental remediation and agricultural sustainability.

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AA-TuP-35 Tailoring the Scavenging Effect of ALD-Al_2O_3 Passivation Layer via Oxidant Engineering for High-Performance Tellurium Transistors*, **Jaeyoon Shim**, Jaemin Jung, In-Hwan Baek,* Inha University, Korea (Democratic People's Republic of)

As the two-dimensional (2D) downscaling of silicon-based semiconductors approaches fundamental physical limits, Monolithic 3D (M3D) integration has emerged as a promising alternative to overcome these challenges. However, realizing high-performance p-type transistors for M3D CMOS integration remains challenging due to the limited hole transport characteristics of conventional oxide semiconductors and the constraint of a low thermal budget (<400℃). Recently, Tellurium (Te) has garnered attention as a next-generation BEOL-compatible p-type material due to its high hole mobility and low-temperature processability, but its rapid and uncontrollable crystallization at room temperature and the formation of an amorphous native oxide degrade device stability and performance. Therefore, an effective passivation strategy is required to enhance the reliability of Te-based thin-film transistors (TFTs). Atomic layer deposition (ALD) is a suitable technique for forming high-quality passivation layers due to its precise thickness control and excellent uniformity. Al_2O_3, with a lower formation energy than tellurium oxide, has been reported to reduce trap density and scavenge the native amorphous tellurium oxide, thereby improving crystallinity. The choice of oxidant in ALD significantly influences the passivation layer quality by affecting the scavenging behavior, chemical composition, and impurity incorporation. Therefore, optimizing the oxidant selection is critical for achieving stable and high-performance Te-based TFTs. In this study, we fabricated Te TFTs and applied ALD passivation using Al_2O_3 with various oxidants (O_3, H_2O, and H_2O_2). By analyzing the electrical performance of the TFTs, we demonstrated that oxidant selection plays a crucial role in modulating the scavenging effect on Te channel layer, thereby impacting trap states, chemical composition, and overall device performance. This study contributes to expanding the selection of ALD oxidants for Te TFT passivation, providing an optimized strategy for high-performance and stable p-type TFTs.

AA-TuP-36 Selective Surface Passivation for Ultrathin and Continuous Metallic Films via Atomic Layer Deposition*, Seong Keun Kim,* KU-KIST Graduate School of Converging Science & Technology, Korea University, Republic of Korea*; Han Kim, Taeseok Kim,* ***Minseok Kim****, Jihoon Jeon, Gwang Min Park,* KU-KIST Graduate School of Converging Science and Technology, Korea University, Republic of Korea*; Sung-Chul Kim, Sung Ok Won,* Korea Institute of Science and Technology (KIST), Republic of Korea*; Ryosuke Harada,* TANAKA, Japan*; Sangtae Kim,* Department of Nuclear Engineering, Hanyang University, Republic of Korea

Scaling demands in modern electronics increasingly require ultrathin metallic films (<3–4 nm) that maintain high continuity and low surface roughness. However, the inherently high surface energy of metals on dielectric substrates (e.g., Al_2O_3, SiO_2) often promotes island-like growth, making the formation of uniform, continuous ultrathin layers exceedingly difficult. Here, we present a novel strategy to substantially reduce the disparity in adsorption behavior between metallic and dielectric surfaces, thereby enabling the realization of continuous films at significantly lower thickness.

Our approach employs aniline as a small-molecule inhibitor that preferentially adsorbs on existing metallic nuclei rather than on dielectric regions. By introducing an additional inhibitor-injection step prior to dosing the metal precursor, lateral growth on metal surfaces is effectively suppressed, while nucleation on adjacent dielectric areas is enhanced. Following precursor adsorption, an oxidizing agent (O_3) completes the metal-oxide reaction and removes the inhibitor, restoring surface reactivity for subsequent cycles. Repetitive application of this process significantly increases nucleation density and drastically reduces the film thickness required for achieving continuity.

Using this inhibitor-modified ALD protocol, we demonstrate continuous Ir films at thicknesses as low as ~1 nm and Pt films at ~2.3 nm. Compared to conventional ALD, these ultrathin layers exhibit improved surface smoothness and reduced electrical resistivity. Notably, this approach is especially advantageous for metal precursors with long nucleation delays, indicating its broad versatility across different metal-precursor systems.

Overall, this selective surface-passivation ALD approach pushes the limits of ultrathin metal film deposition, delivering reliable solutions for advanced interconnects, high-density memory electrodes, and other next-generation components. By mitigating metal nucleation challenges on dielectric substrates, it further drives miniaturization and improves device performance in future semiconductor technologies.

AA-TuP-37 Atomic Layer Deposition-Enabled Lateral Conversion of Transition Metal Dichalcogenides for Electrochemical Hydrogen Generation*,* ***Asem Jakyp,*** Nazarbayev University, Kazakhstan*; Aidar Kemelbay,* Lawrence Berkeley National Laboratory*; Arman Tuigynbek, Alexander Tikhonov,* Nazarbayev University, Kazakhstan

Transition metal dichalcogenides (TMDs), a class of van der Waals materials, have gained significant attention for their potential in electronic, optoelectronic and catalytic applications due to their highly tunable electronic and optical properties. However, achieving wafer-scale, precisely controlled synthesis of TMDs remains a critical challenge for scalable device integration. In this work, we present lateral conversion, a novel synthesis approach that enables the fabrication of patterned TMD structures with precise thickness control at lithographically defined locations. The method is facilitated by atomic layer deposition (ALD), which ensures angstrom-level thickness precision, large-area uniformity, and versatility in selecting metal oxides for subsequent conversion into TMDs for catalytic applications. The lateral conversion process involves the chalcogenation of ALD-deposited metal-oxide films, sandwiched between silica layers. This configuration effectively protects the TMD basal plane from contamination and oxidation, while simultaneously exposing catalytically active edge sites — an essential feature for efficient electrocatalysis. We demonstrate the fabrication of lithographically defined WS_2, MoS_2 and their alloys using lateral conversion, with in-depth characterization via Raman spectroscopy, photoluminescence (PL) mapping, and scanning electron microscopy (SEM). The catalytic efficiency of the synthesized TMDs is evaluated using a three-electrode electrochemical setup to assess their performance in the hydrogen evolution reaction (HER). The ALD-enabled precise thickness and composition control, patterning capability, scalability, and catalytic performance of this approach establish lateral conversion as a promising platform for the large-scale synthesis of TMD-based electrocatalysts.

AA-TuP-38 Low-Temperature Thermal Atomic Layer Deposition of Gallium Nitride Thin Films*,* ***Jian Heo****, Yerim Choi, Hyeji Kim, Okhyeon Kim, Hye-Lee Kim, Won-Jun Lee,* Sejong University, Republic of Korea

Gallium nitride (GaN), a wide direct bandgap III-V semiconductor, is widely used in power electronics and optoelectronic devices, such as high electron mobility transistors (HEMTs) and light-emitting diodes (LEDs). GaN films are typically grown at high temperatures using metal-organic chemical vapor deposition (MOCVD). However, thermal atomic layer deposition (ALD) offers an alternative method for high-quality GaN growth at lower temperatures, making it suitable for deposition on temperature-sensitive substrates and devices while avoiding plasma-induced damage. Despite extensive research on the plasma-enhanced ALD (PEALD) of GaN, low-temperature thermal ALD of GaN remains largely unexplored. In this study, GaN films were deposited by thermal ALD at temperatures below 250°C, and their properties were systematically analyzed. Self-limiting growth was confirmed by alternating exposure to a Ga precursor and ammonia. At 200°C, the growth rate was 1.3 Å/cycle, and the refractive index was 2.13, which is close to that of polycrystalline GaN (2.19 [1]). In addition, the deposited GaN films exhibited a stoichiometric composition with minimal impurities. Step coverage, density, crystallinity, and optical bandgap were investigated at different deposition temperatures to evaluate the effect of deposition temperature on the film properties.

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AA-TuP-39 High-Performance p-Type SnO Thin Film Transistor with Raised Source/Drain using Dry Etching Method*,* ***Jaemin Jung****, Jaeyoon Shim, InHwan Baek,* InHa University, Korea (Democratic People's Republic of)

Tin monoxide (SnO) has emerged as a promising p-type oxide semiconductor for back-end-of-line (BEOL) complementary metal-oxide-semiconductor (CMOS) integration due to its high hole mobility, which originates from the hybridization of Sn 5s and O 2p orbitals in the valence band. [1] However, the formation of a Schottky barrier at the oxide semiconductor/metal interface results in high contact resistance at the source/drain (S/D) regions, limiting device performance. Increasing the channel thickness can be an effective approach to reducing contact resistance. However, it inevitably leads to trade-offs, including increased off-current and significant negative shift of threshold voltage (V_{th}), which ultimately degrades electrical performance. To address this issue, Si, Mengwei, et al. proposed a raised S/D structure for n-type ITO thin-film transistors (TFTs) using a recessed channel formed by wet etching.[2] However, its isotropic etching profile induces unintended channel undercut, which may degrade device performance. Moreover, the excessively high etch rate of wet etching is not suitable for precise nanometer-scale channel thickness control. In contrast, dry etching methods such as reactive ion etching (RIE) and atomic layer etching (ALE) enable precise etch-depth control due to their anisotropic etching profiles and superior nanoscale patterning capability, making them highly suitable for recessed channel formation. Therefore, optimizing dry etching processes is essential for fabricating high-performance p-type SnO TFTs with a raised S/D structure. In this work, we optimized the dry etching process for ALD-deposited SnO thin films using Cl-based gases by analyzing the surface roughness and chemical composition to refine the etching conditions. Also We fabricated SnO TFTs with a raised S/D structure and systematically evaluated the impact of recessed channel thickness on device electrical performance. Furthermore, we investigated the dependence of contact resistance on SnO film thickness and demonstrated high-performance SnO TFTs through optimized recessed channel engineering. This study presents a novel approach for atomic-scale processing of p-type SnO TFTs, paving the way for their application in BEOL CMOS integration.

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[2] Si, Mengwei, et al. *ACS nano* 14.9 (2020): 11542-11547.

AA-TuP-40 Gain Enhancement of Microchannel Plate Detectors via ALD Coatings Inside the Channels, *Sun Gil Kim, **Min Seop Song**, Hyun Mi Kim, Ki Hun Seong, Sung Kyu Jang, Jong Hyun Choi,* Korea Electronics Technology Institute (KETI), Republic of Korea*; Yu Bin Nam,* Kyonggi University, Republic of Korea*; Jeong Gil Na, Kyung Hwan Jeong,* JJ CNS, Republic of Korea*; Seul Gi Kim, Hyeong Keun Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea

In semiconductor manufacturing equipment, time-of-flight mass spectrometry (ToF-MS) is widely employed for real-time process exhaust gas monitoring. This technique determines mass-to-charge ratio based on ion flight time, offering high sensitivity and rapid analysis capability. One of the essential components in ToF-MS, the Microchannel Plate (MCP), serves as an electron multiplication and signal amplification device, enabling efficient detection and amplification of ion signals.

Conventional MCPs are fabricated from lead glass, where a SiO_2 emissive layer is formed during glass fabrication, facilitating electron multiplication. However, despite materials such as MgO and Al_2O_3 exhibiting superior secondary electron emission (SEE) properties compared to SiO_2, conventional deposition techniques such as physical vapor deposition (PVD) and chemical vapor deposition (CVD) have limitations in achieving uniform coating inside MCP channels. In contrast, atomic layer deposition (ALD) technology enables precise and uniform coating of materials with excellent electron multiplication properties even within the narrow MCP channels, thereby enhancing MCP performance. In this study, we developed the ALD process to deposit Al_2O_3 as a resistive layer and MgO as an emissive layer inside MCP channels. Bis(ethylcyclopentadienyl)magnesium ($Mg(EtCp)_2$) was used as the precursor for MgO, TMA(Trimethylaluminum) ($Al(CH_3)_3$) for Al_2O_3, and Deionized water (H_2O) as the reactant.

Film thickness and density were analyzed using an ellipsometer and X-ray reflectometry (XRR). Additionally, X-ray photoelectron spectroscopy (XPS) was employed to examine the elemental composition and Mg/O ratio across different film thicknesses. The crystal structure was characterized using X-ray diffraction (XRD), while high-resolution transmission electron microscopy (HR-TEM) was utilized to investigate the microstructure of the deposited films. Moreover, the secondary electron emission (SEE) coefficient of MgO thin films under various process conditions was measured using a γ-focused ion beam (γ-FIB) system, and based on these results, the optimal process parameters and film thickness were determined.

This study is expected to serve as a key reference for material selection in emissive and resistive layers of MCP. Future research will explore various oxide thin-film combinations and novel materials, not only to enhance MCP gain but also to improve MCP lifetime and noise characteristics, thereby contributing to overall performance advancements. Moreover, the findings can be applied across various industrial and research fields, including time-of-flight mass spectrometry (ToF-MS) and image intensifiers.

AA-TuP-41 Effects of Alkali-Metal Doping on Aluminum-Silicate Coated Titanium Oxide Thin Film Transistors Prepared by Atomic Layer Deposition, ***Ryo Miyazawa**, Haruto Suzuki, Hibiki Takeda, Bashir Ahmmad Arima, Fumihiko Hirose,* Graduate School of Science and Engineering, Yamagata University, Japan

Thin-film transistors (TFTs) are used as pixel-control switching devices in displays. In this study, we developed surface-sensitive TFTs with 16 nm-thick titanium oxide channel for high mobility. The fabricated TFTs exhibited significant current amplification in the milliampere range with Na doping. We used aluminum-silicate films prepared by room temperature atomic layer deposition (RT-ALD) as the sodium adsorption layer. We reported the experimental results at the ALD/ALE conference 2024. It was reported that aluminum-silicate films exhibited adsorption abilities not only for Na but also for K and Cs. On the other hand, the Na-doped TFTs might be a contamination sources for other Si devices in LSI. Hence, in this study, we examined K and Cs doping instead of Na for the TFTs. In the conference, we will also discuss on the operation mechanism.

TiO_2 films were deposited on a Si substrate with a thermally grown SiO_2 layer by ALD. The TiO_2 thickness was set at 16 nm, with tetrakis(dimethylamino)titanium (TDMAT) as a Ti precursor. Plasma-excited humidified argon generated with an RF power of 500 W was employed as the oxidizing agent. The films underwent heat treatment at 500 °C for 30 minutes under the atmosphere for crystallization. Subsequently, Ti electrodes with a thickness of 100 nm were fabricated by electron-beam evaporation using a metal mask. For the gate electrode, the oxide film was selectively removed, followed by indium (In) deposition. Finally, a 10 nm-thick aluminum-silicate layer was formed as an alkali-metal adsorption layer via RT-ALD. Tris(dimethylamino)silane (TDMAS) and trimethylaluminum (TMA) were used as the precursors of Si and Al, respectively. The plasma power for oxidation during this process was 100 W. Figure 1 presents a schematic of the TiO_2-TFT with aluminum-silicate as the alkali metals adsorption layer.

Figure 2 shows the I-V characteristics of TiO_2-TFT after immersion in CsCl solutions. Even in the case of cesium doping, we confirmed current enhancement to the same milliampere level as with sodium. On the other hand, it was difficult to confirm the saturation region. We assume that the contact resistance limits the output currents [1]. In the conference, we discuss the effects of alkali metals on TiO_2-TFT.

AA-TuP-42 Influence of Atomic-layer-deposited MoNx Layers on Ferroelectric Properties of Hf-Zr-O Capacitors, *Jeong Hwan Han, **Jeong min Han**, Wangu Kang,* Seoul National University of Science and Technology, Republic of Korea

Ferroelectric (FE) materials have attracted significant attention for next-generation memory technologies, such as ferroelectric random-access memory (FeRAM), which offers advantages over flash memory, including higher speed and lower power consumption. Among various FE materials, HfO_2-based materials with a fluorite structure have been particularly notable due to their stable ferroelectricity even at sub-10 nm thicknesses, low leakage current resulting from a large bandgap (>5 eV), and excellent compatibility with CMOS technology. However, since HfO_2-based ferroelectrics are multi-phase materials containing both FE and non-FE phases, they tend to exhibit relatively low remnant polarization (2Pr) compared to conventional perovskite-based ferroelectrics, which limits their memory performance. Recent studies have focused on enhancing the 2Pr of $HfZrO_x$ (HZO) by methods such as doping, oxygen vacancy engineering, and in-plane tensile stress. Among these, oxygen vacancies have been shown to promote the crystallization and stabilization of the ferroelectric orthorhombic phase of HZO during rapid thermal annealing.

In this study, we investigate the enhancement of ferroelectric properties in HZO by introducing atomic-layer-deposited (ALD) MoN_x thin films. To evaluate the ferroelectric performance of HZO, metal-ferroelectric-metal (MFM) capacitors with a Pt/HZO/TiN structure were fabricated, and ALD MoN_x films were inserted at different locations (HZO/BE bottom interface, middle of HZO, and TE/HZO top interface). The impact of MoN_x films and their positioning on the ferroelectric properties and reliability of HZO was assessed. Through this investigation, we identified the optimal insertion condition for ALD MoN_x films to achieve superior ferroelectric performance in HZO.

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AA-TuP-43 Enhanced Stability of Ultrathin Mo-Passivated RuO2 Bottom Electrodes for TiO2-Based DRAM Capacitors, *Han Jeong Hwan, **Choi Seon Gu**, Lee Jae Hyeon,* Seoul National University of Science and Technology, Republic of Korea

As dynamic random access memory (DRAM) capacitors continue to scale down to enhance integration density, maintaining sufficient capacitance for reliable operation has become increasingly difficult due to structural constraints. This challenge necessitates the development of new high-k dielectric materials. Among potential candidates for metal-insulator-metal (MIM) capacitors, rutile TiO_2 stands out with a high dielectric constant of 70–170 and the ability to grow epitaxially on a bottom electrode with a matching rutile structure. Consequently, the advancement of compatible electrode materials is crucial for integrating these new dielectrics. Ruthenium oxide (RuO_2) is a promising metal oxide electrode for TiO_2-based MIM capacitors due to its rutile structure, low resistivity (~35 μΩ·cm), and high work function (~5.1 eV). However, during the atomic layer deposition (ALD) of TiO_2 on RuO_2 electrode, exposure to the Ti precursor and O_3 oxidant caused repeated reduction and etching of the RuO_2 surface, resulting in degradation of its morphology, structure, and electrical properties.

To address this issue, this study introduces an ultrathin Mo-passivated RuO_2 (Mo/RuO_2) bottom electrode to mitigate RuO_2 surface degradation during the ALD TiO_2 process. The crystalline structure and surface morphology were characterized using grazing incidence X-ray diffraction (GAXRD) and atomic force microscopy (AFM). TiO_2-based MIM capacitors were fabricated on the Mo/RuO_2 electrode, and X-ray fluorescence (XRF) and Auger electron spectroscopy (AES) analyses were conducted to evaluate the initial TiO_2 growth behavior and compositional variations. These analyses confirmed that the Mo interlayer effectively suppressed the reduction and etching of RuO_2. The ultrathin Mo layer facilitated the epitaxial growth of rutile TiO_2, improved interfacial and dielectric properties of ALD TiO_2, and significantly improved the device reliability.

Acknowledgements

This work was supported by the Technology Innovation Program(RS-2024-00509266, Development of Next-generation dielectric and electrode process equipment for logic 1nm or less and memory xnm level) funded By the Ministry of Trade Industry & Energy(MOTIE, Korea) and Korea Institute for Advancement of Technology(KIAT) grant funded by the Korea Government(MOTIE) (RS-2024-00409639, HRD Program for Industrial Innovation)

AA-TuP-44 Towards Ultra-Low Resistivity of Titanium Nitride PEALD Layers Grown on an Amorphous SiO_2 Substrate with Aluminum Nitride Interfacial Layer*, Valentina Korchnoy,* Technion Israel Institute of Technology, Israel*; Inna Popov,* The Hebrew University of Jerusalem, Israel*; Yael Etinger,* Technion Israel Institute of Technology, Israel*; Michael Lisiansky,* Tower Semiconductors, Israel

TiN layer is an important electrode material for modern electronic devices due to its low resistivity, scalability, and compatibility with CMOS technology. The plasma Enhanced Atomic Layer Deposition (PEALD) technique is widely used for growing uniform and conformal thin layers of TiN. The resistivity of thin TiN PEALD film is strongly influenced by the underlying substrate. Thin TiN layer of ultra-low resistivity (~ 10.5 µΩ.cm) has been achieved by PEALD on a sapphire substrate with AlN interfacial layer (IL) [1]. This resistivity is close to the bulk value. Such a low resistivity of the 14 nm TiN film can be attributed to its quasi-epitaxial manner of growth on AlN IL and low defect density of the layer. The perfect lattice matching between the (0001) sapphire substrate, AlN IL, and TiN is a dominant factor in the TiN layer performance. The AlN IL as thin, as 8 nm, is enough to grow a well-textured quasi-epitaxial TiN film. However, in TiN grown on an amorphous substrate (SiO_2) with AlN IL of the same thickness, the quality of the TiN layer is significantly worse, because TiN turned out to be poorly textured. As a result, its resistivity becomes approximately an order of magnitude higher than that of TiN grown on a sapphire substrate with the same thickness of AlN IL. This result was attributed to the poor structural performance of the AlN seed layer grown on an amorphous substrate (small polycrystal size without clear texturing).

The atomic layer annealing (ALA) technique used for the deposition of AlN layer supplies additional energy to stimulate surface reactions, increase the metal adatoms mobility and densification of the deposited film. Another factor that can improve the AlN IL quality is the layer thickness. As shown in [2], an increase in the thickness of the AlN layer leads to enhancement of its crystallinity.

The goal of our study is to determine the critical AlN IL thickness that provides a well-textured “seed” layer for subsequent deposition of ultra-low resistivity TiN films for electronic device applications. We suppose that the performance of on-grown TiN film will be close to those obtained on a sapphire substrate.

The AlN layers of 12 and 66 nm thickness were deposited by PEALD, using N_2/Ar plasma on 100 Å thermal oxide layers grown on a Si (001) substrate. The layers were characterized by XRD, XRR, TEM and spectroscopic ellipsometry. Structural analysis of the layers shows that PEALD AlN IL with a thickness of ~60 nm grown on amorphous SiO_2 substrate provides a well-structured template for the subsequent deposition of quality TiN films with low resistivity.

AA-TuP-45 High-Performance Tio2 Hardmask for sub-10 Nm Advanced Memory Patterning*, Heongyu Lee,* *Seul-Gi Kim, Cheongha Kim, sumin Lee, Hyun-mi Kim, Sun Gil Kim, Jong Hyun Choi, Hyeongkeun Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea

Si-based spin-on-hardmask (SOH) has been widely used in semiconductor processes; however, as the half-pitch approaches 10 nm, issues related to the deterioration of final wafer patterning quality arise due to deformation caused by the insufficient elastic modulus during etching or cleaning processes. To address this issue, new hardmask materials, including Ti, Zr, and W, have been proposed for application in sub-10 nm advanced memory processes.

In this study, TiO_2 is proposed as an alternative hardmask material to resolve major deformation problems in semiconductor patterning processes. TiO_2 exhibits a high elastic modulus, making it resistant to deformation, along with excellent corrosion resistance to oxygen-based plasma ans high etch selectivity over photoresist and carbon layers. It is also expected to exhibit superior optical properties and outgassing performance.

To enhance coverage over the spin-on-carbon (SOC) hardmask, an amorphous TiO_2 thin film was deposited using a plasma-enhanced atomic layer deposition (PEALD) process. Using tetrakis(dimethylamino)titanium (TDMAT) and O_2 plasma, an ALD window in the range of 100–250°C was identified, with a growth per cycle of 0.5–0.6 Å/cycle, and a refractive index close to 2.4. Transmission electron microscopy was employed to analyze the microstructure and composition of amorphous TiO_2. The elastic modulus of TiO_2 and its etch selectivity over SOC were estimated, confirming its suitability as a new hardmask material.

This study verifies the suitability of PEALD TiO_2 as a high-performance hardmask material, demonstrating its potential to replace Si-SOH and contribute to improved wafer yield through its superior mechanical properties.

AA-TuP-46 Machine Learning-Driven Thermal Budget Analysis for Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ Capacitors*, Minjong Lee,* University of Texas at Dallas*; Jongmug Kang,* Kangwon National University, Republic of Korea*; Dushyant Narayan, Geon Park, Dan Le,* University of Texas at Dallas*; Seungbin Lee, Hyeonghong Min, Gwanghyeon Jang, Si Joon Kim,* Kangwon National University, Republic of Korea*; Jiyoung Kim,* University of Texas at Dallas

Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ (HZO) devices have gained significant attention for their potential in non-volatile memory applications. ALD-grown HZO films exhibit robust ferroelectric properties and compatibility with back-end-of-line (BEOL) processes, making them promising candidates for next-generation electronics. However, achieving optimal ferroelectric behavior is highly dependent on annealing temperature, which influences phase formation and crystalline. Proper thermal treatment is essential for stabilizing ferroelectric performance within the orthorhombic phase, with ~400 °C identified as the optimal temperature for 10 nm HZO films.[1] Thus, precise control over the annealing process is critical for enhancing the performance and reliability of ferroelectric HZO-based devices. This study introduces a machine learning (ML)-driven thermal budget analysis to extend the range of annealing conditions explored for ferroelectric HZO devices.

Previous studies on low-temperature ferroelectricity in HZO films have shown that annealing at 300 °C for 48 hours is sufficient to crystallize the ferroelectric phase.[2] This low thermal budget process for ferroelectric crystallization is believed to be closely linked to both annealing temperature and time. However, a comprehensive exploration of all possible annealing conditions is practically unfeasible, as each experimental run incurs substantial time, cost, and additional labor and analysis expenses.[3] This challenge makes the integration of ML technologies particularly promising for improving cost-efficiency in process development by minimizing the required volume of experimental data. ML techniques provide deeper insights into a broader range of annealing conditions, even with a limited dataset. For example, while experimental data covers an annealing temperature range of 300 to 400 °C, ML analysis extends predictions to 200 to 500 °C. To further improve efficiency and robustness, this study integrates the Johnson-Mehl-Avrami-Kolmogorov (JMAK) model to correlate HZO crystallization kinetics with ML-based predictions. The combination of this model with ML optimization minimizes prediction errors and enhances the overall reliability of the ML model. The presentation will cover these promising approaches, along with electrical properties, technical methodologies, and experimental design.

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AA-TuP-47 Energy Storage Performance of Field-Induced Ferroelectric Al_2O_3-Inserted $Hf_{-0.5}Zr_{0.5}O_2$ Thin Films for Electrostatic Supercapacitors*, Jonghoon Shin*, *Dong Hoon Shin, Haengha Seo, Kyung Do Kim, Seungheon Choi, Tae Kyun Kim, Heewon Paik, Haewon Song, Seungyong Byun, In Soo Lee, Cheol Seong Hwang,* Seoul National University, South Korea

The growing global energy demand requires the development of efficient and reliable energy storage systems.[1] Electrostatic dielectric supercapacitors have attracted significant attention due to their high power density, fast charge/discharge speeds, high operating voltages, and excellent cycling and thermal stability.[1] Identifying ferroelectric (FE) materials that maximize both energy storage density (ESD) and efficiency by achieving high saturated polarization (P_S), low remnant polarization (P_r), large breakdown field (E_{BD}), and slim hysteresis loop is crucial.[2] Achieving fast charging and discharging speeds is also essential for rapid energy storage and release.

$Hf_{1-x}Zr_xO_2$ thin films are promising candidates due to their well-established atomic layer deposition (ALD) processes, lower leakage current (bandgap: ~5.5 eV), and low crystallization temperatures (400-550 °C). Field-induced ferroelectric (FFE) materials are particularly promising for energy storage applications due to their reversible field-induced phase transition between the non-polar tetragonal phase (t-phase, space group: $P4_2/nmc$) and polar orthorhombic phase (PO-phase, space group: $Pca2_1$), enabling significant energy to be charged and discharged.[3] Consequently, FFE thin films display antiferroelectric-like double hysteresis loops in the polarization-electric field measurements, characterized by high P_s and low P_r.[3] Hence, enhancing energy storage performance requires maximizing the t-phase.

This study investigated the impact of Al_2O_3 doping on the structural and chemical characteristics, and the energy storage performance of atomic layer deposited $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films. By adjusting the number of Al_2O_3 dopant cycles and layer insertion positions, optimized Al_2O_3-inserted HZO films achieved a record-high ESD of ~138 J cm^{-3} among $(Hf,Zr)O_2$-based thin films, with a high efficiency of ~80%. (Figure 1) The films maintained stable energy storage performance over 10^9 cycles at 6.0 MV cm^{-1} without electrical breakdown. (Figure 2) A single Al_2O_3 cycle (~0.12 nm), uniformly diffused at multiple locations within the HZO matrix, suppressed the monoclinic phase (m-phase, space group: $P2_1/c$) and stabilized the t-phase. This structure enhanced the FFE switching, decreased the hysteresis loop area, and increased the breakdown field (above ~8.0 MV cm^{-1}). In contrast, thicker Al_2O_3 layers (~0.24-0.36 nm) formed continuous, non-diffusive layers that hindered FFE t-phase stabilization. These findings highlight the critical role of precise Al_2O_3 insertion in maximizing the energy storage capabilities of HZO thin films.

AA-TuP-48 Atomic Layer Deposition of Ru-Ir Binary Alloy Thin Films for Advanced Interconnects, *Se-Hun Kwon, **Yeong-Seo Cho,** Myung-Jin Jung,* Pusan National University, Republic of Korea

Copper (Cu) has been predominantly used as an interconnect material in semiconductor Back-End-of-Line (BEOL) processes. However, it faces significant challenges due to a drastic increase in resistivity when the line width decreases below 10 nm. To address this issue, it is essential to develop new interconnect materials with a low Figure of Merit (FoM; $\rho_0\lambda$) and high cohesive energy compared to Cu that minimize electron scattering and reduce line resistance. Currently, single-metal candidates such as Ru, Co, and Mo has been extensively studied using atomic layer deposition (ALD) techniques as potential alternatives to Cu due to their favorable FoM characteristics and cohesive energies. However, the ALD of these single metals has shown limited improvements in resistivity compared to Cu.

Herein, therefore, we propose an alternative ALD binary alloy, Ru-Ir, as a new advanced interconnect material based on its FoM characteristics, which is capable of achieving lower resistivity than Cu at line widths below 10 nm. Since both Ru and Ir possess lower FoM values compared to Cu and share the same valence, they are expected to minimize the increase in resistivity when forming an alloy. Additionally, the Ru-Ir binary alloy has a wide solid solubility range, allowing effective control of the mean free path. To investigate this new advanced interconnect material, we systemically examined the effect of compositions and thickness on the electrical resistivity of ALD Ru-Ir binary alloy thin films. And, it was carefully compared with those of Cu interconnect material. In this presentation, the detailed optimization of ALD Ru-Ir binary alloy interconnects will be discussed with an appropriate theoretical explanations, aiming to address the resistivity increase issue of Cu at interconnect width less than 10 nm, and ultimately to develop a metallization material that outperforms Cu in future interconnect applications.

AA-TuP-49 Nanolaminated Al_2O_3/ZrO_2 film using Atomic Layer Deposition to enhance corrosion resistance on SUS304 steel, *Se-Hun Kwon, **Jae-Hyun Kim,*** Pusan National University, Republic of Korea

Atomic layer deposition (ALD), which utilizes self-limiting surface reactions by alternately exposing precursors and reactants to a surface, has recently been investigated as a method to form thin, defect-free films. This ALD method of thin film deposition has the advantages of precise thickness control on the nm scale, excellent step coverage on complex surface morphology, and large-area deposition, which is required in industries that use large surface area materials. In this study, Al_2O_3 and ZrO_2 laminated thin films were deposited on SUS 304 Substrates using ALD technology to improve corrosion resistance in high NaCl environments such as seawater. Using ALD technology, Al_2O_3 was deposited as an amorphous, grain-free thin film to effectively block the migration of salt, a corrosive medium, into the bulk Stainless steel under the thin film, and ZrO_2 thin films, a highly corrosion-resistant oxide material was alternately deposited between the Al_2O_3 films to form a lamination structure. To form laminated Al_2O_3/ZrO_2 thin films, one supercycle consisting of two subcycles was used for deposition. The the number of repetitions of each subcycle was adjusted to form thin films with the targeted thickness.

ALD-deposited thin films were measured using an ellipsometer, transmission electron microscope (HRTEM) and X-ray diffraction (XRD). And to evaluate the corrosion resisting performance in high-salt environments such as seawater, which is one of the many corrosive media, a potentiostatic polarization test and potentiodynamic test was conducted in 3.5 wt% NaCl electrolyte, and the corrosion properties were evaluated according to the film material, film structure, and film thickness.

AA-TuP-50 Impact of Al Gradient Doping on HfO_2 Based Metal – Insulator – Metal DRAM Capacitor, ***Taelim Lee,** Jungwoo Bong, Hosung Lee, Seongmin Jin, Keun Heo,* Jeonbuk National University, Republic of Korea

With the growing demand for higher data storage and faster processing, improving the capacitance of metal-insulator-metal (MIM) capacitors has become increasingly critical. This study examines the impact of aluminum (Al) gradient doping on the dielectric constant of HfO_2-based MIM capacitors. Compared to uniform doping, gradient doping more effectively promotes the transition of HfO_2 to its high-k tetragonal phase, resulting in enhanced capacitance. Various parameters, including annealing temperature, capping layers, and ALD conditions, were explored to optimize high-k performance. MIM capacitors with both gradient and uniform doping were fabricated and tested under annealing conditions of 400 °C, 500 °C, and 600 °C. The results show that gradient doping significantly reduces leakage current by an order of magnitude. While the uniformly doped capacitors exhibited a dielectric constant of ~44.7 and an EOT of 0.96 nm, gradient doping led to a dielectric constant of ~60.7 and an EOT of 0.71 nm, marking a 35.8% increase in dielectric constant and a 0.25 nm reduction in EOT. These findings demonstrate the potential of gradient doping as an effective approach to improving MIM capacitor performance for high-capacitance functional applications.

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AA-TuP-51 Aero-TiO2 Three-Dimensional Nanoarchitecture for Photocatalytic Degradation of Tetracycline, ***Sebastian Lehmann,** Kornelius Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany*; Vladimir Ciobanu, Tatiana Galatonova, Tudor Braniste, Ion Tiginyanu,* National Centre for Materials Study and Testing, Moldova (Republic of)

One of the biggest issues of wide bandgap semiconductor use in photocatalytic wastewater treatment is the reusability of the material and avoiding the contamination of water with the material itself. In this paper, we report on a novel TiO_2 aeromaterial (aero-TiO_2) consisting of hollow microtetrapods with $Zn_2Ti_3O_8$ inclusions. Atomic layer deposition has been used to obtain particles of unique shape allowing them to interlock thereby protecting the photocatalyst from erosion and damage when incorporated in active filters. The performance of the aero-TiO_2 material was investigated regarding photocatalytic degradation of tetracycline under UV and visible light irradiation. Upon irradiation with a 3.4 mW/cm^2 UV source, the tetracycline concentration decreases by about 90% during 150 min, while upon irradiation with a Solar Simulator (87.5 mW/cm^2) the concentration of antibiotic decreases by about 75% during 180 min. The experiments conducted under liquid flow conditions over a photocatalyst fixed in a testing cell have demonstrated the proper reusability of the material.

AA-TuP-52 Enhanced Reliability and Low-Voltage Operation in $Hf_{0.5}Zr_{0.5}O_2/ZrO_2/Hf_{0.5}Zr_{0.5}O_2$ Stack Compatible with Back-End of Line Process, ***Yinchi Liu,** Hao Zhang, Jining Yang, Xun Lu, Shiyu Li, Yeye Guo, Yiwen Yu, Hao Zhu, Lin Chen, Hongliang Lu, Shijin Ding, Wenjun Liu,* Fudan University, China

HfO_2-based ferroelectric devices have garnered significant attention in embedded memory due to their exceptional CMOS compatibility as well as sub-10 nm scalability. Nevertheless, poor crystallization and high driving field in Zr-doped HfO_2-based ferroelectric materials ($Hf_{0.5}Zr_{0.5}O_2$, HZO) during low temperature annealing (< 400 °C) make it challenging to balance ferroelectricity and reliability in practical applications. Here, the back-end of line (BEOL) compatible HZO/ZrO_2/HZO stack and the corresponding capacitors were fabricated. Compared to the conventional HZO film, the HZO/ZrO_2/HZO stack exhibits superior remanent polarization ($2P_r$) of 39.6 μC/cm^2 and 53.8 μC/cm^2 under 2 MV/cm and 4 MV/cm, respectively. By integrating ZrO_2 middle layer (ML) into HZO films, robust reliability was achieved, including a large breakdown electric field of 2.73 MV/cm in 10-year time-dependent dielectric breakdown (TDDB) lifetime, as well as excellent endurance characteristic with a $2P_r$ of 38.04 μC/cm^2 after 4.34×10^9 cycles at 2 MV/cm and no breakdown after 6×10^{10} fatigue cycles at 1.5 MV/cm. It is believed that ZrO_2 ML could introduce additional strain at a low annealing temperature below 350 °C and improve the proportion of the ferroelectric phase in the HZO/ZrO_2/HZO stack. Then, the thickness of the ferroelectric thin films was further scaled down to sub-6 nm. The capacitor with the sub-6 nm HZO/ZrO_2/HZO stack annealed at 400 °C shows a superior $2P_r$ of 26.3 μC/cm^2 under only ±1.25 V sweeping, while the conventional HZO film presents nonferroelectricity. The enhanced ferroelectricity stems from the increased ferroelectric phase proportion with ZrO_2 insertion. Moreover, the capacitor with a HZO/ZrO_2/HZO stack also achieved an excellent endurance with a $2P_r$ of 27.1 μC/cm^2 after 10^{11} cycles without breakdown and only ~12% $2P_r$ degradation at 85 °C. The robust reliability is ascribed to the suppressed generation of defects and domain pinning under the low operating voltage. The sub-6 nm HZO/ZrO_2/HZO stack presents great potential for BEOL compatible nonvolatile memories in advanced process nodes.

AA-TuP-53 Design of Crystalline InGaO Channels with High-Temperature Stability via Thermal ALD Process Parameter Variations, *Hye-Jin Oh,* Hanyang University, Korea; *Dong-Gyu Kim,* Hanyang University, Republic of Korea; *Tae Woong Cho, Hae Lin Yang,* Hanyang University, Korea; *Jihyun Kho, Yurim Kim, Bong Jin Kuh,* Samsung Electronics Co., Republic of Korea; *Jin-Seong Park,* Hanyang University, Korea

Oxide semiconductors have garnered interest as potential materials to address the issues caused by the scaling down of dynamic random-access memory devices.[1] However, high-temperature stability is a critical requirement for applying oxide semiconductors to memory devices.[2] To overcome the challenges of high-temperature instability in oxide semiconductors, it is essential to maintain a similar crystal structure regardless of the annealing temperature. Here, we proposed an optimized crystalline InGaO (IGO) film for high temperature stability by engineering atomic layer deposition process parameters, ozone concentration, and deposition temperature. Our results reveal that high-temperature stability can be secured by using elevated ozone concentrations and deposition temperatures in IGO deposition. Notably, IGO deposited at 300℃ shows little change in the main (222) intensity when annealed at 700℃ compared to 400℃, and a highly c-axis aligned (222) plane is observed. The field-effect transistor with an IGO active layer deposited at 300℃ showed minimal changes in electrical parameters after annealing at 700℃ (μ_{FE}: 58.4 to 68.7 cm^2/Vs) and demonstrated excellent PBTS stability (ΔV_{th}: 0.15 V) at 3 MV/cm, 95℃. These outcomes suggest the possibility of utilizing oxide semiconductors in memory devices that require managing high-temperature thermal budgets.

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AA-TuP-54 Advancements in ALD for DRAM: High-Performance Films for Capacitor and Electrode Applications, ***Tejinder Singh,*** Eugenus, Inc.

As DRAM technology continues to scale to meet the increasing demands of high-performance computing, artificial intelligence, and data-intensive applications, maintaining capacitance while reducing cell dimensions presents a significant challenge. The aggressive scaling of DRAM unit cells necessitates innovations in high-k dielectric materials and electrode films to ensure high charge storage capability, low leakage currents, and excellent step coverage in high-aspect-ratio structures. Atomic Layer Deposition (ALD) has emerged as the key enabler for advanced DRAM capacitor and electrode fabrication, offering precise thickness control, excellent conformality, and superior material quality. Eugenus, a leader in ALD technology, has developed next-generation solutions for DRAM capacitor and electrode deposition, leveraging its Sierra, Lassen, and Whitney ALD platforms. These systems enable the deposition of advanced materials such as ZrO_2, HfO_2, Al_2O_3, and ferroelectric $HfZrO_x$ for high-k capacitor stacks, as well as TiN, VN, and TSN for bottom and top electrodes. The Sierra ALD system, optimized for high-step coverage metal deposition, provides excellent process uniformity and throughput for TiN/VN electrodes, ensuring low resistance and high reliability in ultra-scaled DRAM architectures. The Lassen ALD system delivers high-quality dielectric films with superior conformality and electrical performance, enabling next-generation capacitor structures with minimal leakage and high breakdown strength. Additionally, the Whitney ALD system supports MoN electrode formation and gapfill applications, further enhancing DRAM performance by reducing resistance and improving integration flexibility.

This technical presentation will be focused on film properties, characterization, and device results. Key advancements in these ALD platforms include optimized precursor delivery, multi-station process modules, and improved reactor designs for high-aspect-ratio structures exceeding 50:1. These innovations enable step coverage exceeding 95% while maintaining excellent film quality, meeting the stringent demands of advanced DRAM fabrication. This presentation will discuss the technical advancements of Eugenus ALD solutions and their impact on future DRAM scaling, providing insights into high-volume manufacturing strategies for next-generation memory devices

Author: Tejinder Singh, Ph.D, Chief Technology Officer, Eugenus, Inc

AA-TuP-55 Optimization of Low-Temperature PEALD for High-Performance TiO_2/SiO_2 Optical Coatings, ***Duy Thanh Cu,*** *Guan-Yu Ke,* National Central University, Taiwan; *Wen-Hao Cho,* Taiwan Instrument Research Institute, National Applied Research Laboratories, Taiwan; *Chien-Cheng Kuo,* National Central University, Taiwan

The study introduces a revolutionary low-temperature plasma-enhanced atomic layer deposition (PEALD) technique for fabricating high-quality, stress-minimized anti-reflective coatings (ARCs). This innovative method operates at a remarkably low temperature of 70℃, challenging traditional high-temperature deposition processes and yielding superior optical coatings with reduced residual stress.

The optimized process at 150 W plasma power produces high-quality optics with an average reflectivity of 0.35% in the visible spectrum while maintaining low stress, a significant achievement for low temperature deposited optical coatings. Focusing on titanium dioxide (TiO_2) and silicon dioxide (SiO_2) stacking using PEALD at 70℃, the research addresses high-temperature deposition challenges and mechanical stress issues for polymer substrates.

A notable stress compensation effect is observed between TiO_2 films (tensile stress ~220 MPa) and SiO_2 films (compressive stress ~-35 MPa). This combination strategy results in a remarkably low total stress of 48 MPa for multi-layer ARCs, marking significant progress in stress control for optical coatings. Interestingly, findings reveal that carbon and nitrogen incorporation into TiO_2 films occurs, with carbon doping does not have significant impact on the film absorption.

The use of common, cost-effective materials like SiO_2 and TiO_2 enhances the scalability of this approach for industrial applications. The stress-reduction effect persists even with thickness variations up to 9.6%, demonstrating real-world applicability.

These films exhibit low defect density, an amorphous structure, and surface smoothness approaching one atomic monolayer (~0.2 nm), indicating high optical quality comparable to high-temperature deposited films. This low-temperature PEALD technique not only advances optical coating technology but also expands possibilities for coating temperature-sensitive substrates and complex 3D structures, promoting applications in flexible electronics, advanced optical components, and next-generation display devices.

AA-TuP-56 Analysis of the Ambipolar Conduction of Atomic-layer-deposited Tin Monoxide Thin-Film Transistors with Indium Tin Oxide Electrodes, *Cheolseong Hwang,* ***Sahngik Mun,*** *Seoryong Park, Yonghee Lee, Sukin Kang, Jinheon Choi, Jaewon Ham, Juneseong Choi,* Seoul National University, Republic of Korea

The increasing demand for higher-density NAND Flash memory has driven dimensionality scaling and device structure transition from two-dimensional to three-dimensional (3D). Conventional polysilicon channel has shown deteriorated electrical characteristics as the channel thickness reached sub-10 nm in the 3D NAND Flash structure, prompting the exploration of alternative channel materials, with metal oxide semiconductors emerging as strong candidates. For a metal oxide semiconductor to function as a channel material in NAND Flash memory, it must support the conduction of both holes and electrons because they must be injected from the channel to the charge trap layer to erase and program the cells. When adopted as a channel material in NAND flash memory, n-type oxide semiconductors such as InGaZnO have demonstrated effective electron conduction and programming capabilities. However, they lack holes, making the erase operation challenging.

Tin monoxide (SnO) is an appealing contender for this purpose due to its relatively small indirect bandgap of 0.7 eV, which allows for the contact metal's Fermi level to be close to both the conduction band minimum (CBM) and valence band maximum (VBM). In addition, the energy band structure, comprising Sn 5p orbitals at the CBM and hybridized Sn 5s and O 2p orbitals at the VBM, provides a metallic character in both band edges, facilitating the conduction of both holes and electrons.

This study explores the possibility of applying atomic-layer deposited (ALD) SnO as a channel material in 3D NAND Flash. ALD SnO exhibits intrinsic p-type conduction characteristics due to the formation of tin vacancies, which act as shallow acceptor states and generate holes. Previous research has primarily focused on utilizing ALD SnO's p-type conduction characteristics. On the contrary, the high density of defect states within the bandgap and the significant electron injection barrier limits the n-type conduction in ALD SnO thin-film transistors (TFTs).

This work modulates the source/drain (S/D) electrodes to achieve electron conduction in ALD SnO TFTs. Indium tin oxide was adopted as the S/D electrode material, enhancing electron conduction and enabling ambipolar conduction characteristics. Furthermore, a mobility extraction method under electron-hole recombination conditions is proposed. The electron-hole recombination is an unavoidable phenomenon in ambipolar TFTs, where electron and hole conduction co-occurs. Therefore, considering the application of ambipolar ALD SnO as a channel material in 3D NAND Flash, the influence of electron-hole recombination phenomena on carrier mobility was analyzed.

AA-TuP-57 Catalyst Engineering and Synthesis via Atomic Layer Deposition*, **Xinhua Liang,*** Washington University in St. Louis

Heterogeneous catalysts enable numerous chemical transformations of fossil resources (such as natural gas, methane, liquid petroleum, and coal) into useful products. Typically, heterogeneous catalysts consist of small metal particles dispersed on a high-surface-area porous oxide support. Atomic layer deposition (ALD) has primarily been used for the formation of oxide thin films with precise atomic-layer control. Due to the unique nucleation process during the first few cycles of ALD, it can also be employed to prepare highly dispersed metal nanoparticles or even single metal atoms. In this presentation, I will discuss our recent progress in the preparation of metal and bimetallic nanoparticles using ALD, as well as ALD thin film modified catalysts for various catalytic reactions, such as dry reforming of methane and selective hydrogenation.

AA-TuP-58 Enhancement of Stress Distribution through Patterned Island Design Using Atmospheric Pressure Spatial-ALD*, **Min-Seo Kim**, Won-Bum Lee, Chi-Hoon Lee, Jin-Seong Park,* Hanyang University, Korea

Wearable and flexible electronic devices are becoming increasingly important in advanced technologies, such as healthcare monitoring, wearable sensors, augmented reality (AR) displays, and next-generation communication devices. These technologies require display solutions that maintain high reliable performance under mechanical strain. However, conventional active-matrix organic light-emitting diode (AMOLED) displays often experience electrical degradation, fatigue damage under repeated mechanical deformation, posing challenges for commercialization. To overcome these limitations, this study introduces a novel island-bridge structure for oxide thin-film transistors (TFTs) fabricated using atmospheric pressure spatial atomic layer deposition **(AP S-ALD)**. Unlike conventional ALD, **AP S-ALD** enables rapid deposition with continuous precursor and reactant flows separated by inert gases, preserving ALD's self-limiting properties. It simplifies equipment needs, reduces maintenance costs, and supports flexible electronic displays with high efficiency and durability. Using this advanced deposition technique allows for accurate thickness control and excellent step coverage enabling the fabrication of high quality TFTs. Moreover, it significantly enhances mechanical stability while preserving electrical properties, making it a promising solution for next-generation electronic devices.

We evaluated the effect of pattern variation on stress distribution through ANSYS finite element analysis (FEA) simulations, using square, circular, and patterned islands further divided into 4, 8, 12, and 16 sub-patterns. The results demonstrated that circular and patterned islands reduced stress distribution compared to conventional square islands. This novel patterned island-bridge structure shows reduction of maximum stress distribution on the TFT regions. Based on these findings, oxide TFT devices were fabricated and tested using AP S-ALD to experimentally verify the results. The devices maintained stable electrical performance under 30% mechanical strain, outperforming square island designs. This enhanced strain tolerance indicates a lower risk device failure under prolonged deformation. By utilizing the patterned island-bridge structure to enhance mechanical stability, this study presents a strategic design approach for next-generation stretchable electronics.

AA-TuP-59 Demonstration of Reliable Ferroelectric Memory with Optimized 4 Nm-Thick $Hf_{1–X}Z_{Rx}O_2$ Films and an Ultra-Thin Al_2O_3 Capping Layer*, **Han Sol Park,** Cheol Seong Hwang,* Seoul National University, Republic of Korea

Ferroelectric Zr-doped HfO_2 ($Hf_{1-x}Zr_xO_2$) thin film was recognized for its robust ferroelectric properties down to nano-scale thickness and compatibility with complementary metal oxide semiconductor (CMOS) technologies[1]. However, the widespread application of the $Hf_{1-x}Zr_xO_2$thin film as ferroelectric random access memory (FeRAM) is impeded by its high coercive field (E_C), which leads to a high operation voltage[2].Developing ferroelectric $Hf_{1-x}Zr_xO_2$ thin film operating at a voltage as low as ~1 V without compromising memory performance for highly integrated FeRAM technologies is urgently required.

The operation voltage can be decreased by decreasing the film thickness. However, when the$Hf_{1-x}Zr_xO_2$ film thickness decreases to as low as~5 nm, non-ferroelectric tetragonal phase stability increases due to the dominance of its low surface energy effect[3]. Moreover, meeting low thermal budget requirements in back-end-of-line processing becomes difficult in thinner films due to rapidly increasing crystallization temperature with decreasing thickness[4]. Such a high annealing temperature degrades the interface of the ferroelectric layer with the electrode films, undermining the reliability of thin films.

This study reports experimental optimization of the thickness scaling for $Hf_{1-x}Zr_xO_2$ thin films for stable operation at low voltage with high reliability. By adjusting ozone dose time, Zr ratio, crystallization annealing temperature, and TiN capping electrode thickness, the ferroelectric properties of the 4nm-thick film were significantly enhanced without compromising reliability. Furthermore, the high leakage current of the 4 nm-thick $Hf_{1-x}Zr_xO_2$ decreased ~10^2 times by capping an ultra-thin Al_2O_3 layer (< 5 Å). Optimized 4nm-thick $Hf_{1-x}Zr_xO_2$ thin film showed great potential in FeRAM applications with a $2V_C$ of ~0.8 V and double remanent polarization ($2P_r$) of ~25 μC/cm^2 at an applied voltage of ±1 V with a switching endurance of 10^{11}, which conforms to the giga-bit density FeRAM requirements.

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AA-TuP-60 Zirconium Carbide (ZrC_x) Thin Films as Next-generation Diffusion Barriers for Cu and Ru Interconnects Prepared by Plasma Enhanced Atomic Layer Deposition*, **Minjeong Kweon**, Chaehyun Park, Sang bok Kim, Soo-Hyun Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

Zirconium(Zr)-based materials have attracted significant interest in semiconductor applications, such as diffusion barriers, gate electrodes, and high-temperature electronic devices, due to their high thermal stability (T_m for Zr: 1850℃, ZrC: ~3420℃, ZrN: ~2980℃), low resistivities (Zr: ~42, ZrC: ~43, ZrN: ~12 μΩ·cm), and chemical stability. While the ALD (atomic layer deposition) process of zirconium nitride (ZrN) has been somewhat studied, a research on the ALD process of zirconium carbide (ZrC_x) has not been reported yet so far.In this study, we, for the first time, investigated the ALD process for ZrC_x thin film using a showerhead-type PE-ALD reactor (IOV dX1 PEALD, ISAC Research, Korea). A nitrogen-free zirconium precursor was used as the precursor, while H_2 plasma served as the reactant. The deposition was carried out at a chamber pressure of approximately 1 Torr within a temperature range of 150–450 °C. The optimal deposition temperature was found to be 300 °C where a self-limiting growth was confirmed with a saturated growth rate of ~ 0.2 Å/cycle. The resistivity of ALD-ZrC_x film was as low as ~ 300 μΩ·cm with the rock-salt crystal structure.The properties of ALD- ZrC_x films deposited under optimized conditions were analyzed using various characterization techniques, including XRD, XRR, XPS, 4-point probe, RBS, TEM, and UPS. To assess the potential of ALD-ZrC_x films as practical diffusion barriers in interconnect applications, their ability to prevent the diffusion of Cu and Ru during metallization was evaluated. The results of this study highlight the potential of ZrC_x thin films for next-generation semiconductor technology and contribute to the foundation for future application-oriented research.

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AA-TuP-61 Centralized Bulk Precursor Delivery by Means of Direct Liquid Injection

Ehsan Mohseni*, Johannes Grübler, Joerg Koch,* SEMPA SYSTEMS GmbH, Germany

Deposition techniques such as chemical vapor deposition (CVD) and atomic layer deposition (ALD) are particularly suitable for the deposition of specific elements delivered by precursor chemicals. They achieve industrial standards for film thickness, uniformity, and purity for coatings much more reliably and reproducibly than physical deposition and wet chemical techniques. This is particularly true for depositions on 3D surfaces. Both techniques, which are used in the semiconductor, photovoltaic and optoelectronic industries, among others, require a precise and reliable supply system of precursor materials, which poses several difficulties. Only 10% of industrially available precursors are gaseous, while about 80% are in the form of powders or crystals [1]. Solid precursors are the most challenging among others because the sublimation rate is directly related to the free surface area, which changes as sublimation progresses, resulting in a non-constant mass transport rate during the deposition. In addition, most of the available precursors have safety requirements.

Non-gaseous precursors are commonly delivered by evaporation. This is conventionally realized using bubbler or vapor draw technologies, where a carrier gas passes through or by the precursor, and becomes saturated before being delivered. The vapor delivery rate depends on the temperature, pressure, and in case of the bubbler, the carrier gas flow. Increasing the latter may lead to temperature instability and fluctuations in delivery rate and precursor concentration. Because of this thermodynamic limitation, the use of bubblers is recommended when low precursor consumption is required, and typically each deposition reactor requires its own bubbler. Moreover, downstream insulation is often necessary to avoid condensation [2].

Direct liquid injection (DLI) is an alternative vapor delivery technology in which the precursor is kept at room temperature and only the required amount is vaporized and injected into the reactor [3]. Unlike bubbler technology, the supply rate in DLI is not limited by the vapor pressure. This makes it particularly interesting for precursors with low thermal stability and low vapor pressure. Fully automated with high-precision flow and pressure controllers, DLI allows high-throughput precursor supply while maintaining an adjustable concentration range both below and above atmospheric pressure level. This allows one DLI system to be used as a central supply unit for multiple reactor chambers, resulting in a compact design and reduced footprint. Here we present our latest DLI technology designed for liquid as well as solid precursors.

AA-TuP-62 Highly-Conductive ALD-WCx Thin Films Using a New Fluorine-Free W Precursor for Cu & Ru Interconnects

Dongbeom Seo*, Soo-Hyun Kim, Sang Bok Kim,* Ulsan National Institute of Science and Technology, UNIST, Republic of Korea

Tungsten-based materials (W, WN_x, WN_xCy, WC_x) exhibit an exceptional hardness, good chemical and thermal stability, and low resistivity. Due to these outstanding properties, tungsten-based thin films have been extensively investigated as Cu diffusion barriers, adhesion layers for interconnects, and metal gates. Tungsten-based thin films are predominantly deposited using WF_6 as a precursor for a long time. However, WF_6 generates toxic and corrosive hydrogen fluoride (HF) as a reaction byproduct. The F impurities in the deposited film result in the etching of underlying substrates and defect formation which can degrade the performance and reliability of devices. To address these challenges, the deposition of W-based thin films using fluorine-free tungsten (FFW) precursors has become crucial, and substantial research efforts are actively advancing this field. [1, 2] In this study, WCx thin films were deposited by plasma enhanced atomic layer deposition (PEALD) using a new FFW metalorganic precursor and H_2 plasma as the reactant, at the deposition temperature ranged from 200 to 300 ℃. Self-limiting growth behavior was observed for both precursor pulsing and reactant pulsing at 250 ℃ of the deposition temperature, with the saturated growth rate of approximately 0.4 Å/cycle. The ALD-WC_x film deposited at 250 ℃ was identified as a nanocrystalline structure with a face-centered cubic β-WC_{1-x}phase by XRD and XPS analyses. Remarkably, the resistivity of ALD-WC_x film at the optimized deposition condition was as low as ~190 μΩ·cm, which shows its potential for various applications including a diffusion barrier/glue layer for Cu and Ru metallization as well as a gate or capacitor electrode material for advanced 3D devices.

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AA-TuP-63 Germanium Doping for Electrical Modulation of Ferroelectric $HfZrO_4$ Using Atomic Layer Deposition

Jared McWilliams*, Sunil Ghimire, Charlene Chen, Ray Meck, Nguyen Vu,* Merck KGaA, Darmstadt

Since its first discovery, ferroelectricity in hafnia-based oxides has seen significant improvement using the large-scale, manufacturing-friendly atomic layer deposition (ALD) method, making them the most promising candidate for advancing non-volatile memory technology.[1] Among all compositions, the 1:1 ratio alloy $HfZrO_4$ (HZO) is the most studied compound due to the low thermal budget required to achieve satisfactory electrical performance. However, its further technical adoption has been hindered by the high operating voltage of HZO,resulting in high energy dissipation and early device failure. Significant efforts have been invested towards understanding switching mechanisms and predicting potential dopant candidates to reduce the coercive voltage of HZO. [2]

This work demonstrates, for the first time, the experimental validation of Germanium-doped HZO since the theoretical prediction by Chae *et al.*[3] Electrical behaviors such as polarization switching, leakage, and voltage-dependent capacitance are taken into account along with physical characterizations to elucidate the mechanisms behind the ferroelectric switching and the reduction in the coercive field of Ge-doped HZO. Different doping strategies to achieve desirable ferroelectric characteristics are also presented, highlighting the importance of dopant concentration and the location of dopant atoms within the device stack. The advantage of using precursors with wide ALD windows is also discussed to emphasize further the role of precursor choices in maintaining a low thermal budget for the fabrication process of doped HZO.

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AA-TuP-64 Trap Density Reduction in High-k Dielectrics: A Dual Approach with ALD Optimization and HPDA, *Taewon Hwang*, *Su-Hwan Choi, Chang-Kyun Park, Jin-Seong Park,* Hanyang University, Korea

The semiconductor industry has advanced through continuous device scaling, improving speed and integration density. However, scaling introduces challenges such as short-channel effects and increased leakage currents due to tunneling in thin insulators. High-k dielectrics with permittivities exceeding Si_3N_4 (k ~7), such as Al_2O_3 (k ~9), HfO_2 (k ~25), and ZrO_2 (k ~25), have been introduced to address these issues. Al_2O_3 offers thermal stability, while HfO_2 and ZrO_2 enable tunable properties through their crystalline phases. However, defects in high-k materials—such as grain boundaries and impurities—form leakage pathways, while interface traps degrade electrical performance by increasing trap-assisted tunneling and instability. Addressing these defects is critical to enhancing device reliability.

Hydrogen annealing effectively passivates traps, reducing interface trap density and improving electrical properties. However, traditional forming gas annealing (FGA) at high temperatures can cause oxygen scavenging and structural degradation. High-pressure hydrogen annealing enhances hydrogen incorporation at lower temperatures, mitigating these issues. Deuterium annealing (D_2) also provides stronger and longer-lasting passivation due to its higher bond strength and lower diffusivity than hydrogen.

This study employs a dual approach to minimize defects: (1) optimizing atomic layer deposition (ALD) to reduce bulk defects and (2) applying high-pressure deuterium annealing (HPDA) to enhance interface stability. Increased ALD pressure and ozone flow promote Cp-ligand combustion, reducing impurities and bulk trap density. HPDA facilitates deuterium diffusion into bulk and interface regions, significantly lowering defect densities. D-SIMS confirmed successful deuterium incorporation across different high-k materials. HPDA reduced hysteresis and interface trap density for HfO_2, and ZrO_2 from 0.39 V and 3.98×10^{11}, and 0.44 V and 5.21×10^{11} $eV^{-1}cm^{-2}$ to0.38 V and 2.05×10^{11}, and 0.40 V and 5.16×10^{11} $eV^{-1}cm^{-2}$, respectively. Charge pumping confirmed that HPDA-incorporated deuterium does not contribute to mobile charge, ensuring long-term reliability.

These results demonstrate HPDA’s effectiveness in defect reduction, offering a promising strategy for improving the performance and stability of high-k dielectrics in next-generation semiconductor devices.

* Author for correspondence: jsparklime@hanyang.ac.kr [mailto:jsparklime@hanyang.ac.kr]

AA-TuP-65 ALD-Al_2O_3 Buffer Layer, a Key Component for Realizing Stretchable Thin Film Transistor Arrays, *Jaehyun Moon*, *Bock Soon Na,* Electronics and Telecommunication Research Institute (ETRI), Republic of Korea; *Sangmin Lee, Taek-Soo Kim,* Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea; *Seong-Deok Ahn, Seung-Youl Kang,* Electronics and Telecommunication Research Institute (ETRI), Republic of Korea

1.Reality Devices Research Division, Electronics and Telecommunication Research Institute (ETRI), Daejeon 34129, Rep. of Korea

2.Advanced Device Technology, ICT, University of Science and Technology (UST), Daejeon 34113, Rep. of Korea

3.Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Rep. of Korea

*: kang2476@etri.re.kr [mailto:kang2476@etri.re.kr]

In this work, bearing the importance of stretchability in the field of emerging electronics, we describe and demonstrate a scheme which is useful to make stretchable oxide TFT array. Integration of stiff inorganic devices on soft and compliant polymer substrates is technically demanding. In this regard, we highlighted the crucial roles of conformably ALD- Al_2O_3 buffer layer on a wavy compliant surface, which not only enables TFT processes but also mechanically withstands cyclic stretching. Substrates bearing surface waviness are advantageous to sustain externally induced strain. Rather than letting the system to evolve to bear wrinkles, it is advantageous to use a platform on which wrinkles are already formed. In this regard, we fabricated the oxide TFT array separately on a PI/glass substrate using reliable vacuum deposition and photolithographic processes. Using a laser lift off (LLO) process, the PI/TFT array was detached, and laminated on a pre-stretched compliant substrate. Upon releasing the pre-stretched substrate, a wavy PI/TFT array was formed. The mechanical properties of ALD- Al_2O_3 film of 150 nm thickness was directly measured to have a Young’s modulus of ~130 GPa. TFTs on our array can withstand stain 13 % and metal buses fully conductive up to cyclic strain of 30 %.

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AA-TuP-66 Optimization of High-*k* Gate Insulators for Amorphous IGZO channel-based 3D DRAM: Materials and Process Development, *Seonyeong Park*, *Jisang Yoo,* Yonsei University, Korea; *Jeongwoo Park, Pilsang Yun, Daewon Ha,* Samsung Electronics Co., Republic of Korea; *Hyungjun Kim,* Yonsei University, Korea

As device scaling accelerates, the conventional planar dynamic random access-memory (DRAM) structures are transitioning into 3D DRAM architectures. Various issues arise while converting the traditional Si-based transistors to 3D structures. For example, using single crystal Si requires over 100 layers of Si/SiGe epitaxial growth, but the complexity of 3D stacked structures makes them unsuitable for large-scale manufacturing. Polycrystalline Si, commonly used in V-NAND, faces issues like leakage current and degradation between cells due to grain boundaries. Amorphous Si offers process advantages but suffers from poor electron mobility and defects.

To address these problems, amorphous oxide semiconductors (AOS) have emerged as potential alternatives. Specifically, amorphous Indium Gallium Zinc oxide (a-IGZO) has gained attention because it can be deposited by physical vapor deposition (PVD) and atomic layer deposition (ALD), making it suitable for mass production. Additionally, a-IGZO has fewer issues with leakage current and degradation compared to polycrystalline and amorphous Si, and it meets the required electron mobility of 2~10 cm^2/Vs needed for 3D DRAM. However, research on a-IGZO has primarily focused on the channel material, while the gate insulator (GI) and source/drain (S/D) contact materials and processes remain underdeveloped.

In particular, ALD-based GI, which are preferred for their conformal deposition capability in 3D structures, face challenges when high-*k* GI directly deposited onto a-IGZO. Traditional high-*k* GIs cause leakage current due to a low conduction band offset, and direct reactions between the a-IGZO channel and ALD precursors can lead to trap states (oxidant vacancy, V_O) at the channel interface.

Therefore, our research focuses on optimizing the direct deposition of high-k GIs onto a-IGZO. We have explored various oxide materials and precursor-oxidant combinations to find the best process for reducing leakage current and improving device performance. After confirming basic ALD growth characteristics, we used techniques like X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) to analyze thin film properties. We also fabricated metal-oxide-semiconductor (MOS) capacitors and a-IGZO channel field-effect transistors (FETs) to evaluate their performance.

AA-TuP-67 Polarity-Induced Threshold Voltage Shift in Ovonic Threshold Switch Device Based on Atomic Layer Deposited Germanium Selenide for Vertical Three-Dimensional Selector-Only Memory, *Jeong Woo Jeon*, *Byongwoo Park, Sangmin Jeon, Sungjin Kim, Wonho Choi, Gwangsik Jeon,* Seoul National University, South Korea; *Junyoung Lim, Yonghun Sung, David Ahn,* SK Hynix, Korea; *Cheol Seong Hwang,* Seoul National University, South Korea

This study investigates the fabrication and electrical performances of vertical selector-only memory (V-SOM) devices with atomic layer deposited conformal $Ge_{0.6}Se_{0.4}$ films for scalable storage-class memory applications. The bias polarity played a crucial role in stably inducing the polarity-induced threshold voltage (V_t) shifts originated by the asymmetric contact area between the vertical tungsten bitline (BL) and tungsten wordplane (WP). When a positive voltage was applied to the BL and the WP was grounded, stable switching occurred for initial forming, resulting in repeatable V_t readings. Conversely, applying a negative voltage caused subsequent V_t values measured under positive bias to be higher than those measured only with positive bias. The read voltage value between two V_t states provided sufficient current contrast, where a lower V_t state exhibited higher current (indicating the SET state), and a higher V_t state exhibited lower current (indicating the RESET state). The memory window (ΔV_t), the difference between the RESET and SET V_t values, showed minimal dependency on chalcogenide film thickness and cell area but increased with on-current amplitude. Cross-sectional analysis revealed polarity-sensitive elemental migration in amorphous films, driven by the electronegativity difference of Ge and Se. Compositional changes induced a gradient mobility edge, validated through subthreshold conduction analysis and subsequent modeling of field-induced non-equilibrium carrier distribution using a modified Poole-Frenkel equation. These results confirm the influence of band modulation on subthreshold conduction and ΔV_t, supporting the feasibility of the $Ge_{0.6}Se_{0.4}$ film-based V-SOM devices for vertical crosspoint architectures.

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AA-TuP-68 Designing Low-Thermal-Budget Hafnia-Based Ferroelectrics Capacitors*, **Peng Yuan**, Xufang Zhang, Jing Zhang,* North China University of Technology, China

In just over a decade, HfO_2-based ferroelectric thin films have progressed from early research stages to a potential candidate for integration into backend-of-line (BEOL) processes, with the possibility of industrialization.Acting as the dielectric in the 1T1C unit for ferroelectric random-access memory (FeRAM) or Dynamic random-access memory (DRAM), HfO_2-based ferroelectric thin film should be compatible with the thermal budget requirement (<400°C) of BEOL processes, especially in advanced nodes. However, achieving the necessary properties for these films typically requires rapid thermal annealing at temperatures above 400°C. Consequently, the pursuit of a low thermal budget (<400°C) for HfO_2-based ferroelectric materials has become a significant focus in the field. Despite this, achieving both high remanent polarization (P_r) and endurance within a low thermal budget remains a considerable challenge.

In this work,we provide a comprehensive study of atomic layer deposition (ALD) techniques for obtaining low-thermal-budget hafnia-based ferroelectric capacitors, including doping element, deposition temperature, and interface engineering. Additionally, we demonstrate ferroelectric hafnium-gallium oxide annealed at 400°C with high remanent polarization (P_r) and good endurance. Ferroelectric capacitors based on $Hf_xGa_{1+x}O_2$ thin films demonstrated high remnant polarization ($2P_r > 25\mu C/cm^2$), and good endurance for 10^9 cycles, making it fully compatible with BEOL processes.

AA-TuP-69 Low Resistivity Amorphous/Polycrystalline Titanium Nitride Multilayer Thin Films by Plasma-Enhanced Atomic Layer Deposition for Metal Diffusion Barrier*, Christophe Vallee, **Van Long Nguyen**, Natalya Tokranova,* University at Albany-SUNY

Titanium nitride (TiN) has attracted significant interest in microelectronics due to its excellent chemical resistance, thermal stability, and low resistivity. [1] It is widely used as a metal gate in CMOS technology, electrode material in DRAMs, and metal diffusion barrier. [2-4] Traditionally, TiN thin films are deposited using physical vapor deposition (PVD) or chemical vapor deposition (CVD). However, as device geometries become more complex and shrink to nanometer scale, halogen-free atomic layer deposition (ALD) processes are preferred due to their angstrom scale controllability, superior step coverage, and reduced risk of metal corrosion. To obtain low-resistivity TiN films, plasma-enhanced ALD (PE-ALD) is more effective than conventional thermal ALD due to improving TiN crystallinity and minimizing oxygen and carbon impurities. Additionally, the plasma with substrate biasing can further improve film quality thanks to the presence of energetic ions. In this study, we demonstrate a low-resistivity TiN multilayer thin film composed of alternating amorphous and polycrystalline TiN layers, deposited by using supercycles of PE-ALD (**Figure S1a**). The amorphous layers, an effective metal diffusion barrier due to its disordered structure making complex pathways for metal atoms to diffuse through, continue to interrupt diffusion pathways via grain boundaries of polycrystalline layers which have low electrical resistivity. As a result, the multilayer structure film can exhibit improved barrier properties and electrical resistivity (**Figure S1b**). The PE-ALD processes were carried out at 250ºC using tetrakis(dimethylamido)titanium (TDMAT) with Ar plasma for amorphous TiN layers, and TDMAT with $N_2/H_2/Ar$ plasma for polycrystalline TiN layers. Our initial results indicate a promising research direction; however, further investigation and optimization are required for both TiN single-layer and multilayer structures.

AA-TuP-70 Influence of Thermal Annealing on Interdiffusion and Electrical Characteristics of Ferroelectric FETs Interface of IGZO/HZO*, **HyeJoo Kang**,* Ajou University, Republic of Korea*; Seung Wook Ryu, Dohee Kim, Jongyoung Lee,* SK Hynix, Korea*; Il-Kwon Oh,* Ajou University, Republic of Korea

Due to the physical processing limitations of dynamic random access memory (DRAM) capacitors, various memory devices for capless DRAM are being explored. Among these, ferroelectric field effect transistors (Fe-FETs) using ferroelectricity properties stand out as promising candidates for capless DRAM technology. Recently, research has focused on Fe-FETs utilizing hafnium zirconium oxide (HZO) as the ferroelectric material and indium gallium zinc oxide (IGZO), known for its extremely low off-current, as the channel material.[1] However, high-temperature annealing is often required to induce the desirable ferroelectric phase in HZO. This annealing process can lead to interdiffusion of elements at the interface between the HZO and IGZO layers, potentially forming unwanted phases and defects.[2] These issues can negatively impact the electrical properties and overall performance of the devices.[3] Therefore, addressing and mitigating interdiffusion at the interface during annealing is crucial for maintaining device stability and performance. Understanding the mechanisms of interdiffusion and developing strategies to minimize its effects are essential for the reliable fabrication of Fe-FETs.[4]

In this study, we investigate the impact of annealing temperature on interdiffusion at the IGZO/HZO interface and the electrical device characteristics of Fe-FET using IGZO/HZO. To evaluate the effect of annealing temperatures ranging from 350°C to 750°C on interdiffusion at the IGZO/HZO interface, we used secondary ion mass spectrometry (SIMS) and confirmed that extreme interdiffusion occurs at temperatures above 550°C. The crystallinity of HZO, essential for its ferroelectric properties, was examined using grazing incidence X-ray diffraction (GI-XRD) on an MSFM device structured as TiN/IGZO/HZO/TiN. Additionally, polarization versus voltage (P-V) measurements were conducted on the MSFM device after annealing to evaluate its polarization characteristics. We fabricated Fe-FETs utilizing IGZO/HZO and evaluated the device characteristics, including field-effect mobility (μ_{FE}), I_{on}/I_{off}, subthreshold swing (SS) and memory window. We anticipate that this research will contribute to studies involving Fe-FETs using IGZO and HZO.

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AA-TuP-71 Plasma Enhanced Atomic Layer Deposition of HfO_2 with Applying DC Bias*, **Hee Jun Yoon**, Taeyoon Lee, Hyeongtag Jeon,* Hanyang University, Korea

As semiconductor devices become scaled down, it is important to maintain the high capacitance in dynamic random access memory (DRAM). It was studied that shrinking the thickness could increase capacitance, but it has many problems such as leakage current. Since there are limits to reducing the thickness or increasing the area, it is important to find materials with high dielectric constants to enhance the capacitance. Therefore, there are many high-k materials like Al_2O_3, and ZrO_2, but research of high k material is still being studied.[1]

Hafnium oxide (HfO_2) has been suggested as next generationhigh k material. HfO_2 has monoclinic, cubic, and tetragonal phases and the monoclinic phase has a kvalue of ~20, but the tetragonal phases has a value of ~40, therefore it is important to obtain HfO_2 with a tetragonal phase.

In the case of high-k material, it is important to deposit thin film for DRAM capacitors and the conformality, uniformity, quality must be good. Conventionally, chemical vapor deposition (CVD) has problems about requiring high temperature, poor uniformity. To meet these requirements, atomic layer deposition (ALD) has been studied for better uniformity and conformality, but plasma enhanced atomic layer deposition (PEALD) has been used for lowering process temperature and its good reactivity of radicals.[2]

However, unlike conventional PEALD, we introduced the DC bias with PEALD. When a positive DC bias is applied, the sheath region of plasma is reduced, allowing radicals to reach the substrate more easily. As a result of the high reactivity of these radicals, high-crystallinity HfO_2 can be deposited.

In this study, $HfO\text{-}_2$ was deposited using cyclopentadienyl-tris(dimethylamino) hafnium (Cp-Hf) and O_2 remote plasma. Process window and composition of film were evaluated by spectroscopy ellipsometry (SE), auger electron spectroscopy (AES) respectively. Film density and crystallinity were evaluated by X-ray reflectometry (XRR), X-ray diffraction (XRD). X-ray photoelectron spectroscopy (XPS) was utilized for chemical binding state and analysis of step coveragein 3D structure was done with Transmission electron microscopy (TEM).

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AA-TuP-72 Development of High-Performance 2 nm In_2O_3 Thin-Film Transistors via BEOL-Compatible ALD Process Using DBADMIn Precursors*,*

In-Hwan Baek, ***InHong Hwang,*** Inha University, Republic of Korea

Indium oxide has emerged as a promising channel material for thin-film transistors (TFTs), extending from display backplane applications to low-leakage DRAM transistors and monolithic 3D integrated circuits (M3D ICs) integration. The low thermal budget of atomic layer deposition (ALD) renders it compatible with M3D fabrication, thereby preventing thermal damage to underlying layers. The capability of ALD to enable conformal deposition on 3D structures has facilitated the scaling of 2T0C DRAM, demonstrating the feasibility of $4F^2$ and $2F^2$ architectures.[1] Additionally, the inherent low off-current of oxide semiconductors makes them well-suited for low-power consumption devices. In this research, we demonstrate high-performance TFTs using a 2 nm-thick indium oxide channel layer. The high mobility of the TFTs was achieved along with outstanding bias stress stability. These results highlight the scalability and applicability of indium oxide TFTs for next-generation memory devices.

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AA-TuP-73 Influence of Process Conditions on Stability and Plasma Resistance of ALD Y_2O_3 Thin Films*,*

Min Joo Koo, *Hyun Mi Kim, Hye Young Kim,* Korea Electronics Technology Institute, Republic of Korea*; Chang sub Park, Yong Soo Lee,* KoMiCo, Republic of Korea*; Sung Kyu Jang, Jong Hyun Choi, Seul Gi Kim, Sun Gil Kim, Hyeong keun Kim, Ji hun Kim,* Korea Electronics Technology Institute, Republic of Korea

As semiconductor devices continue to scale down, the demand for advanced chamber coatings in etching and deposition equipment has grown. Atomic Layer Deposition (ALD) is widely used for this purpose due to its excellent film uniformity, conformality, and precise thickness control. While Al_2O_3 has been the standard chamber coating material, Y_2O_3 is gaining attention for its superior plasma resistance, high secondary electron emission, and strong etch resistance against fluorinated plasmas. However, ALD Y_2O_3 processes using H_2O as a reactant show lower reproducibility and higher variability than O_2 plasma or O_3-based processes, making it essential to address these challenges for stable film deposition.

This study developed an ALD Y_2O_3-H_2O process using a liquid precursor and analyzed the impact of process temperature on thin film properties and plasma resistance characteristics. In ALD, process temperature significantly influences film composition, surface morphology, and thickness uniformity, making its optimization crucial. To improve the reproducibility and stability of the ALD Y_2O_3-H_2O process, three approaches were employed. First, the purge time was extended to minimize the influence of residual reactive gases and byproducts remaining in the chamber after reactions. Second, an initial 40-cycle H_2O pulse-exclusive process was introduced to reduce variability in the early growth phase and stabilize the initial process conditions. Additionally, process temperature was evaluated to examine their impact on process stability and thin film formation. To ensure a comprehensive analysis, all three approaches were conducted alongside time-of-flight-mass spectrometry (TOF-MS) monitoring, which provided real-time insights into gas-phase species and reaction byproducts, aiding process evaluation. This method aimed to improve process reliability by ensuring consistency in the early growth stage. Plasma resistance evaluations were conducted using CF_4, O_2, and Ar gases gases under plasma exposure to investigate the effects of temperature variations and H2O process stabilization on the durability of Y2O3 film.

This study is expected to enhance the understanding of the Y precursor H_2O reactant process and contribute to optimizing process conditions. By improving process reliability and reproducibility, the findings can support the development of high-quality thin films for various applications.

AA-TuP-74 Increasing Quality of ALD-Grown Nitrides Through Atomic Layer Annealing*,*

Bas van Asten, TU Delft, Netherlands

B. van Asten

Kavli Institute of Nanoscience, Delft University of Technology, Delft, The Netherlands

Superconducting nitrides, such as titanium nitride, are one of the promising materials used as resonators within the fabrication of superconducting quantum computers. Typically, these resonators are used to detect and read the quantum state of qubits [1]. Through plasma enhanced atomic layer deposition these superconducting nitrides can be grown. One of the techniques proposed to increase the quality of these films is atomic layer annealing (ALA), where after every ALD cycle a thermal source is used to heat the grown layer. The effect of this anneal is similar to high temperature deposition, but has less of a toll on the thermal budget of the underlying sample. The quality of this deposition has shown to allow for low temperature epitaxial growth [2]. In this work, we characterize the superconducting TiN films by comparing the critical temperatures of films grown with ALA-ALD, using a plasma source to provide local heating. By looking at resistivity and x-ray diffraction of various films, the effects of ALA on the crystallinity of the films is investigated.

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AA-TuP-75 Plasma-Enhanced and Thermal Atomic Layer Deposition of Superconducting Nitride Thin Films*,*

Zahra Ahali, *Sanaz Zarabi,* Beneq Oy, Finland*; Ziying Wang, Peter Liljeroth,* Aalto University, Finland*; Otto Laitinen,* Beneq Oy, Finland

Atomic layer deposition (ALD) is a promising technique for fabricating superconducting thin films with precise control on thickness and uniformity. Superconducting thin films are increasingly relevant to the semiconductor industry, where they enable advancements in ultra-sensitive sensors, cryogenic computing, and quantum technologies. Their integration with semiconductor-based devices offers new possibilities for high-speed, low-power electronics and next-generation computing architectures (1-3).

In this study, we systematically investigate the deposition of superconducting (TiN) films using both thermal ALD and plasma-enhanced ALD (PEALD) to understand how deposition conditions influence superconducting properties. By employing NH3/N2 plasma reactants, we explore the effects of key process parameters—including plasma exposure time, gas flow ratios, and plasma power—on film characteristics such as resistivity and superconducting transition temperature. The films were deposited on silicon wafer substrates and thoroughly characterized to assess their structural and electrical properties. X-ray diffraction (XRD) was used to evaluate the crystalline state of the films, while scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM) were employed to analyse film thickness and morphology (2-3).

Our results provide insights into how ALD mode impacts superconductivity in these films, highlighting the role of process parameters in optimizing superconducting performance. This study contributes to the broader understanding of ALD-based superconducting material fabrication, offering valuable data for future process optimization and material development.

Keyword: Superconducting, Thin film, ALD, Plasma, Optimization.

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Affiliation:

1.Beneq Oy, Espoo, Finland

2.Department of Applied Physics, Aalto University, Espoo, Finland

AA-TuP-76 Effect of Interfacial Layer on Ferroelectricity of Hf$_{1-x}$Zr$_x$O$_2$ Thin Films in MFIS Structure*, Hyo-Bae Kim*, *Ji-Hoon Ahn,* Hanyang University, Republic of Korea

Ferroelectrics offers new opportunities for the development of the next generation semiconductor devices such as memristors for neuromorphic computing, replacement of NAND flash, and FeFET for 2T DRAM devices. Hafnia based ferroelectrics are theoretically advantageous ferroelectrics for device scaling, due to their several advantages, such as CMOS compatibility, stable remanent polarization even below 10 nm, and unit cell-by-unit cell dipole control. Nonetheless, some challenges must be overcome to fabricate stable ferroelectrics devices, including presence of unnecessary interlayer (e.g., dead layers), and unstable ferroelectric crystallinity at thin scales. In particular, unnecessary interfacial layer contributes to the formation of depolarization fields, charge trapping/detrapping, and atomic ratio mismatches, thereby complicating the deposition of stable ultra-thin ferroelectrics. In this study, we investigated the alteration of ferroelectric properties resulting from the intentional insertion of interfacial layer between Hf$_{1-x}$Zr$_x$O$_2$ and Si substrate in MFIS structure capacitors. Measured the electrical properties and crystallinity of the thin ferroelectric capacitors (below 3 nm) and confirmed ferroelectric properties regardless of the annealing process. These results suggest that selective growth or suppress of the interfacial layer can effectively enhance the ferroelectric phase in ultra-thin films.

AA-TuP-77 Lanthanum ALD Precursors for the Application fo High-κ Gate Dielectrics*, I-Cheng Tseng*, *Yong-Jay Lee,* Industrial Technology Research Institute, Taiwan

Rare-earth metal compounds exhibit unique electronic and magnetic properties, making them widely used in semiconductors, manufacturing, and the chemical industry. As transistors continue to shrink, rare-earth oxides are becoming increasingly important in microelectronics due to their wide band gaps, high dielectric constants, and excellent thermal stability. Atomic layer deposition (ALD) further enables transistor miniaturization.

In this study, we synthesized a lanthanum (La) ALD precursor for depositing La_2O_3 thin films, La_2O_3 has a higher dielectric constant, compare to conventional SiO_2, which can replace SiO_2 as a gate dielectric in field-effect transistor and serve as capacitor layers in next-generation dynamic random-access memory (DRAM).

AA-TuP-78 Charge Trapping Memory Structure with Low Interface Defect Density of <10^{12} cm-2 eV-1 via Remote Plasma-Based Hydrogen Post-Treatment*, ChanHee Lee*, *Hee chul Lee,* Department of Advanced Materials Engineering, Tech university of korea

HfO_2 and ZrO_2, as high k dielectric materials, hold significant promise for replacing silicon nitride-based charge trapping layer (CTL) in conventional NAND flash memory. This potential is attributed to their high trap densities, substantial conduction band offsets relative to the tunneling oxide (TO), and thin equivalent oxide thickness (EOT). Previous studies have demonstrated that remote plasma (RP) deposition causes less damage than conventional direct plasma methods, thereby improving device performance. In our prior work, RP deposited HfO_2 and ZrO_2 exhibited a relatively low interface defect density (D_{it}) of 1.3×10^{12} cm^{-2} eV^{-1}, as measured by the Castagné–Vapaille method.

In this study, we investigate the effect of hydrogen plasma treatment (HPT) on HfO_2 and ZrO_2 to reduce D_{it} to approximately ~10^{11} cm^{-2} eV^{-1} range. Specifically, we employed remote plasma with a power of 1.9 kW at 2 Torr to activate hydrogen (5% H_2/Ar), applying a 30 second treatment for two cycles prior to high k deposition. Devices with the structure p-Si/SiO_2(~2 nm)/high-k(10 nm)/Al_2O_3(10 nm)/Au were then fabricated using either HfO_2 or ZrO_2 as the high k layer.

Capacitance–voltage (C–V) measurements were performed on these devices, and D_{it} was extracted via Berglund integration. Notably, the HPT treated devices exhibited similar C–V characteristics under both high frequency (1 MHz) and low frequency (1 kHz) conditions, indicating a very low interface defect density, especially in the shallow trap region. Furthermore, under a rapid thermal annealing (RTA) condition of 400°C for 20 minutes, ZrO_2 showed a D_{it} of 1.75×10^{11} cm^{-2} eV^{-1} and a memory window (MW, extracted using a ±4 V voltage sweep) of 0.4805 V, while HfO_2 exhibited D_{it} and MW values of 2.76×10^{11} cm^{-2} eV^{-1} and 0.4752 V, respectively.

In conclusion, our findings demonstrate that remote plasma deposition combined with hydrogen plasma treatment offers significant advantages for fabricating CTM(charge trapping memory) devices with low defect densities, achieving D_{it} values of as low as ~10^{11} cm^{-2} eV^{-1} range. Moreover, optimizing process parameters such as plasma power (which is closely correlated with radical density) and RTA conditions can make it feasible to further reduce D_{it} below 10^{11} cm^{-2} eV^{-1} and enhance the MW to above 1.5 V.

AA-TuP-79 Plasma-Pretreated ALD Growth of Platinum Catalysts on Carbon Nanotubes for Polymer Electrolyte Membrane Fuel Cell Applications*, Junmo Koo,* Korea Maritime and Ocean University, Republic of Korea*; Joon Hyung Shim,* Korea University, Republic of Korea

Platinum (Pt) catalysts are essential for polymer electrolyte membrane fuel cells (PEMFCs), but their high-cost limits commercialization. Atomic layer deposition (ALD) provides precise control over Pt catalyst growth, optimizing efficiency and stability. This study explores the impact of oxygen plasma pretreatment on Pt ALD growth on carbon nanotube (CNT) supports. Without plasma treatment, Pt formed uniformly as small nanoparticles, whereas plasma-treated CNTs exhibited sparsely distributed larger Pt clusters due to preferential nucleation sites. Electrochemical testing revealed that catalysts grown on plasma-treated CNTs exhibited higher electrochemical surface area (ECSA) and improved fuel cell performance. The larger, well-distributed Pt particles enhanced charge transfer and oxygen reduction reaction (ORR) efficiency, leading to more stable and higher power generation compared to bare CNT-supported catalysts. Our findings demonstrate that oxygen plasma pretreatment effectively modulates Pt nucleation during ALD, improving catalyst utilization and durability. This approach provides a scalable and efficient route for optimizing Pt catalyst deposition in next-generation fuel cells.

AA-TuP-80 Impact of Zr-Precursor Ligand Design on Interfacial and Electrical Properties of ALD-Grown ZrO_2Thin Films*, Hyeong Jun Kim*, *Haram Yang, Woongkyu Lee,* Department of Materials Science and Engineering, Soongsil University, Republic of Korea

The development of next-generation logic devices and dynamic random access memory (DRAM) capacitors requires achieving sufficient capacitance to compensate for the decreasing electrode area due to device scaling. High-k dielectric materials have emerged as a promising solution, with ZrO_2 attracting significant attention for its excellent dielectric properties: ~20 in the monoclinic phase, ~47 in the tetragonal phase, and ~37 in the cubic phase. Additionally, ZrO_2 exhibits high chemical stability and a large bandgap (~5.8 eV), contributing to stable leakage current properties. The Cp-based Zr precursor Cp-Zr(NMe_2)$_3$, primarily used for the atomic layer deposition (ALD) of ZrO_2, offers high thermal and chemical stability. However, it requires prolonged O_3 exposure time, which inevitably lead to the formation of a low-k interfacial layer by bottom electrode oxidation, degrading capacitor performance. Consequently, novel precursors have been developed for further optimized ALD process to minimize the interfacial defect formation during high-k dielectric deposition.

In this study, an ALD process using the MePrCp-Zr(NMe_2)$_3$ precursor (UP Chem Co.) and O_3 was developed, confirming ALD growth behavior across a wide process temperature range of 150-300 °C. A comparison of ALD saturation times at 300 °C between the conventional Cp-Zr(NMe_2)$_3$ and MePrCp-Zr(NMe_2)$_3$ revealed that the MePrCp-Zr(NMe_2)$_3$ exhibited higher reactivity, enabling growth of ZrO_2 thin films with shorter O_3 exposure time than Cp-Zr(NMe_2)$_3$. A planar capacitor with a (top) 60 nm Pt/ ZrO_2/ 100 nm TiN (bottom) structure was fabricated, and electrical properties revealed ~ 0.5 nm decrease in equivalent oxide thickness (EOT) when using MePrCp-Zr(NMe_2)$_3$ compared to Cp-Zr(NMe_2)$_3$. This indicates the interfacial property improvement by the suppression of the low-k TiON layer, which forms between ZrO_2 and the bottom electrode. Furthermore, etching damage of Ru substrates during ZrO_2 deposition on them using different precursors and O_3 was examined to evaluate the feasibility as next-generation electrode materials.

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AA-TuP-81 Mitigating Crystallinity Degradation and Leakage Current of Rutile TiO_2 Dielectric Thin Films via Mg Doping, ***Seungwoo Lee**, Soomin Yoo, Chaeyeong Hwang,* Kyung Hee University, Republic of Korea*; Hansol Oh, Daeyeong Kim, Yongjoo Park,* SK Trichem, Republic of Korea*; Woojin Jeon,* Kyung Hee University, Republic of Korea

Further scaling is needed to reduce the production cost of dynamic random-access memory (DRAM), and adopting higher dielectric constant (*k*) materials as the insulators in DRAM capacitors is necessary to ensure sufficient capacitance for robust operation within limited design rules. TiO_2 is an attractive candidate due to its *k* value (>100) in the rutile phase and atomic layer deposition (ALD) compatibility but is challenged by its poor leakage current characteristics due to its low bandgap (~3 eV). For this reason, suppressing leakage current through conduction band offset control between TiO_2 and the electrode film was effective, such as Al doping. However, since ALD-grown Al_2O_3 is usually amorphous at typical ALD process temperatures, Al doping degraded the crystallinity of TiO_2, thereby reducing the capacitance density.

Therefore, in this presentation, we discuss the results of using Mg as a dopant to mitigate the crystallinity degradation of TiO_2 and induce acceptor doping effects such as Al doping. For crystallizing rutile TiO_2, we utilized MoO_2 thin films as a template and an electrode. Mg-doped TiO_2 showed a smaller decrease in *k* value with increasing doping concentration compared with Al-doped TiO_2. Grazing-incidence X-ray diffraction measurement results show that Mg doping did not significantly degrade the crystallinity of TiO_2. Additionally, the leakage current of the TiO_2 dielectric film was suppressed by Mg doping, suggesting that Mg dopant induces the acceptor doping effect like Al dopant.

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AA-TuP-82 Effect of Tungsten Insertion Layer on the Electrical Properties of PEALD HZO Thin Films for Semiconductor Memory Applications, *Hee Chul Lee, Ha Jeong Kim, **Jea Hyuk Choi**,* Semicon Plasma Process LAB, Republic of Korea

Hafnium-zirconium oxide ($Hf_xZr_{1-x}O_2$, HZO)-based thin films exhibit ferroelectricity even at sub-nanometer thicknesses, making them a promising candidate for next-generation non-volatile and low-power semiconductor memory applications. However, defects such as oxygen vacancies within the HZO film can degrade its ferroelectric properties, necessitating further studies on electrode materials and processing conditions to o

In this study, Co-Plasma ALD (CPALD) was employed to deposit HZO films, and the effects of a tungsten (W) insertion layer on the electrical properties of TiN/HZO/TiN capacitors were systematically investigated. The thickness of the tungsten insertion layer was varied (0, 5, 10, and 20 nm) to examine its influence on the structural, electrical, and chemical characteristics of the HZO films. Analysis of the polarization-electric field (P-E) hysteresis curves revealed that introducing the tungsten insertion layer significantly suppressed the wake-up effect, with the highest remanent polarization (2Pr) value of 61.0 $\mu C/cm^2$ observed.

XRD analysis demonstrated that introducing the tungsten insertion layer enhanced the formation of the orthorhombic (o-) phase, which is responsible for ferroelectricity. When the tungsten insertion layer thickness increased up to 10 nm, the o-phase fraction rose from 59.1% to 81.1%, while the tetragonal (t-) phase proportion decreased. This finding strongly correlates with the observed improvement in ferroelectric performance. Furthermore, XPS analysis indicated that incorporating the tungsten insertion layer at the bottom interface reduced oxygen vacancies and improved the crystallinity of the HZO film by decreasing the proportion of sub-stoichiometric Hf 4f and Zr 3d oxide states.

A comparative analysis of electrode configurations revealed that inserting the tungsten layer at the bottom electrode resulted in superior ferroelectric properties compared to the top electrode configuration. The bottom tungsten insertion layer significantly reduced oxygen vacancies, minimizing the wake-up effect and enhancing device reliability. The highest 2Pr value was obtained when tungsten was inserted at both the top and bottom electrodes, indicating optimal ferroelectric performance.

This study demonstrates that the tungsten insertion layer plays a crucial role in improving the ferroelectric characteristics of HZO films, particularly by mitigating oxygen vacancy-related defects at the electrode interface. The electrode configuration and processing conditions proposed in this research are expected to serve as a valuable foundation for next-generation semiconductor memory technology advancements.

AA-TuP-83 The Impact of Chromium Ion Implantation on ALD Lead Chalcogenide Thin Films, *Haifeng Cong,* Old Dominion University*; Charlotte Poterie, Jean Francois Barbot,* Universite de Poitiers-CNRS, France*; **Helmut Baumgart**,* Old Dominion University

Inherently the synthesis of semiconducting materials by Atomic Layer Deposition ALD produces only intrinsic undoped films which require the introduction of small amounts of impurities for doping to change them into extrinsic semiconductors. Apart from various in-situ diffusion doping techniques like delta doping during the ALD process, post deposition doping by ion implantation affords the best control of dose and doping profile. The present study investigates the impact of 180 keV Cr^+ ion implantation on the properties of semiconducting ALD lead chalcogenide thin films to improve their thermoelectric figure of merit. The implantation was accomplished with 180 keV Chromium ions at a given fluence of 5×10^{15} ions cm^{-2} to reach a desired 1% Cr doping level. The energy of the incident ions was tuned using stopping and range of ions in matter (SRIM) simulations to produce an implant peak around the projected range centered on the ALD film thickness. The thermoelectric PbTe thin films have been synthesized on silicon substrates covered with native oxide by ALD using lead (II)bis(2,2,6,6-tetramethyl-3,5-heptanedionato) ($Pb(C_{11}H_{19}O_2)_2$), and (trimethylsilyl) telluride ($(Me_3Si)_2Te$) as ALD precursors for lead, and tellurium and Nitrogen as the carrier and purge gas. The Si native oxide surface was functionalized before ALD PbTe thin film deposition to ensure reproducible chemisorption of the ALD precursor compounds. The growth temperature during ALD was varied over a range from 130ºC to 170ºC. The Lead precursor was volatilized at a temperature of 170 ºC and the Tellurium precursor was heated at 45 ºC. The chamber base pressure was kept at 500 mTorr.Several physical characterization techniques among them SEM and EDS have been employed to determine the ALD PbTe thin film characteristics before and after Chromium ion implantation. X-ray diffraction analysis reveals that the films exhibit a polycrystalline structure with simple cubic crystallites. Atomic force microscopy analysis was employed to determine the surface properties of the films, including surface topology, root mean square (RMS) roughness, grain height, and average size. For the electrical characterization we report the effects of the ion implantation on the resistivity ρ(T) as a function of temperature, the electrical conductivity, the Hall mobility, and the Seebeck coefficient.

AA-TuP-84 Atomic Layer Deposition of Zirconia and Titania Inhibit Sintering in Pt Catalysts Under Oxidative Reaction Conditions, ***Bang Nhan**,* Department of Chemistry, Stanford University*; Shyama Mandal,* Department of Chemical Engineering and SUNCAT Center for Interface Science and Catalysis, Stanford University*; Jacob Smith,* Oak Ridge National Laboratory*; Gennaro Liccardo,* Department of Chemical Engineering and SUNCAT Center for Interface Science and Catalysis, Stanford University*; Sydney Richardson,* Mechanical Engineering, Stanford University*; Frank Abild-Pedersen,* SLAC National Accelerator Laboratory*; Miaofang Chi,* Oak Ridge National Laboratory*; Matteo Cargnello, Stacey Bent,* Department of Chemical Engineering and SUNCAT Center for Interface Science and Catalysis, Stanford University

Platinum-group elements are widely used in heterogeneous catalysis due to their exceptional activity, making them essential for applications such as emission control and electrocatalytic hydrogen evolution reaction (HER). However, their scarcity necessitates strategies to optimize metal utilization and enhance catalyst stability. Under extreme thermal and oxidative conditions, small Pt nanoparticles (NPs) sinter over time, leading to catalyst deactivation and subsequently, metal efficiency reduction.

Several strategies have been implemented to minimize sintering, such as encapsulating Pt NPs within a metal oxide framework. However, full control over the encapsulation process is still needed. Atomic layer deposition can meet the needs for growing conformal thin films with Angstrom-level precision on high-aspect-ratio substrates. In this study, we explored ALD-grown zirconia and titania as encapsulation shells for Pt catalysts. Colloidally synthesized Pt NPs were first supported on amorphous alumina (Pt/Al_2O_3), followed by ALD growth of zirconia [tetrakis(dimethylamino) zirconium and water] and titania [tetrakis(dimethylamino) titanium and water] overlayers, achieving a GPC of 1.4 Å/cycle for both processes.

The hydrothermal stability of the ALD-modified catalysts was evaluated using propene (C_3H_6) oxidation as a model reaction for residual hydrocarbon combustion. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)revealed that after hydrothermal aging at 850°C for 4 hours, the particle size of the ALD-coated catalysts remained unchanged, while the control Pt/Al_2O_3 catalyst experienced significant sintering. Arrhenius plots collected at steady-state C_3H_6 conversion showed that the ALD-modified catalysts exhibited improved stability and enhanced activity, whereas the control catalyst lost up to fivefold of its initial activity. Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) indicated that this improvement stems from the formation of under-coordinated Pt sites as small nanoclusters within the ALD overlayers during thermal aging. The enhanced stability is attributed to the physical barrier imposed by the ALD coatings, which suppresses Ostwald ripening of oxidized Pt species under reaction conditions. The zirconia-based catalysts show higher activity than the titania-based catalysts, a difference attributed to the microstructure of the ZrO_2 film. Overall, these findings highlight the effectiveness of ALD-grown zirconia and titania overlayers in stabilizing Pt catalysts, offering a promising strategy for enhancing catalyst durability and performance in high-temperature applications

AA-TuP-85 Thin Conductive Cu Films by Post-Reduction of Atomic Layer Deposited CuO, ***Maria Gabriela Sales**, Neeraj Nepal, Peter Litwin, David Boris, Scott Walton, Virginia Wheeler,* U.S. Naval Research Laboratory

Interconnect applications in microelectronics has helped spur the need to develop robust and scalable atomic layer deposition (ALD) processes for copper (Cu). For this application space, the unique advantage of ALD is being able to conformally coat high aspect ratio via structures due to its self-saturating nature and precise thickness control. Reported ALD recipes for pure Cu typically rely on reactions between a metal-organic Cu precursor and a reducing reactant, including different chemical compounds for thermal ALD or a reducing plasma for plasma-enhanced ALD (PEALD). However, these conventional Cu ALD processes have very low growth rates of 0.1-0.5 Å/cycle, at best. As is typical of other metal ALD recipes, traditional ALD of metallic Cu requires the deposition of at least 20-40 nm in order to achieve full grain coalescence and a conductive film.

In this work, we report on an alternative way of obtaining conductive Cu films through the use of an in-situ plasma reduction. Initially, copper (II) oxide, or CuO, is deposited by PEALD at a substrate temperature of 150 °C, using copper(I)-N,N'-di-sec-butylacetamidinate ($[Cu(^sBu\text{-}amd)]_2$) and Ar/O_2 plasma as precursors. The growth rate for this CuO recipe is 0.3 Å/cycle, which is higher than what is obtained for pure Cu using the same precursor (0.1 Å/cycle). Grown CuO films have a low concentration of incorporated ligands and a smooth surface morphology. Following CuO ALD, the CuO film is exposed to reducing plasma pulses containing a mixture of Ar and H_2 gas. This reduction with Ar/H_2 plasma exposure is performed in-situ, without removing the CuO sample from the ALD reactor. To characterize the films, spectroscopic ellipsometry (SE), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and contactless sheet resistance measurements were performed.

In this talk, we will discuss various parameters in the Ar/H_2 reducing plasma, such as total exposure time, pulse lengths, and number of reducing plasma cycles, and investigate how they affect key properties of the resultant Cu film, such as chemistry, morphology, and resistivity. Additionally, we report on utilizing supercycles of CuO ALD and reducing plasma pulses to grow thicker (30 nm) Cu films with low resistivity. To date, our most optimal CuO-then-post-reduction procedure yielded a 30 nm Cu film with a root mean square (RMS) roughness of 3.3-3.5 nm and a resistivity of 3.8 µΩ cm, which is only a factor of 2 greater than for bulk Cu.

AA-TuP-86 Enhanced Dielectric Properties of HfO2 Thin Films Produced Via Novel Catalytic Atomic Layer Deposition Process, ***Sara Harris**, Dane Lindblad, Aaron Wang, Arreliane Dameron, Matthew Weimer,* Forge Nano

Optimized high-κ dielectric materials are widely utilized as gate oxides and dielectric barriers in compound semiconductor devices such as GaN HEMT and MEMS [1]. Monolithic high-κ dielectric materials have inherent performance tradeoffs demonstrated by hafnium oxide (HfO_2) which has a high dielectric constant but a low breakdown voltage and high leakage current limiting overall efficacy as a dielectric barrier[2]. Composite materials such as $HfAlO_x$ can improve dielectric performance by combining the high dielectric constant of HfO_2 with the wider band gap and higher breakdown voltage of aluminum oxide (Al_2O_3) unlocking capabilities for next generation dielectric materials [2]. Atomic layer deposition (ALD) exploits precise control over self-limiting surface chemistry allowing for discreet nanolayers that can be tailored to optimize bulk film dielectric performance with a level of control that is not possible via other deposition techniques (CVD and PVD). This work demonstrates HfO_2 thin films deposited via ALD with enhanced dielectric properties achieved through the addition of a novel catalytic conversion step known as a CRISP Process. HfO_2 deposited via the CRISP process has 29% higher GPC, 7% higher density, more ideal stoichiometry, 44% less carbon impurity and larger crystal grains when compared to films growth with O_3 alone. In pursuit of high performing dielectric materials several compositions of ALD deposited nanolaminates were studied through the incorporation of small amounts of Al_2O_3 into bulk HfO_2. Discreet nanolayer formation is demonstrated via cross sectional scanning electron microscopy (SEM) shown in Figure 1. With varying amounts of Al_2O_3, dielectric constant, κ, can be increased from 16.2 to 19.2, the dielectric strength (breakdown voltage) can be increased from 6.9 to 7.8 MV/cm, and the leakage current density can be reduced from $3.3x10^{-9}$ to $8.1x10^{-12}$ J at 60Vm. Figure 2 demonstrates leakage current density and dielectric constant improvements for various compositions of CRISP and ozone based HfO_2 nanolaminate thin films. Work is ongoing to tune layer composition for the best overall performance. In the future, full characterization in GaN HEMT devices is planned for both the $HfO_2 – O_3$ and HfO_2 – CRISP processes.

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AA-TuP-87 MoO2Cl2: how the first large volume solid precursor has been enabled for HVM, ***Jeffrey Yoder**,* Air Liquide

The semiconductor industry is adopting Molybdenum (Mo) to replace Tungsten for some leading edge device applications to improve performance across NAND, logic, and DRAM. MoO2Cl2 is being chosen for the largest volume application in 3D NAND manufacturing due to its high vapor pressure and superior ability for word line gap-fill. In a first-of-its-kind development for a solid precursor, bulk vapor delivery systems enable the distribution of the molecule from the sub-fab to the process tools versus the use of small packaging installed inside the tool. The use of bulk systems serves to lower the customer total cost of ownership (TCO) while freeing up the valuable fab tool deck space. This talk will review the key aspects of the MoO2Cl2 application, manufacturing, supply chain, and enabling high volume manufacturing with sub-fab bulk vapor delivery systems.

AA-TuP-88 Mitigation of Surface Dielectric Loss in Superconducting Quantum Devices via Combined Atomic Layer Etching and Deposition, ***Neha Mahuli**, Joaquin Minguzzi, Jiansong Gao, Omar Reyna, Sandra Diez, Victor Ly, Guillaume Marcaud, Matthew Hunt, Jefferson Rose, Loren Swenson, Oskar Painter, Ignace Jarrige,* Amazon

We present a surface treatment that integrates atomic layer etching (ALE) and atomic layer deposition (ALD) to mitigate the dielectric loss in superconducting quantum devices. We report the application of this dry process to aluminum (Al)-based coplanar waveguide resonators and transmon qubits. We show that ALE of Al_2O_3 at 300°C, performed using alternating exposures of trimethylaluminum (TMA) and HF-pyridine, not only conformally removes the native metal oxide but also effectively cleans the surface by eliminating organic residues from all exposed regions, including sidewalls and silicon (Si) surfaces. Subsequent ALD of Al_2O_3 at the same temperature enables controlled regrowth of a uniform, high-purity dielectric on the metal surfaces. Our characterization of the surface chemical properties points to a significant reduction in fabrication-induced contamination and the formation of a thinner, Al-rich oxide layer that resembles pristine native Al oxide. We show that the application of this treatment to our devices is correlated with a reduction in dielectric loss at single-photon power levels by a factor of two, achieving transmon coherence times exceeding 0.4 ms — the highest reported for this geometry to date. Ongoing work aims to extend this approach to remove the native Si oxide, explore alternative low-loss dielectric encapsulation layers, and further isolate the individual contributions of ALE and ALD to these performance gains.

Area Selective ALD
Room Event Hall - Session AS-TuP
Area Selective ALD Poster Session

AS-TuP-1 Advancing AS-ALD of WSe_2 Through Nature-Inspired Engineering, ***Kylee Lamberson**, Chih-hung Chang,* Oregon State University

Area-selective atomic layer deposition (AS-ALD) of WSe_2 offers significant promise for advancing electronic and energy technologies. Our research introduces an innovative approach that combines microreactor-assisted nanomaterial deposition (MAND) with nature-inspired chemical engineering (NICE) to achieve safe, efficient, and lithography-free deposition with enhanced temporal resolution of nanomaterials like WSe_2. Drawing inspiration from the ovipositor mechanism of the parasitic wasp Diachasmimorpha longicaudata, we developed a bio-inspired seed pretreatment strategy to optimize substrate surface preparation. This method utilizes a deposition nozzle to locate the seed material precisely, mimicking the wasp's ability to find a host organism for egg deposition. In our MAND system, selenium is generated in situ via a reaction between solid selenium powder and forming gas, eliminating the need for hazardous bulk storage of H_2Se. Tungsten is introduced through pulsed heating of solid $W(CO)_6$, generating tungsten carbonyl molecules. Then, alternating flows of $W(CO)_6$, inert gas, and H_2Se facilitate the selective deposition of WSe_2 onto micro- and nanoscale seeds. Seed shape and chemical properties were optimized using insights from literature and density functional theory (DFT) simulations. By varying source transport rates, we studied the nucleation and growth of WSe_2, enabling detailed analysis of growth kinetics and process optimization. Advanced characterization techniques, including scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS), were employed to validate and refine the process. This work highlights the transformative potential of integrating NICE and MAND for scalable, safe, and efficient AS-ALD of WSe_2, paving the way for innovative advancements in semiconductor manufacturing and energy technologies.

AS-TuP-2 Advancements in Area-Selective Deposition by Merck: From Fundamental Principles to Industrial Applications

Isiah Liu, Merck KGaA, Darmstadt, Taiwan*; Lanxia Cheng, Tingmin Wang, Matthew MacDonald, Bhushan Zope,* Merck KGaA, Darmstadt*; Chang-won Lee,* Merck KGaA, Darmstadt, Korea (Democratic People's Republic of)*; Masashi Jinguji, Xinjian Lei,* Merck KGaA, Darmstadt

Area Selective Deposition (ASD) processes have gained significant attention due to the limitations of current lithographic techniques in fabricating advanced semiconductor devices, particularly as device dimensions continue to shrink. For the development of future semiconductor nodes, a critical process is required to selectively grow thin films on specific surfaces while preventing deposition on others. This process must effectively differentiate between surfaces to ensure precise material deposition. To address these challenges, Merck has developed systematic concepts based on the surface reactions involved in selective deposition, which require a comprehensive understanding of surface chemistry and the reactivity of inhibitors to passivate non-growth areas. The inhibitor layer plays a crucial role in the ASD process by acting as a protective barrier, selectively preventing deposition on undesired regions of the substrate while ensuring material growth occurs only on the targeted surfaces. These surface reactions were initially explored through molecular modeling and subsequently confirmed through application tests and in-situ metrologies. Through extensive studies, the optimal selection of inhibitors, coupled with the development of the ASD process, has been successfully achieved, enabling precise control over material deposition in advanced semiconductor fabrication. This progress has led to the development of several novel ASD processes that have attracted significant interest within the industry, demonstrating the ability to selectively passivate dielectric (SiO2, Si3N4, Si) and metal (Cu) substrates. This breakthrough offers a promising solution for the precise control of material deposition, representing a critical advancement for the fabrication of next-generation semiconductor devices.

AS-TuP-3 Comparative Study of Experimental and DFT Calculations of Trimethylaluminium Adsorption on SiO_2, SiN, and Si for Area-Selective Deposition

Genki Hayashi, *Ni Zeyuan, Yumiko Kawano, Shinichi Ike, Shuji Azumo,* Tokyo Electron Technology Solutions Limited, Japan

Area-Selective Deposition (ASD) is an attractive process for semiconductor manufacturing[1]. It utilizes the differences of the surface chemical reaction between a precursor molecule and different substrates. Surface reaction simulations are useful tools for screening appropriate ASD precursors[2]. In this study, we investigated the validity of adsorption energy calculation using density functional theory (DFT) by comparing the calculation with the process outcomes.

We calculated the adsorption energy of Trimethylaluminium (TMA) molecule on H-terminated Si, OH-terminated SiO_2, and NH-, OH- and F-terminated SiN substrates (Fig1(a)). Here, TMA is a well-known precursor that is often used for Al_2O_3 deposition, and the choices of these surface terminations were based on the usual dilute HF (DHF) treatment prior to precursor introduction to remove native oxides[3]. It is widely known that H (OH) terminated surface was formed for Si (SiO_2) surface after DHF. For SiN surface, it was found from X-ray photoelectron spectroscopy (XPS) measurement (Fig1(b)) that fluorine was clearly detected on the surface, suggesting that not only OH and NH but also non-negligible amount of F was terminated on the surface, which is consistent with the previous study [3]. The calculated adsorption energy (Fig1(a)) was lower in order of the SiO_2(-OH), SiN(-OH), SiN(-NH), Si(-H), and SiN(-F) cases. This suggested that TMA is most likely to adsorb on the SiO_2(-OH) surface, whereas most unlikely to adsorb on SiN(-F) surface.

To compare the simulation results with experiments, we actually introduced TMA to Si, SiO_2, and SiN substrates in a chamber after DHF. Fig1(c) shows the XPS results (Al 2p) of these substrates after TMA flow. The largest amount of Al (resulting from TMA adsorption) was observed on the SiO_2 substrate, which agrees with the speculation from the simulation results. For SiN substrate, we also performed H_2O dipping treatment for 12.5 h at maximum after DHF, and consecutively, TMA flow experiment. As shown in Fig2(a) (XPS results), amount of fluorine decreased for 12.5-h H_2O dipping, suggesting that -F is replaced by -OH. Corresponding to this, it was found from XPS measurement (Fig2(b)) that amount of Al increased. This experimental result is consistent with the adsorption energy calculation (Fig1(a)) where TMA is more likely to adsorb on SiN(-OH) than on SiN(-F). These results demonstrate the usefulness of the DFT calculations to estimate selectivity in developing ASD.

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AS-TuP-4 An Automated Adsorption Simulation Workflow for Efficient High-Throughput Molecule Screening for Area-Selective Deposition

Zeyuan Ni, *Michitaka Aita,* Tokyo Electron Technology Solutions Ltd., Japan*; Ayuta Suzki,* TEL Technology Center, America, LLC*; Genki Hayashi, Yumiko Kawano, Shinichi Ike, Shuji Azumo,* Tokyo Electron Technology Solutions Ltd., Japan

Area-selective deposition (ASD), a "chemical patterning" method that can reduce the fabrication cost and achieve novel structures beyond lithography, is gathering increasing global interests from researchers in semiconducting industry.[1–3] One of the key items to realize ASD on two specific types of areas is the selection of reactants and/or inhibitors from over thousands of candidate molecules. Compared to experiments, the first-principles simulation is a more accessible approach with lower cost and higher speed. Yet, a thorough simulation for an adsorption event requires searching for several most energetically favorable saddle points (i.e. transition states) in the potential energy surface, which makes it demanding in computation resources for high-throughput exploration.

In this work, we developed a simple surrogate automatic simulation workflow for evaluation of a molecule's adsorption behavior on surfaces by using density functional theory (DFT) software VASP and automation packages fireworks and atomate[4]. First, we performed manual simulations of the adsorption behavior for N-(Trimethylsilyl)dimethylamine (TMSDMA) C5H15NSi on 7 types of surfaces by using the NEB method. It is found that the activation energy E_a is almost in proportion to the adsorption energy after molecule dissociation, which is denoted as E_{d_ads}. (Fig. 1) Such empirical relationship is similar to the well-known Bell-Evans-Polanyi principle[5], so we believe E_{d_ads} can serve as a reasonable surrogate metric for E_a.

Accordingly, an automatic E_{d_ads} simulation workflow that can break molecules into fragments and search for the most stable adsorption configuration automatically has been implemented (Fig. 2) and tested for 4 types of molecules on Ru and hydroxyl-terminated SiO2 (SiO2-OH) surface. For each molecule-substrate pair, multiple adsorption configurations have been investigated, from which the most stable one is chosen to represent the final adsorption energy of the molecule on the specific surface (Fig. 3). Within the 4 molecules we investigated, we find that the difference of alkynes' adsorption energies on Ru and SiO2-OH is the largest, outperforming TMSDMA, carboxylic acids, and pyridine. Alkynes could be promising inhibitors blocking Ru surface compared to SiO2-OH.

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AS-TuP-5 Self-Assembled Inhibitor for Area-Selective Deposition on Cu Interconnects to Lower Contact Resistance

*, **Yun Ki Kim,*** Samsung Electronics, Republic of Korea*; Sang Chul Youn,* Samsung Electronics Co., Republic of Korea

Beyond the 5nm node, the limitations in producing nanostructures for chip production have necessitated the adoption of new materials for Cu interconnects, as the existing Ta/TaN systems have structural limitations and performance issues that hinder their effectiveness. To overcome these challenges, area-selective atomic layer deposition (ALD) techniques are employed, wherein self-assembled monolayers (SAMs) are utilized to deactivate ALD growth on pre-patterned surfaces. In this study, SAM inhibitors were used to selectively block TaN layer formation on Cu interconnects, resulting in a significant reduction in contact resistance by approximately 63%. This reduction is primarily attributed to the prevention of direct TaN deposition on Cu, with a selectivity ratio of 2.85. Furthermore, the optimal thickness for both the SAM and TaN layers was determined to be 200 °C. At last, the long-term stability in a wide range of temperature (-20–60 °C) for 18 months was investigated, and verified the suitability for mass production chips.

AS-TuP-6 Optimization of Small Molecular Inhibitors for Area-Selective Atomic Layer Deposition by Controlling Alkyl Chain Length

*, **EunChong Cho,*** Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; Hae Lin Yang,* Hanyang University, Korea*; Jung-Hoon Lee,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea*; Jin-Seong Park,* Hanyang University, Korea*; Youngkwon Kim,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

This study addresses the limitations of conventional self-assembled monolayers (SAMs) in area-selective atomic layer deposition (AS-ALD) by investigating small molecular inhibitors (SMIs) for vapor-phase deposition. SMIs were designed based on trimethoxyphenylsilane (TMPS) with varying alkyl chain lengths (n = 1-6) interposed between the phenyl and silicon. The SMIs were characterized using nuclear magnetic resonance (NMR) spectroscopy and evaluated for passivation effectiveness through water contact angle (WCA) measurements on SiO2 substrates and AS-ALD experiments. The WCA of SMIs with shorter alkyl chains (n = 1-3) was higher than TMPS, while those of SMIs with longer chains (n = 4-6) were lower. To evaluate the selectivity of SMIs in AS-ALD experiments, we first deposited SMI on SiO2 and TiN substrates, followed by VO2 deposition. SiO2 was used as a non-growth area, while TiN served as a growth area. As a result, the shorter chain SMIs (n = 1-3) achieved over 85% selective inhibition efficiency on SiO2 relative to TiN, in contrast to TMPS showing ~67% efficiency. The optimal selective inhibition efficiency of about 90% was observed for n = 2. In contrast, longer chain SMIs (n = 4-6) exhibited diminishing selective inhibition efficiency, correlated well with WCA results. This study provides valuable insights for future SMI designs in AS-ALD applications, contributing to the advancement of nanoscale semiconductor fabrication techniques.

AS-TuP-7 Area-Selective Atomic Layer Deposition of Amino Silane-Based Small Molecule Inhibitor for Enhancement of Selectivity

*, **Jae Hun Hwang,** EunChong Cho, Youngkwon Kim,* Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

Area-selective atomic layer deposition (AS-ALD) is one of the next-generation technologies that enable bottom-up fabrication, in contrast to the traditional top-down fabrication used in semiconductor manufacturing. AS-ALD has the potential to reduce the number of lithographic patterning steps considerably. Furthermore, AS-ALD enables angstrom-level accuracy in specific regions of substrates with diverse chemical properties when fabricating thin film devices. In this study, we applied small molecular inhibitors (SMIs) in AS-ALD to address the issues of low volatility and uniformity in gas-phase processes of conventional self-assembled monolayers (SAMs). We compared two SMIs, trimethoxyphenylsilane (TMPS) and tri(dimethylamino)phenylsilane (TDMAPS), containing methoxides and dimethylamines as the head groups that can interact with the substrates.

The synthesized SMIs were characterized using nuclear magnetic resonance spectroscopy. SMIs were deposited using ALD, and water contact angle measurements were performed on four substrates (SiO2, SiN, TiN, and Cu) to evaluate the coverage and passivation effectiveness. After depositing a Ru film on the SMIs-coated substrate using the Ru precursor $[Ru(II)(\eta^5\text{-}C_7H_7O)(\eta^5\text{-}C_7H_9)]$, the film thickness was measured via X-ray fluorescence analysis. X-ray photoelectron spectroscopy was performed to conduct a precise elemental analysis of Ru. TDMAPS deposited on SiO2 and SiN substrates showed 100% selectivity for 150 cycles of Ru deposition, while deposition occurred on Cu and TiN substrates after a slight nucleation delay, confirming the substrate-specific chemo-selectivity. In particular, the TDMAPS-coated SiO2 and SiN showed higher selectivity of Ru precursors compared to those of TMPS, which is attributed to the of higher reaction rates amino groups with the substrate. This study demonstrates the importance of the head groups of SMIs to enhance the selectivity in AS-ALD and provides guidelines for the design of SMIs.

AS-TuP-8 Substrate-Driven Selectivity in Area-Selective Atomic Layer Deposition of ZnO: A Theoretical Investigation

*, **Semin Kim,** Yeseul Son, Taeyoung Kim, Soo-Hyun Kim, Byungjo Kim,* UNIST, Republic of Korea

As semiconductor devices continue to scale down while demanding higher performance, precise process control and a fundamental understanding of atomic-scale surface reactions become essential. Area-Selective Atomic Layer Deposition (ASALD) has emerged as a promising technique, enabling material growth in designated regions by leveraging surface chemical properties. Unlike conventional ALD, ASALD eliminates the need for additional patterning steps, inherently achieving selective deposition at the nanoscale. This makes ASALD particularly relevant for next-generation semiconductor devices, where precise material placement is critical, such as in 3D-integrated circuits and functional thin-film applications.

Zinc oxide (ZnO), a transparent conductive oxide, has garnered significant interest due to its excellent electrical and optical properties. It is widely used in next-generation semiconductor devices, transparent electrodes, optoelectronic components, and gas sensors. While previous studies on ZnO ASALD have primarily focused on inhibitor-based selective deposition, the influence of inherent substrate properties on ZnO film growth and incubation cycles remains largely unexplored.

In this study, Density Functional Theory (DFT) and molecular dynamics (MD) simulations were conducted to examine how different substrate compositions (SiO_2, Ti, Cu, and Ru) influence ZnO ALD precursor adsorption. To better capture realistic surface configurations, a machine learning force field (MLFF) was implemented, enabling MD simulations that more accurately reflect atomic interactions. Additionally, extensive DFT calculations were performed to quantify the intricate interactions occurring at different surfaces. The analysis revealed substantial variations in precursor-surface interactions, including significant differences in adsorption energies during physisorption. Furthermore, discrepancies in ligand exchange reaction energies were observed, leading to notable shifts in ZnO growth kinetics depending on the substrate. These differences directly impacted incubation cycles, providing a theoretical foundation for substrate-driven selectivity in ZnO ASALD.

By leveraging these insights, we establish a theoretical framework for understanding how chemical reactants interact with different surfaces and how substrate characteristics can be intentionally modified to induce inherent selectivity. This work highlights the importance of a strong theoretical foundation in optimizing atomic layer processing for unprecedented selectivity, offering a pathway to precise pattern control in advanced semiconductor manufacturing.

AS-TuP-9 Inherent Area-Selective Atomic Layer Deposition of Molybdenum Carbide for Bottom-up Semiconductor Manufacturing

*, Jeong Hwan Han, **Min Seok Kim,** Ji Sang Ahn,* Seoul National University of Science and Technology, Republic of Korea

With the increasing demand for higher integration and enhanced performance in semiconductor devices, area-selectiveatomic layer deposition (AS-ALD) is playing a crucial role. AS-ALD is a technology that can precisely depositnanometer-level thin films in desired areas, effectively addressing issues that may arise during unnecessary pattern formation or processing. Particularly, selective deposition of metal materials in metallization, and further advanced packaging, where multiple layers of metal need to be deposited sequentially, has the advantage of implementing more complicated structures. Molybdenum carbide (MoC_x) is gaining attention as a promising material for the next generation semiconductor manufacturing due to its excellent mechanical and electrical properties as well as high thermal and chemical stability, there are few reports on Mo-based materialsfor AS-ALD.

In this study, we developed molybdenum carbide (MoC_x) thermalALD using a novel combination ofMo precursor and co-reactant, and conducted analysis of the film properties. Notably, itwas observed that the film growth behavior varied depending on the substrates by analyzing Mo areal density and film thickness. MoC_x films growth was effectively suppressed on Al_2O_3 substrate, whereas significant film deposition was observed on Cu substrate. Despite being a dielectric substrate, the SiO_2 substrate showed similar growth behavior to Cu, suggesting these processes preferred to suppress MoC_x deposition on Al_2O_3. The MoC_x process achieved ~10.4 nm selective deposition on Cu over Al_2O_3 (94.2 % selectivity) and ~13.9 nm on SiO_2 over Al_2O_3 (92.8 % selectivity).These findings demonstrate the feasibility of selective deposition on different substrates, particularly with Al_2O_3 as non-growth area (NGA). This study aims to present an effective approach to overcome technical limitations in next-generation device manufacturing by proposing a method for ASD not only in metal-dielectricapplications but also between dielectrics through theinherentAS-ALD process of molybdenum carbide.

Acknowledgements

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AS-TuP-10 Photo-Assisted Atomic Layer Deposition of Metallic Nickel*, **Yupu Tang**, Ion Lambrou, Ville Jokinen, Ville Miikkulainen,* Aalto University, Finland

Photo-assisted atomic layer deposition (Photo-ALD) provides a fundamentally new approach for inherently selective thin film growth, leveraging photo-induced activation rather than traditional surface activation or deactivation methods. In this work, we demonstrate that Ni Photo-ALD achieves selective deposition on a broad range of semiconducting metal oxide substrates, while completely suppressing growth on insulating surfaces—a improvement over previously reported Cu-based processes, which were limited to grow on fewer substrates. The unique optical and chemical interaction between photo, the precursor, and the semiconducting surfaces allows for selective activation, enabling Ni selective growth without the need for external inhibitors or complex patterning steps. This work not only demonstrates the versatility of Ni Photo-ALD across diverse oxide substrates but also highlights its potential as a scalable technique for selective material growth in advanced fabrication processes.

AS-TuP-11 Logic Applications of Area Selective Deposition beyond 1.4nm*, **Hoon Seok Seo**, Kang Sub Yim,* Samsung Electronics, Republic of Korea

The scaling of semiconductor devices has significantly increased transistor density, which has improved the performance of various electrical devices ranging from computers to smartphones. Through such an evolutionary miniaturization, a semiconductor manufacturing technology has required more fine deposition and patterning techniques. However, in the existing nano- fabrication processes based on lithography, it is highly challenging to form an accurate pattern alignment and limited to handle interfacial phenomena inside device. Accordingly, the semiconductor industry has intensively focused on 'area selective deposition (ASD)'. It provides a powerful technique to yield area-selective interfaces of metal/low-k material by using the self-aligned molecules as an inhibitor. In this article, we discussed the application of ASD into logic products. In particular, we introduced the evaluation results for the reverse selective barrier metal (RSBM) and fully aligned via (FAV) that are being applicable to the backend of line (BEOL).

AS-TuP-12 Impurity-Free Accelerators in Atomic Layer Deposition: Driving the Growth of Low-Resistivity Ultrathin Iridium Films*, Se-Hun Kwon, **Myung-Jin Jung**,* Pusan National University, Republic of Korea

Iridium (Ir) has a low figure of merit ($\rho_0 \times \lambda$) and a high melting temperature, so it has recently been spotlighted as a very important copper (Cu) alternative interconnect material in next-generation semiconductor devices. In particular, atomic layer deposition (ALD) enables the deposition of ultra-thin, conformal, and uniform films with excellent step coverage, even in highly complex or narrow trench structures of several-nm dimensions, due to its inherent self-limiting characteristic. In this regard, ALD-Ir is considered one of the most suitable metallization processes for advanced semiconductor interconnect applications.

To develop a reliable ALD-Ir process with improved film quality, considerable efforts have been made. Recently, an ALD-Ir process exhibiting low electrical resistivity and negligible oxygen impurities was reported using Tricarbonyl (1,2,3-η)-1,2,3-tri(tert-butyl)-cyclopropenyl iridium ($C_{18}H_{27}IrO_3$ or TICP) precursor and oxygen [1]. However, despite these advantages, this TICP precursor exhibits a long incubation period and high nucleation delay, making it difficult to deposit extremely thin and continuous Ir films on the hydroxyl-terminated oxide surface.

Therefore, in this study, a method for depositing highly uniform and continuous ALD-Ir thin films with low resistivity even on oxide materials was explored by significantly reducing the incubation period and promoting nucleation through impurity-free accelerators under simple process conditions. This additional step does not change the existing device structure while enabling the formation of high-quality Ir thin films with strong resistance to external impurities. Furthermore, we systematically compared and analyzed the nucleation and growth behavior, as well as film properties, of ALD-Ir on the oxide surface under process conditions with and without the accelerator. As a result, we successfully obtained ultrathin ALD-Ir films with superior uniformity, low surface roughness, and low resistivity, even on oxide surfaces.

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Emerging Materials
Room Event Hall - Session EM-TuP
Emerging Materials Poster Session

EM-TuP-1 A Novel Topological Semi-Metal: MoP Pathfinding for Future Interconnects at Nanoscale*, **Jeong-Seok Na**, Kyle Blakeney, David Mandia, Jeremie Dalton,* LAM Research

Metal interconnect resistance increases as devices continue to shrink, which poses challenges for metallization schemes in future device nodes.

Topological semi-metals (TSMs) were recently introduced and have demonstrated promising resistivity scaling performance at nanoscale. This is due to their unique properties related to topologically protected surface states and suppressed electron backscattering. MoP is considered one of promising candidates due to its high carrier concentration (~10^{23} cm^{-3}) and relatively low bulk resistivity (~9 $\mu\Omega\cdot cm$) compared to other TSMs.

We describe the fundamental problem of metal resistivity increasing as interconnect dimensions shrink. Recently, some materials have been observed to show an unconventional resistivity decrease with decreasing dimensions. Among these topological semi-metals, MoP is a promising candidate. There have been few reports about MoP synthesis process that is compatible with interconnect applications.

In this study, we investigate the growth behavior and film properties of MoP using thermal ALD process. First, we compared different reducing agents in the ALD of MoP films. Second, comprehensive film characterization was conducted to evaluate resistivity and crystal phase/structure using 4-point probe, XPS depth profile, AR-XPS, GI-XRD and XRR analyses. The selective growth was tested to evaluate bottom-up gapfill in via structures over a wide temp range for both logic and memory applications. Finally, we discuss the need for thermal stability studies and nanoscale device characterization in order to prove the resistivity scaling benefits of MoP films.

EM-TuP-2 Vapor Phase Infiltration of Poly(1-Trimethylsilyl-1-Propyne) with Trimethylaluminium*, Jonathan Jenderny,* Applied Electrodynamics and Plasma Technology, Ruhr-University Bochum, Germany*; Nils Boysen,* Fraunhofer Institute for Microelectronic Circuits and Systems, Duisburg, Germany*; Florian Preischel,* Inorganic Materials Chemistry, Ruhr-University Bochum, Germany*; Teresa de los Arcos,* Technical and Macromolecular Chemistry, Paderborn University, Germany*; Aleksander Kostka,* Center for Interface-Dominated High-Performance Materials, Ruhr-University Bochum, Germany*; Peter Awakowicz,* Applied Electrodynamics and Plasma Technology, Ruhr-University Bochum, Germany*; Jean-Pierre Glauber,* Leibniz Institute for Solid State and Materials Research, Germany*; **Harish Parala**,* Institute for Materials Chemistry, Leibniz Institute for Solid State and Materials Research, IFW Dresden, Germany*; Anjana Devi,* Institute for Materials Chemistry, Leibniz Institute for Solid State and Materials Research, Germany

Inorganic–organic hybrid materials are gaining importance for different applications, combining the advantages of both organic and inorganic materials. Vapor phase infiltration (VPI) has emerged as a promising technology for the synthesis of hybrid materials. In the field of polymeric gas separation membranes, a common problem is long-term stability, as filtered gases can lead to material deterioration or swelling [1]. In addition to increasing the membrane stability, VPI has also been shown to beneficially impact the separation performance, e.g., when infiltrating polymer of intrinsic microporosity 1 (PIM-1) with trimethylaluminium (TMA) [2].

In this study, VPI of poly(1-trimethylsilyl-1-propyne) (PTMSP) with TMA is investigated. PTMSP was chosen due to its exceptionally high free volume and its organic nature, featuring a carbon-carbon double bond as functional group. Saturation of the precursor inside the polymer is attained after already 60 seconds of infiltration time inducing significant densification of the material as observed by transmission electron microscopy (TEM). Water contact angle measurements indicate a shift towards hydrophilic behaviour after infiltration. Depth profiling using time-of-flight secondary ion mass spectrometry (TOF-SIMS) shows accumulation of aluminium (Al) in the PTMSP polymer. The presence of Al was detected along the whole polymer, confirming that the VPI process affects the whole polymer and is not limited to the sub-surface or the gradient layer region. Depending on the infiltration time, a significant densification of the porous structure was observed that directly influences the selectivity of the gas permeation, up to a complete blocking for long infiltration times. These results represent the first VPI process of a polymer featuring only a C-C double bond and outline the versatility of the VPI technique, being applicable for both gas-barrier and membrane applications in the future.

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EM-TuP-3 Study of (TaN)1-XCx Electrode to Investigate Its Impact on OTS Selector Devices*, **Minkyu Lee**, Taeyoon Lee,* Yonsei University, Korea

Conventional transition metal nitrides (TMNs) have gained significant attention in the field of memory devices due to their low resistivity and high thermal & chemical stability. In particular, tantalum nitride (TaN) has been widely applied in various memory industries owing to its high melting point, uniform resistivity, and diffusion barrier properties. However, recent research in the direction of reducing the reset current in phase change memory (PCM) faces limitations with TaN due to its low resistivity. Therefore, it is essential to study materials that can control resistivity while having low roughness and good adhesion with the substrate. Carbon, an element with a small atomic size, can be incorporated into TMN materials to modulate their resistivity and control surface roughness through grain size variations. Here, we demonstrate novel $(TaN)_{1-x}C_x$ electrodes that can adjust electrical resistivity depend on the compositions of carbon. X-ray diffraction (XRD) patterns were analyzed to confirm each crystal lattice and peak shift. Applying measured XRD patterns, full width half maximum (FWHM) and grain sizes were extracted using Debey-Scherrer equation. To visualize crystal structure and amorphous state of $(TaN)_{1-x}C_x$ films, transmission electron microscope (TEM) was employed along with the diffraction pattern using fast fourier transform (FFT).

EM-TuP-4 Study for Deposition of CuI onto Indium-Gallium-Zinc-Oxide for Light Detection Application*, **Woosuk Sohn**, Taeyoon Lee,* Yonsei University, Korea

IGZO phototransistors have been recently paid attentions in various fields such as displays, image sensors, and wearable devices, owing to their high charge mobility and photosensitivity. Although the IGZO phototransistors are widely recognized, some improvements are required as they can detect a limited wavelength range of visible light due to the wide bandgap of IGZO (approximately 3.7–3.8 eV). Generally, the bandgap of IGZO can be adjusted by introducing impurities, however, such approaches often lead to performance degradation by decreasing the mobility of transistor and raising the threshold voltage and subthreshold swing. In this study, we developed a CuI/IGZO phototransistor capable of detecting light in the whole visible range by utilizing copper iodide (CuI), a p-type semiconductor material widely used in photodetectors, solar cells, and LEDs. As p-type CuI is spin-coated on the n-type IGZO layer, a pn junction and a type-II bandgap structure can be formed, which leads to an increase in the number of electrons and holes generated by light and enhances the photocurrent. Also, zinc (Zn) was additionally doped to prevent the degradation of performance of CuI TFTs due to the volatility of iodine, and enhance the on-off current ratio of the transistor. For the gate dielectric, spin-coated Al_2O_3 was employed instead of SiO_2, yielding better device stability. While the Al_2O_3 layer was not deposited by atomic layer deposition (ALD), it still provided sufficient insulating properties. Future work could incorporate ALD-based thin-film deposition to achieve improved thickness uniformity, interface control, and large-area process scalability. In fact, ALD has shown promise in uniformly doping IGZO and CuI thin films and controlling defects, suggesting that it can further enhance the responsivity and detectivity of CuI/IGZO phototransistors. The proposed device has great potential for applications in photo-memory and neuromorphic device, presenting innovative advancements in fields such as artificial intelligence, autonomous driving, and smart devices.

EM-TuP-5 Networking Density Effects on the Patterning Performance of Resists Deposited via Hybrid MLD*, **Long Viet Than**, Giulio D'Acunto, Stacey F Bent,* Stanford University

The implementation of extreme ultraviolet (EUV) lithography in semiconductor manufacturing promises to extend Moore's Law by enabling the patterning of sub-8 nm feature sizes. However, further device scaling is dependent on the implementation of EUV-tailored photoresists that meet requirements in sensitivity, resolution, and line edge roughness. With feature sizes approaching the nanometer scale, stochastic variation in the photoresist molecular structure also affects pattern quality, resulting in the need for new resist chemistries with uniform chemical distribution.

Metal-organic thin films deposited via hybrid molecular layer deposition (MLD) are a promising class of materials to address the challenges of designing new EUV-compatible resist chemistries, by incorporating EUV-absorbing metal centers into the polymer network while exhibiting Å-level thickness control and atomic-scale homogeneity. In this work, we investigated a series of hybrid MLD-derived aluminum alkoxide (alucone) resists, deposited via trimethylaluminum (TMA) and a series of alcohol counter-reactants (glycerol, ethylene glycol, and sequential dosing of methanol/ethylene glycol). This process yielded thin films that are chemically akin, as demonstrated by X-ray photoelectron spectroscopy (XPS), but exhibit notable differences in networking/crosslinking density. Electron beam lithography, an established proxy for EUV, was used to evaluate how these structural differences affect their patterning performance. All three alucone resists exhibited negative-tone patterning, attributed to the loss of organic ligands and to the formation of inorganic alumina. We found that decreasing the crosslinking density improves the resolution limit, ultimately achieving 14 nm lines in 1:1 line/space patterns with alucone containing methanol/ethylene glycol linkers. The variation observed between these hybrid materials underscore the importance of structure-property relationships for the rational design of metal-organic EUV resists.

ALD Applications
Room Halla Hall AB - Session AA1-WeM
Catalyst and Fuel Cell Applications

Moderators: Ji Hwan Ahn, POSTECH, **Hao Van Bui**, Phenikaa University

8:00am **AA1-WeM-1 Atomic Layer Deposition for Highly Durable Hydrogen Fuel Cells: from Catalyst to Cell***, Xiao Liu, Hang Liu, Yuxin Gao, Jianhua Wu,* ***Rong Chen,*** Huazhong University of Science and Technology, China **INVITED**

The widespread application of hydrogen fuel cells relies heavily on high performance oxygen reduction reaction catalysts. When facing with complex and harsh operational conditions, traditional Pt-based catalysts always surfer from serious electrochemical corrosion or poisoning of sulfonic acid groups at the catalyst or cell level. In this talk, we will present controllable synthetic strategies of advanced catalysts for highly durable hydrogen fuel cells based on atomic layer deposition. A series of highly stable Pt-based alloy catalysts are prepared by ultrathin metal oxide coating and post-annealing process, which could avoid the agglomeration of catalyst particles caused by high ordering temperature. The strategies of sub-surface single atom precise doping and selective passivation of nitrided TiO_2 are developed to prevent the corrosion of low coordination or unsaturated sites on the surface Pt catalysts. At the cell level, spatially confined ultrafine Pt-based alloy in porous carbon support could effectively improve the performance of fuel cells by reducing oxygen transport resistance. Besides, the corrosion resistance of stainless-steel bipolar plate is enhanced by Al_2O_3/TiO_2 nanolaminates composited with niobium-doped amorphous carbon coating. As a very promising thin film technique, ALD has shown its potential to address challenges in hydrogen fuel cell from all aspects.

8:30am **AA1-WeM-3 Interfacial Properties of ALD-Grown In_2S_3 Catalysts in CO_2 Electroreduction***, Järi Van den Hoek,* University of Antwerp, Belgium*; Femi Mathew, Ruben Blomme,* Ghent University, Belgium*; Lieven Hintjens, Brend De Coen,* University of Antwerp, Belgium*; Eduardo Solano,* ALBA synchrotron, Spain*; Matthias Minjauw,* Ghent University, Belgium*; Nick Daems, Daniel Choukroun,* University of Antwerp, Belgium*; Christophe Detavernier,* Ghent University, Belgium*; Tom Breugelmans,* University of Antwerp, Belgium*;* ***Jolien Dendooven,*** Ghent University, Belgium

Electrochemical reduction of CO_2 is a promising strategy for sustainable production of high-value chemicals like formate, a valuable feedstock in the textiles, food and chemicals industries. In CO_2 electrolysers, selective catalysts that suppress the competing hydrogen evolution reaction (HER) are essential, along with a well-defined triple-phase boundary (TPB) at the gas diffusion electrode (GDE)/catalyst/electrolyte interface to enhance CO_2 mass transfer. Beyond intrinsic catalytic properties, interfacial factors such as surface roughness and hydrophobicity impact the TPB region and performance. To investigate these effects, we employed plasma-enhanced (PE-) and thermal (T-)ALD of In_2S_3 on GDEs, creating model catalysts without ionomers or binders [1].

The ALD processes used $In(acac)_3$ and H_2S (plasma) precursors at a substrate temperature of 180 °C. Saturated growth was confirmed on Si substrate, achieving 0.28 and 0.17 Å/cycle for PE- and T-ALD, respectively. Both films were crystalline, with the PE-In_2S_3 film displaying a tetragonal structure and the T- In_2S_3 film a cubic structure. Next, In_2S_3 films were successfully deposited on GDEs, as confirmed by XPS and XRF mapping. Cross-sectional SEM-EDS revealed the penetration of In and S 100 µm deep inside the GDE, in contrast to superficial deposits by conventional coating methods. The PE-In_2S_3 and T-In_2S_3 electrocatalysts showed a comparable surface roughness and electrochemical active surface area. The hydrophobicity was studied via water contact angle (CA) measurements. Compared to the bare GDE (151.0°), the CA of T-In_2S_3 exhibited a limited decrease to 128.8°, whereas PE-In_2S_3 displayed a significantly diminished value of 76.9°, indicative of plasma-induced modification of the underlying PTFE-rich GDE surface. Thus, the hydrophobicity decreased drastically for PE-In_2S_3.

The T-In_2S_3 films achieved a formate Faradaic efficiency of more than 90% at 1 A cm^{-2} in a flow-by electrolyzer. In contrast, PE-In_2S_3 exhibited reduced electrochemical activity and selectivity, attributed to its higher wettability. The increased hydrophilicity caused excessive penetration of the electrolyte into the GDE, resulting in a shift in the TPB, limiting CO_2 diffusion to the catalyst layer and promoting HER over formate production. On the other hand, the conformal coverage provided by T-ALD together with its favourable hydrophobic interfacial properties stabilized the TPB region, allowing for long-term stability of up to 30 h. These findings contribute to the understanding of how catalyst interfacial properties promote activity and stability in CO_2 electroreduction.

[1] Van den Hoek et al. Adv. Energy Mater. 2025, 2404178.

8:45am **AA1-WeM-4 Scaling Up Platinum on Carbon Catalyst Fabrication for Proton Exchange Membrane Water Electrolysis***,* ***Peter Michael Piechulla****, Mingliang Chen, Sophie van Beusekom,* Delft University of Technology, Netherlands*; Mena-Alexander Kräenbring, Fatih Özcan, Doris Segets,* University of Duisburg-Essen, Germany*; Ruud van Ommen,* Delft University of Technology, Netherlands

Wind and solar have in recent years become the cheapest sources of electricity; however, their intermittency is still an obstacle to further capacity expansion. Hydrogen generation through proton exchange membrane water electrolysis (PEMWE) is a promising solution to this problem but requires scarce platinum group metal catalysts to facilitate the half-reactions at the electrodes, which may soon become a bottleneck for scale-up. Hence, the catalyst is typically deposited sparsely onto a support material (e.g., Pt-loaded carbon, Pt/C), thereby increasing surface area of the catalytically active metal. With incipient wet impregnation as a scalable and thus industrially accepted method, morphology and dispersion of Pt is difficult to control. In contrast, ALD enables Pt/C fabrication at atomic level precision, but is so far only employed in lab scale experiments[1].

In this contribution, we demonstrate the manufacturing of highly active Pt/C catalysts for PEMWE through ALD on particles in a fluidized bed reactor (FBR-ALD), and investigate the upscaling potential of the process[2]. The process is carried out at atmospheric pressure, such that no expensive and difficult to scale vacuum systems are required from the outset. First, we tailor catalysts with a nanometer scale dispersion of Pt on carbon using sub-gram scale batches of catalyst. The catalyst is analyzed for its morphology via TEM imaging and screened for electrochemical performance via cyclic voltammetry measurements to obtain the electrochemically active surface area. Second, to evaluate the performance of the most promising ALD-made Pt/C catalysts under realistic conditions, we manufacture cathode catalyst layers and characterize their performance and durability in a laboratory-scale PEMWE system. Finally, we transfer the FBR-ALD process to a larger scale reactor (>10 g batches of catalyst), where we investigate saturation behavior and utilization of the $MeCpPtMe_3$ precursor through residual gas analysis. In addition to fundamental insights, we thereby gain an indication of economic efficiency of the process. In conclusion, we demonstrate that ALD manufacturing of high performance Pt/C catalyst is a scalable process.

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9:00am **AA1-WeM-5 Platinum Promoted Cobalt based Fischer-Tropsch Thin-Film Catalysts***,* ***Muhammad Hamid Raza****, Avela Kunene, Imane El Arrouji,* PVcomB, Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Berlin, Germany*; Catalina E. Jiménez,* Department Interface Design, HZB, Berlin, Germany*; Alexander Steigert, Martin Muske, Tobias Köhler, Ali Shan Malik,* PVcomB, Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Berlin, Germany*; Marcus Bär,* Department Interface Design, HZB, Berlin, Germany. Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (HI ERN), Erlangen, Germany. Dept. Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Erlangen, Germany*; Nicola Pinna,* Department of Chemistry and The Center for the Science of Materials Berlin, Humboldt-Universität zu Berlin, Berlin, Germany*; Rutger Schlatmann, Daniel Amkreutz,* PVcomB, Helmholtz-Zentrum Berlin für Materialien und Energie (HZB), Berlin, Germany

The Power-to-Liquids (PtL) approach can produce sustainable fuels by utilizing Fischer-Tropsch (FT) processes to convert green hydrogen and carbon dioxide. While FT is a promising technology for producing sustainable fuels, high-performance catalysts are crucial to its success. Thin film catalysis offers opportunities to tailor the catalysts properties by design that are pre-adapted to specific chemical environment for their targeted application. FT benefits from thin film catalysts by reducing the amount of active materials, streamlining activation phase and enhancing selectivity toward desired end products. We report a cobalt-based thin-film FT catalyst synthesized by a combination of different deposition techniques including atomic layer deposition (ALD), plasma enhanced chemical vapour deposition (PECVD), magnetron sputtering and successive ionic layer adsorption and reaction (SILAR). Mn/MnO$_x$ and Pt are studied as promoters and enhancers toward FT while considering cobalt as the FT active material. The size of platinum particles is controlled by number of ALD cycles. An ultra-low amount of Pt grown by 5ALD cycles is loaded onto the stack of cobalt based heterostructures (Mn-Co-SiO$_x$/Al) to study the effect of platinum as reduction promotor. The reduction behaviour of cobalt in the presence of Mn and Mn-Pt in oxidation-reduction conditions is investigated using *in-situ* synchrotron grazing incident X-ray diffraction. It is revealed that platinum promotes the reduction of cobalt species (spinel-Co$_3$O$_4$ to Co^0) as indicated by a significant lowering of the reduction temperature to 350 °C while the addition of Mn retards the reduction of CoO to Co^0. Temperature-programmed reduction (TPR) studies further confirm the effect of Pt on promoting the reduction of Co$_3$O$_4$ at lower temperatures to the FT active phase. These well-defined Pt-Mn-Co-SiO$_x$/Al hierarchical heterostructures represent a promising thin film FT catalyst system with significantly enhanced FT activity. Clear structure−property correlations required to insight-driven scale up the process, will be presented.

9:15am **AA1-WeM-6 Selectively Located Pt Clusters on Au/CeO$_2$ for Highly Robust Water-Gas Shift Reaction via Atomic Layer Deposition***, **Xiao Liu**, Yuanting Tang, Bin Shan, Rong Chen,* Huazhong University of Science and Technology, China

CO impurities in hydrogen derived from fossil fuel reforming present a substantial barrier to efficiency and environmental impact. This challenge underscores the importance of the water-gas shift (WGS) reaction, a critical process for purifying hydrogen for fuel cell applications. Au catalysts have shown outstanding low temperature catalytic activity toward WGS reaction, but they are struggling with the durability concerns.We fabricate a depth-controlled TiO$_2$ nanotrap via area-selective atomic layer deposition (ALD) method to balance the activity and anti-sintering properties of Au nanoparticles.[1] It exhibits enhanced sintering resistance while retaining an activity similar to that of pure Au catalyst. The average size of sintered Au (8.4 ± 2.7 nm) is three times smaller than that of pure Au catalyst (21.1 ± 7.1 nm) after calcination in air at 700 ºC. Based on the area-selective ALD method, Pt clusters are selectively located on Au/CeO$_2$ to activate the interfacial active sites poisoned by intermediate species.[2] The selective method effectively avoids the coverage of Au surface sites by Pt atoms and maintains the low temperature catalytic activity of Au/CeO$_2$ catalyst. Durability test indicates that the Pt-activated Au/CeO$_2$ catalyst shows superior durability in WGS atmosphere (200 ºC), which only attenuates 7.9% (from 78.0% to 70.1%) after 150 h. The analysis of surface intermediates and density functional theory calculations reveal that the introduction of Pt ensures the regenerative capacity of Au/CeO$_2$ active sites by facilitating the decomposition of intermediate species and the desorption of CO$_2$.

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9:30am **AA1-WeM-7 Fluorine-Free and Freestanding Bipolar Membranes Based on Metal-Oxide Ald-Coated Electrospun Nanofibers for Water Electrolysis and Fuel Cells***, **Arnaud Demore**, Damien Voiry,* IEM - CNRS, France*; Philippe Miele,* IEM - ENSCM, France*; Mikhael Bechelany,* IEM - CNRS, France

As the demand for green hydrogen production grows, processes such as water electrolysis are among the most promising technologies. However, several limitations remain unresolved yet, Proton Exchange Membrane Water Electrolysis (PEMWE) relies on noble metal (IrO$_2$ for OER in acidic conditions) and Anion Exchange Membrane Water Electrolysis (AEMWE) can use earth-abundant metals for the OER in alkaline conditions, but HER is limited by to the lack of available protons at the cathode. In this context, simultaneously achieving a high-pH OER and a low-pH HER is desirable and this is precisely one of the opportunities offered by bipolar membranes (BPM). When operated in reverse bias, BPMs can maintain a pH gradient across the electrochemical cell by dissociating water into protons and hydroxide ions. This allows for optimized reaction conditions at both anode and cathode, reducing catalyst costs. A BPM consists of two ion exchange layers of opposite polarity, separated by a catalytic layer. Water dissociation (WD) occurs at the interface of those two ion exchange layers known as bipolar junction. Water dissociation efficiency directly impacts energy consumption and overall cell performance. Additionally, while some catalysts have shown the ability to dissociate water effectively, the current deposition processes often produce a thick catalytic layer that can lead to delamination, catalyst leakage, further affecting long-term stability and performance. Therefore, our objective is to implement an efficient catalytic layer for WD, as thin as possible, in order to minimize catalyst usage while maintaining a strong bond to the polymer. A combination of Atomic layer deposition (ALD) and Electrospinning (ES) methods appears well suited to achieve this goal. ALD is a low temperature process that allows a precise control of thickness, conformity and uniformity of deposited layer, providing a chemically strong bonded layer even on polymer surfaces. ES is a cost effective method for producing high-surface-area, tunable, fluorine-free polymer nanofibers. By using quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (Q-PPO) and sulfonated polyether ether ketone (S-PEEK), two ion exchange polymers of opposite polarity, TiO$_2$ ALD-coated nanofibers were produced and further processed to obtain a fully dense bipolar membrane. Bipolar membranes are tested in two compartment H-cell with a four probe electrode set-up, and in electrolysis cells. WD is studied threw Current-Voltage (j-V) measurements to investigate the nature, thickness and distribution of the catalyst to obtain optimal WD performances in the BPM as well as to ensure long-term stability and strong catalyst bonding.

9:45am **AA1-WeM-8 Efficient Alkaline Hydrogen Evolution Reaction with Iridium Nanostructures synthesized by Atomic Layer Deposition***, **Jhonatan Rodriguez Pereira**, Raul Zazpe, Jan Macak,* University of Pardubice, Czechia

The outstanding performance of noble metals such as Pt, Ru, Pd, Ir, etc., for different catalytic applications has been widely demonstrated.[1,2] However, due to their scarcity, efforts have been made to reduce or substitute these noble metals. Atomic Layer Deposition (ALD) is one of the best technique to facilitate loading mass reduction on a support of interest.[3,4] Moreover, ALD is the most suitable technology to decorate with noble metal nanoparticles, high aspect ratio and high surface area substrate architectures.[5]

Surface energy variations between the noble metals and the support surfaces cause the ALD growth to initiate as single atoms, then nanoclusters and as the number of ALD cycles increases nanoparticles (NPs), the agglomeration between NPs dominates over the individual NP size increase, thus developing thin films of relatively higher thickness. These surface energy variations considerably increase the nucleation delay of noble metals. In this sense, our efforts focused on improving the functionality with pretreatments on carbonaceous supports that showed promise in reducing the nucleation delay of Ir deposited by ALD.[6]

It is highly important to choose the right substrates for electrocatalytic applications. Among the available substrates, TiO$_2$ nanotube (TNT) layers and carbon papers (CP) are the best options considering their physiochemical properties, availability, extensive literature and the low costs incurred when using them as support substrates in electrocatalysis. Variations in the morphological aspects of TNT layers and several surface modifications for CPs have received great attention from applied fields due to their enhanced surface area, conductivity and stability.[7–12]

The presentation will introduce and describe the synthesis of Iridium nanostructures by ALD on TNT layers and CP substrates, including the corresponding physico-chemical and electrochemical characterization and the encouraging results obtained for alkaline Hydrogen Evolution Reaction (HER).

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ALD Applications
Room Tamna Hall B - Session AA2-WeM

Display Applications

Moderators: Angel Yanguas-Gil, Argonne National Lab, **Junjie Zhao**, Zhejiang University

8:00am **AA2-WeM-1 Remarkable Productivity and Performance of OLED Encapsulation through Growth Dynamics Control via Atmospheric Pressure Spatial Atomic Layer Deposition*, Chi-Hoon Lee,*** *Kwang Su Yoo, Daejung Kim, Ji-Min Kim, Jin-Seong Park,* Hanyang University, Republic of Korea

The next-generation display industry is evolving beyond conventional liquid crystal displays (LCDs) by eliminating backlights and incorporating organic light-emitting diodes (OLEDs). These advancements have enabled applications in ultra-high-resolution displays for AR/VR, large-area displays, and stretchable/flexible displays. OLEDs commonly adopt low-temperature polycrystalline oxide (LTPO) pixel circuits, which utilize oxide semiconductors with low off-current as switching transistors and low-temperature polycrystalline silicon with high on-current as driving transistors.

Despite their advantages, OLED pixel circuits based on LTPO are susceptible to degradation when exposed to moisture, which can induce phenomena such as metal migration and delamination. Moreover, the infiltration of hydrogen into oxide semiconductors can cause a negative shift in threshold voltage, destabilizing the on/off states of thin-film transistors (TFTs). Therefore, high-performance encapsulation barriers are essential to protect OLED pixel circuits from moisture and hydrogen. Materials such as SiO_2, SiNx, and Al_2O_3 are under extensive investigation for this purpose. Among these, Al_2O_3 is well-known for its low water vapor transmission rate (WVTR) and low hydrogen permeability. Al_2O_3 films can be deposited using various methods, including evaporation, sputtering, plasma-enhanced chemical vapor deposition (PECVD), and atomic layer deposition (ALD).

ALD offers precise thickness control at the nanoscale and excellent conformality over high-aspect-ratio structures. However, conventional ALD processes, based on time-sequential operations, suffer from low deposition rates due to long purge times. Spatial ALD, which shortens the purge step duration, has been identified as a promising solution to overcome this limitation. However, the performance of spatial ALD requires careful optimization of parameters such as substrate speed and separation gas flow.

In this study, we investigated the growth behavior of Al_2O_3 films under various process conditions, focusing on the effects of substrate speed and trimethylaluminum (TMA) partial pressure. The growth behavior was analyzed based on the Langmuir adsorption model and expressed as the difference in growth per cycle (GPC). Four distinct process conditions, labeled A, B, C, and D, were evaluated. A hybrid process, combining the superior film quality of condition A with the high productivity of condition D, achieved exceptional performance metrics: a WVTR of 4.4×10^{-5} g/(m^2·day), hydrogen permeability of 1.7×10^{-4} barrer, and a deposition rate of 37.44 Å/min.

8:15am **AA2-WeM-2 Crystallinity Control through Composition Engineering for High-Performance $MgIn_xO_y$ TFTs via Thermal Atomic Layer Deposition*, Ji-Su Bae,*** *Chi-Hoon Lee,* Hanyang University, Republic of Korea*; Sung-Hae Lee,* Entegris, Republic of Korea*; Jin-Seong Park,* Hanyang University, Republic of Korea

The next-generation display industry is continuously advancing into future technology domains such as AR/VR, free-form displays, large-area displays, and automotive displays. The next-generation display industry holds great promise for oxide semiconductors as new channel materials, owing to their low off-current and high mobility characteristics.Indium-based oxide semiconductors, characterized by high mobility due to their large 5s orbitals, require the introduction of carrier suppressor elements to effectively regulate high carrier concentrations. However, the suppression of charge concentration through the introduction of carrier suppressors is accompanied by a reduction in mobility. To address this issue, extensive research is being conducted on indium-based crystalline oxide semiconductors. The crystallization of indium-based oxide semiconductors has been reported through methods such as post annealing and the introduction of capping layers. This approach can also be extended from a material perspective, for instance, using Magnesium Indium Oxide ($MgIn_xO_y$).

$MgIn_xO_y$, a type of oxide semiconductor, is known to exhibit an inverse spinel crystal structure at a composition ratio of Mg:In = 1:2, which contributes to its high conductivity and enhanced doping efficiency due to the numerous interstitial sites [1]. $MgIn_xO_y$ can be deposited through various methods such as sputtering and spray pyrolysis [2, 3].However, the growth of $MgIn_xO_y$ utilizing ALD, which is renowned for its precise thickness and composition control in the next-generation display industry, has not yet been reported.

In this study, $MgIn_xO_y$with an indium composition range of from 43.3 to 77.0 at% were grown via thermal ALD with ozone as the reactant. It was confirmed that variations in the metal cation composition of $MgIn_xO_y$, controlled through the ALD process, influence the crystallinity of the thin films, which in turn affects the transfer characteristics of the fabricated thin-film transistors. The X-ray diffraction (XRD) analysis revealed the presence of a broad (311) diffraction peak in the $MgIn_xO_y$ thin films, which is associated with an inverse spinel crystal structure. The influence of the average grain size, calculated using the Debye-Scherrer relation for the corresponding plane, on the electrical performance of the TFTs was successfully demonstrated. Then, it is observed that the $MgIn_xO_{-y}$ TFTs with 65.5 at% of indium show excellent device characteristics (V_{th} = -0.1 V, μ_{FE} = ~15 cm^2/V s, S.S = 73.1 mV/dec) and reliability (ΔV_{th} = 0.89 V for PBTS condition).

8:30am **AA2-WeM-3 Nitrogen-Doped SiO_2 Gate Insulator for Enhanced Stability in ALD-IGZO TFTs*, Tae-Heon Kim,*** *Dong-Gyu Kim, Jin-Seong Park,* Hanyang University, Republic of Korea

Silicon nitride (SiN_x) has gained attention as an insulating layer for oxide thin-film transistors (TFTs) due to its high dielectric constant and density, though its high hydrogen content can degrade device reliability. To address this, silicon oxynitride (SiO_xN_y) structures have been explored, leveraging the benefits of both SiO_2 and SiN_x through nitrogen incorporation. Among various doping techniques, atomic layer deposition (ALD) is particularly effective due to its low-temperature process, superior step coverage, and ability to minimize hydrogen-related bonds like Si–OH.

This study proposes a nitrogen doping strategy for SiO_2 gate insulators (GI) using a nitrous oxide (N_2O) plasma reactant to optimize the active layer/GI interface and bulk properties in top-gate bottom-contact (TG-BC) IGZO TFTs. Increasing N_2O plasma power from 100 to 300 W raised the nitrogen concentration in SiO_2 from 0.7 to 2.2 at% but also increased trap densities, leading to a U-shaped threshold voltage (V_{TH}) shift from -4.1 to 4.9 V under positive bias temperature stress (PBTS). Hydrogen annealing effectively reduced the V_{TH} shift from -2.1 to 0.0 V by chemically trapping hydrogen with nitrogen atoms. A hybrid GI structure using N_2O plasma at 150 and 300 W further improved PBTS stability and hydrogen resistance, highlighting the effectiveness of this approach in enhancing IGZO TFT reliability

8:45am **AA2-WeM-4 Engineering Hydrogen Content in SiN_X Thin Films via Precursor Control for Improved Oxide TFTs Characteristics*, Sang-Hyun Kim,*** *Tae Heon Kim, Jin-Seong Park,* Hanyang University, Korea

Atomic layer deposition (ALD) has recently gained significant attention in the fabrication of high-performance display devices due to its self-limiting reaction mechanism, which enables atomic-scale thickness control and uniform thin-film deposition[1]. SiN_X gate insulators offer high dielectric constant and excellent encapsulation properties, enhancing Oxide TFTs performance. However, SiN_X films deposited by conventional CVD methods exhibit high hydrogen content, leading to reliability challenges in oxide TFTs[2]. Recently, ALD-based SiN_X has emerged as a promising solution due to its ability to deposit high-quality thin films compared to CVD, making it suitable for developing low-hydrogen SiN_X. ALD-based SiN_X can improve the mobility and reliability of oxide TFTs, positioning itself as a key material for next-generation high-performance displays.

This study compared TSA and DIPAS precursors to develop hydrogen-engineered SiN_X films for IGZO-TFTs. SiN_X was deposited with plasma power ranging from 100 W to 200 W. TSA exhibited over 3.8 times higher GPC than DIPAS at all power levels due to better chemisorption efficiency and minimal steric hindrance. Optimal films were achieved at 100 W for TSA and 150 W for DIPAS. TSA films showed higher refractive index, higher density, and 35% lower oxygen and 50% lower hydrogen content than DIPAS films. IGZO-TFTs were fabricated using SiN_X (20 nm) and SiN_X (15nm)/ SiO_2 (5 nm). TSA-SiNx-based devices demonstrated superior performance, with a V_{th} of -0.98 V, mobility of 61.8 cm^2/V·s, and zero V_{th} shift under PBTS, due to reduced hydrogen diffusion and trap density. In contrast, DIPAS-based devices exhibited poor V_{th} (-8 V) and reliability.

This study highlights the effectiveness of hydrogen-controlled SiN_x engineering in enhancing the mobility and reliability of IGZO-TFTs. These advancements meet the reliability and performance needs of next-generation displays.

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9:00am **AA2-WeM-5 Remarkable Stability and Hydrogen Resistance on High-Mobility Oxide TFTs via N_2O Plasma Reactant in Atomic Layer Deposition***, **So Young Lim**, Sang-Hyun Kim, Yoon-Seo Kim, Taewon Hwang, Tae Heon Kim, Haklim Koo, Jin-Seong Park,* Hanyang University, Korea

Oxide semiconductor(OS) offers advantages for advanced applications such as high-performance Thin Film Transistors(TFT) and ultra-high-definition displays. Their high mobility, long-range uniformity, and extremely low off-current make them ideal for faster switching speeds, higher power efficiency. The application of ALD to OS fabrication has gained significant attention with reports of high field-effect mobility exceeding 50 $cm^2/V{\cdot}s$. Moreover, ALD provides precise controllability film thickness and composition to produce high-quality thin films. Despite the advancements, trade-off between field-effect mobility and device reliability remains a persistent challenge. Since OSs are highly sensitive to external influences, importance of GI becomes particularly pronounced in protecting them from external components like hydrogen. To mitigate these challenges, robust gate insulators(GIs) are pivotal in protecting OS active layers. Furthermore, researches are conducted to incorporate components to passivate defect sites in thin films.

This study explores N-doped Al_2O_3 as GI deposited by PEALD using N_2O reactant. The N content in the Al_2O_3 films increased linearly with plasma power (100–250 W), from 0.79% to 3.29%. 200W-deposited GI demonstrated a 3% improvement in hard breakdown voltage(7.81 MV/cm at 100 W to 8.08 MV/cm at 200 W) and 90% reduction in trap density compared to the 100W-deposited GI, resulting enhanced hysteresis properties. However, excessive plasma power at 250 W caused plasma damage and excess N content, degrading electrical properties. When applied to high-mobility TFTs, electrical properties were enhanced with increasing N_2O Plasma power. Optimized values include field-effect mobility of 53.45 cm^2/Vs, Vth of -0.03 V and SS of 67.7 mV/dec at 200 W plasma power. Moreover, the reliability under positive bias temperature stress(1h each under a gate electric field strength of 2 MV/cm and at 60℃) was also enhanced exhibiting slight negative Vth shifts of less than 0.18V. Incorporating N into Al2O3 has been demonstrated as an effective method to reduce bulk defects and suppress H diffusion, significantly enhancing device reliability. The hypothesis was validated by observing changes in field effect mobility and Vth value after 350℃ annealing in H-forming gas(H2 4% + N2 96%). This indicates suppressed H diffusion from the ambient into the active layer, thus demonstrating the H resistance of the Al2O3 dielectrics attributed to the increased N content in the GI layer.

Therefore, these findings highlight the potential of N-doped Al2O3 GIs deposited via optimized PEALD, to enhance the reliability and performance of oxide semiconductor-based devices.

9:15am **AA2-WeM-6 Highly Stable Fluorine-Anion Engineered ALD Indium Oxide Thin-Film Transistors towards BEOL Integration***, **Jinxiong Li**, Xinwei Wang,* School of Advanced Materials, Peking University, Shenzhen 518055, China

Back-end-of-line (BEOL) integration with oxide semiconductor thin-film transistors (TFTs) presents a highly promising approach for the continuation of the Moore's Law. To address the critical challenge of the oxygen vacancy (V_O) instability in high-mobility In_2O_3 TFTs, we propose a novel low-thermal-budget fabrication approach to realize fluorinated In_2O_3 (In_2O_3:F) TFTs with remarkable stability [1]. By combining a re-engineered ALD process for ultrathin In_2O_3 films with a novel plasma fluorination strategy, the afforded In_2O_3:F TFTs exhibited a high mobility (μ_{FE}) of 35.9 $cm^2/V{\cdot}s$, a positive threshold voltage (V_{th}) of 0.36 V, and small V_{th} shifts of 49 and −111 mV under positive and negative bias stress conditions, respectively. Density functional theory (DFT) analysis shows that the fluorine doping can stabilize the lattice oxygen and electrically passivate the V_O defects in In_2O_3 by forming the F_OF_i spectator defects. This work demonstrates a BEOL-compatible fabrication approach to achieve both high performance and high stability for the oxide TFTs, thereby highlighting their high promise for advanced BEOL integration.

[1] Jinxiong Li, et al., *Advanced Functional Materials*, 2024, 34 (28), 2401170

9:30am **AA2-WeM-7 High-Pressure Atomic Layer Deposition of Elemental Tellurium for Enhanced P-Type Semiconductors***, Myung Mo Sung, **Dai Tran Cuong**,* Hanyang University, Korea

Tellurium (Te), with its unique helical structure, has emerged as a promising 2D p-type semiconductor. However, traditional deposition techniques face challenges in producing large-area, uniform Te thin films. Atomic Layer Deposition (ALD) offers a potential solution due to its capacity for high-quality, large-scale films. A primary obstacle in ALD-based Te deposition is insufficient nucleation at the initial growth stage, leading to island growth - a result of the low reactivity and bulky ligands of $(Me_3Si)_2Te$ and $Te(OEt)_4$ precursors. To address this, we introduce a novel approach that combines High-Pressure ALD (HP-ALD) with a Multiple-Dosing (MD) technique, promoting the formation of continuous, uniform Te films from the early stages of growth. The resulting Te thin films demonstrate a Hall mobility of 51.2 $cm^2\ V^{-1}\ s^{-1}$, strong stability, and excellent surface coverage. This advancement in Te thin-film fabrication through HP-ALD and MD addresses key challenges, paving the way for integrating Te into next-generation electronic devices.

9:45am **AA2-WeM-8 Ultrathin Sn-Doped in_2O_3 Films for Scalable Semiconductor Transistors***, **Seung Ho Ryu**,* Korea University, Republic of Korea*; Taikyu Kim,* Korea Institute of Science and Technology (KIST), Republic of Korea*; Taeseok Kim, Seong Keun Kim,* Korea University, Republic of Korea

As transistor scaling progresses, ultrathin channel structures are increasingly required to suppress short-channel effects and enhance gate control in advanced device architectures such as FinFETs and gate-all-around (GAA) transistors. However, reducing channel thickness typically leads to severe degradation in conductivity, limiting the electrical performance of thin-film transistors (TFTs). In this study, we investigate an ultrathin Sn-doped In_2O_3 (ITO) channel to overcome this challenge. The uniform Sn doping enhances carrier density and mitigates the conductivity degradation associated with ultrathin channels, ensuring stable electrical performance. As a result, we successfully fabricate enhancement-mode TFTs with a 1.5 nm-thick ITO channel, achieving a high field-effect mobility of 33.4 ± 1.5 $cm^2/V{\cdot}s$, a subthreshold swing of 129 ± 30 mV/dec, and a threshold voltage of 0.3 V. These findings provide a crucial strategy for realizing high-performance oxide TFTs with ultrathin conducting channels, addressing a key challenge in the development of next-generation semiconductor devices.

ALD Applications
Room Halla Hall AB - Session AA3-WeM
Other Energy Applications

Moderators: Sumit Agarwal, Colorado School of Mines, **Rong Chen**, Huazhong University of Science and Technology

10:45am **AA3-WeM-12 Using Area-Selective Ald for Dual Site Catalysis for Photocatalytic Water Splitting***, **Katherine Hurst**, Wilson McNeary,* National Renewable Energy Laboratory*; William Stinson,* Columbia University*; Shane Ardo,* University of California Irvine*; Daniel Esposito,* Columbia University **INVITED**

ALD (Atomic Layer Deposition) of thin films on catalysts can introduce a variety of functionalities in electrochemical systems, effectively altering chemical reactions and outcomes. For example, thin films can enhance the physical stability of a catalyst on a substrate, alter the surface energy through core shell design, passivate catalyst defect sites that create side reactions, among others. Here, we explore strategic deposition of thin oxide coatings by ALD to a enhance reaction selectivity of a co-catalyst system.

Photocatalytic (PEC) water splitting uses a configuration where cocatalysts drive two separate reactions; hydrogen evolution reaction (HER), and hydrogen oxidation reaction (HOR), that are coupled by an active redox mediator to shuttle charge between them. A significant efficiency loss for PEC is caused by high rates of undesired side and back reactions, which are intensified by the proximity of the neighboring oxidation and reduction sites. In this work, we use area selective ALD (AS-ALD) of oxide films to develop tunable interface layers to prevent back reactions that hinder the efficiency.

AS-ALD was used to target growth of an oxide film on one metal of planar dual-metallic-site thin film electrode system with distinct Au regions and Pt regions. Thiol molecules acted as self-assembled monolayers adsorbed on the Au surface, preventing subsequent TiO_2 ALD growth on the Pt regions. After a mild ozone-treatment to remove the thiol molecules, the bare Au surface is exposed. The TiO2 film characteristics and spatial selectivity of growth was characterized by ellipsometry and X-ray photoelectron spectroscopy (XPS). Scanning electrochemical microscopy (SECM) measured suppressed undesired HOR and redox reactions while still permitting the desired HER, verifying the effective blocking methods of the AS-ALD approach. The capability to strategically alter dual-site reaction sites closely spaced provides a promising pathway to enhancing efficiencies in PEC systems.

11:15am **AA3-WeM-14 Impact of Tetrakis(dimethylamido)tin(IV) Degradation on Atomic Layer Deposition of Tin Oxide Films and Perovskite Solar Cells***, Shuang Qui, Augusto Amaro,* University of Victoria, Canada*; Diana Fabulyak,* Avantor, Canada*; Julien Appleby-Millette,* University of Victoria, Canada*; **Cassidy Conover**,* Avantor, Canada*; Dongyang Zhang, Vishal Yeddu, I. Teng Cheong, Irina Paci, Makhsud Saidaminov,* University of Victoria, Canada

Tin oxide (SnOx) films synthesized by atomic layer deposition (ALD) are widely explored in a range of optoelectronic devices, including electrochemical sensors, transistors, and photovoltaics. However, the integrity of the key ALD-SnOx precursor, namely tetrakis(dimethylamido)tin (IV) (TDMASn), and its influence on the properties of the ultimate films remain unexplored. Here, a significant degradation of TDMASn into bis(dimethylamido)tin (II) via the Sn-imine complex is reported, and its impact on the corresponding films and devices is examined. It is found, surprisingly, that this degradation does not affect the growth kinetics and morphology of ALD-SnOx films. However, it notably deteriorates their electronic properties, resulting in films with twice the electrical resistance due to different oxidation mechanisms of the degradation products. Perovskite solar cells employing such films exhibit a significant loss in power conversion efficiency, primarily due to charge transport and transfer losses. These findings urge strategies to stabilize TDMASn, a critical precursor for ALD-SnOx films, or to identify alternative materials to achieve efficient and reliable devices.

11:30am **AA3-WeM-15 Ultrathin Oxygen Deficient SnOx Films as Electron Extraction Layers for Perovskite Solar Modules***, Helen Hejin Park,* korea research Institute of Chemical Technology (KRICT), Korea (Democratic People's Republic of)*; **Joshua Sraku Adu**,* Korea Research Institute of Chemical Technology (KRICT), Korea (Democratic People's Republic of)

The fabrication of high-efficiency, large-area perovskite solar cells necessitate the development of homogeneous charge extraction layers with tunable optoelectronic properties. The characteristics of SnO_x films, deposited via thermal atomic layer deposition (ALD) and plasma-enhanced ALD (PEALD), are influenced by critical parameters such as deposition temperature, precursor pulse and purge durations, extrinsic doping, and post-annealing conditions.[1-3] Despite the homogeneity and conformity of the ALD films, the device performs poorly when compared to ETL generated using colloidal nanoparticle deposition. In this report, we describe the impact of oxygen-deficient tin oxide (SnO_x) thin films as electron extracting layers in perovskite solar modules, deposited by a highly innovative plasma-modified atomic layer deposition (PMALD) tool that allows us to further tune composition, conductivity, and effective work function.Energy-filtered photoemission of electron microscopy (EF-PEEM) shows a remarkably homogeneous surface electronic landscape of the PMALD SnO_x.We examine the impact of PMALD-SnO_x in *n-i-p* device configuration, with poly(triarylamine) (PTAA) as the hole transporting layer, which leads to the improvement in perovskite module power conversion efficiency from 17.9% to 20.1%, with an active area of 23.2 cm^2.Furthermore, devices maintained 92% of their initial efficiency for 2,700 h at 85°C and 85% relative humidity and 96% for 1,000 h under continuous 1 SUN illumination with maximum power point tracking.

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11:45am **AA3-WeM-16 Charge Transport Layers Rafted by Atomic Layer Deposition for Large-Area Perovskite-Based Solar Modules***, **Femi Mathew**,* Institut Photovoltaïque d'Ile-de-France (IPVF), France*; Damien Coutancier,* CNRS-IPVF, France*; Getaneh Gesesse, Marion Provost, Nadia Nazi,* Institut Photovoltaïque d'Ile-de-France (IPVF), France*; Nathanaelle Schneider,* CNRS-IPVF, France

Perovskite solar cells (PSCs) have emerged as promising solar cell technology with rapidly advancing power conversion efficiency (PCE) driven by continuous research and innovation. [1,2] To achieve efficient and stable PSCs, optimal charge transport layers are paramount. Among various vacuum based fabrication techniques, the atomic layer deposition (ALD) technique is a powerful strategy to fabricate pinhole free and electrically continuous charge transport layers with precise thickness control.[3,4] Additionally, for the large-scale production of perovskite modules, the ALD technique is particularly valuable, offering conformal deposition on large-area substrates, making it viable for commercialization.[5]

In this work, we focused on the atomic layer deposition of charge transport layers for 64 cm^2 single junction semi-transparent inverted (PIN) perovskite solar modules. The device structure is built on glass substrate, fluorine-doped tin oxide (FTO) as bottom electrode, NiO_x passivated with self-assembled monolayers (SAMs) as hole transport layer (HTL), perovskite as absorber layer, C60 and SnO_2 as electron transport layer (ETL) and indium tin oxide (ITO) as top electrode. [Fig 1(a)] Among these, the NiO_x and SnO_2 layers were deposited by ALD at low temperatures to ensure compatibility with perovskite absorber material.

Both NiO_x and SnO_2 layers deposited by ALD have been thoroughly investigated for their physicochemical and optoelectronic properties to evaluate their qualification for efficient charge extraction. The crystallinity, surface morphology and chemical composition of the NiO_x and SnO_2 films were investigated. [Fig 2(b&c)] Additionally, optoelectronic properties of the NiO_x and SnO_2 films including transmittance, bandgap and work function were also evaluated. Finally, the solar cell parameters of the device were measured and the champion device obtained PEC of 11% on large area (64 cm^2) perovskite modules. In summary, this work highlights the potential of ALD technique in the fabrication of promising charge-transport layers for next generation photovoltaic cells.

ALD Fundamentals
Room Tamna Hall B - Session AF-WeM

Material Growth I

Moderators: Kivin Im, SK Hynix, **Gregory N. Parsons**, North Carolina State University

10:45am **AF-WeM-12 High Crystallinity Yttrium-Doped ZrO2 under 2 nm Through Atomic Layer Modulation***, **Ngoc Le Trinh**, Bonwook Gu, Wonjoong Kim, Minhyeok Lee,* Incheon National University, Republic of Korea*; Byung-ha Kwak,* Ajou University, Republic of Korea*; Hyun-Mi Kim, Hyeongkeun Kim,* Korea Electronics Technology Institute, Republic of Korea*; Youngho Kang,* Incheon National University, Republic of Korea*; Il-Kwon Oh,* Ajou University, Republic of Korea*; Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

The rapid miniaturization of integrated circuits poses significant challenges for various silicon-based devices, such as DRAM capacitors and 3D transistors, which demand both high capacitance density and low leakage current density. As the device dimensions shrink further, the thin films used in these devices must become even thinner, making it increasingly difficult to preserve their physical properties at such reduced thicknesses. In this work, we studied high crystallinity dielectric thin films with Y-doped ZrO_2 (YZO) less than 2 nm of film thickness. Atomic layer modulation (ALM) based on atomic layer deposition (ALD) was utilized to achieve better compositional uniformity both in-plane and out-of-plane direction at atomic level. In the ALM process, the surface was sequentially exposed to precursors with an intervening purging step between each exposure, followed by a reaction with a counter-reactant, resulting in the growth of the YZO film within a single atomic layer. The ratio of Y and Zr in ALM film was determined by steric hindrance and chemical reactivity of the precursors. To design and interpret the experiment, two theoretical approaches, density functional theory (DFT) and Monte Carlo (MC) simulation were used. The formation energy of the crystalline phase in the ALM films was expected to be lower than in the ALD film. In the ALM film, Y atoms are formed closer to Zr atoms, with Y−O−Zr bonds forming both laterally and vertically within a few atomic layers. Consequently, the ALM film requires a lower energy barrier for diffusion to form theYZO crystalline phase, which enhances film density and improves crystallinity. It was revealed that doping ZrO_2 with Y induces a crystal structure change, leading to a phase transformation from monoclinic to a cubic (111)-plane-dominant phase. Consequently, YZO prepared via ALM shows approximately 250 times lower leakage current density compared to conventional YZO fabricated through ALD at a thickness of 2 nm. This key finding highlights that that YZO achieves both increased dielectric constant and reduced leakage current density at low thicknesses, demonstrating its potential as a promising material for future silicon device applications.

11:00am **AF-WeM-13 ALD Outstanding Presentation Award Finalist: Ultrahigh Purity Plasma-Enhanced Atomic Layer Deposition and Electrical Properties of Epitaxial Scandium Nitride***, **Bruce Rayner**, Noel O'Toole,* Kurt J. Lesker Company*; Bangzhi Liu, Jeffrey Shallenberger,* The Pennsylvania State University*; Jiadi Zhu, Tomas Palacios, Piush Behera, Suraj Cheema,* Massachusetts Institute of Technology*; Blaine Johs,* Film Sense*; Nicholas Strnad,* DEVCOM Army Research Laboratory

Scandium nitride (ScN) by plasma-enhanced atomic layer deposition (PEALD) was demonstrated on silicon (100), sapphire (0001) and magnesium oxide (001) substrates under ultrahigh purity conditions using a new Sc precursor, bis(ethylcyclopentadienyl)scandium-chloride $[ClSc(EtCp)_2]$. Out-of-plane x-ray diffraction patterns indicated single-crystal, cubic phase ScN deposited at 215°C on sapphire (0001) and magnesium oxide (001) substrates; phi-scans confirmed epitaxial growth. The ScN thin films grown on silicon with native oxide were polycrystalline with no preferential orientation. The ScN films showed a nitrogen-to-scandium ratio of approximately 1:1 measured by x-ray photoelectron spectroscopy, with ultra low levels of elemental impurities including 2.5 at.% chlorine, 0.9 at.% carbon and 0.4 at.% oxygen. $ClSc(EtCp)_2$ and N_2-H_2 plasma were evaluated as a ScN co-precursors at substrate temperatures ranging from 200-300°C, where we identified an ALD window between 200–215°C. Images by field emission scanning electron microscopy (FESEM) on 43 nm-thick films grown on untreated silicon revealed columnar grains with lateral sizes ranging from 16-28 nm. ScN conformality across 4:1 aspect ratio silicon trench structures with 312 nm-wide openings was also imaged by FESEM showing a top-to-bottom thickness ratio of 75%. ScN electrical properties were evaluated by performing Hall measurements to determine mobility, free electron concentration and resistivity. For ScN PEALD on magnesium oxide (001), the average mobility was 298 cm^2/Vs with a carrier concentration of 2.35×10^{19} cm^{-3}. The average resistivity was 1.01 mΩ·cm.

11:15am **AF-WeM-14 Microwave Enhanced (ME) ALD of HfO_2***, Jessica Haglund-Peterson, **John Conley**,* Oregon State University

The low temperatures typical of ALD can allow incorporation of impurities from unreacted ligands leading to sub-optimal physical, optical, and electrical properties. Although post deposition annealing (PDA) can help drive off impurities, the temperatures required may exceed thermal budget limits. To maintain low temperature while maximizing film properties, adding energy in-situ *during* each ALD cycle (energy enhanced, EE-ALD) can help drive/speed reactions and reduce impurity incorporation. Indeed, in-situ every cycle rapid thermal annealing improved the density, stoichiometry, electrical, and optical properties of ALD films that could not be achieved by PDA alone.[1-3] Other EE-ALD methods include flash lamp, plasma, UV, laser, and electron beam exposure.[4-9] It has been shown that *post*-deposition microwave annealing (MWA) can improve ALD films,[10] and recently, we introduced *in-situ* microwave enhanced (MWE) ALD.[11] Here we investigate low temperature MWE-ALD of HfO_2.

A Picosun R200 was equipped with a custom MW antenna (MKS) and an MKS SG 1024 solid state MW generator. HfO_2 was deposited at 150˚C using 1/30/0.1/30 sec TEMA-Hf/N_2/H_2O/N_2 ALD cycles. Film thickness and refractive index were modeled using a Film Sense FS-1 mapping ellipsometer. As compared to a control sample without MW exposure, adding 30 s in-situ 400 W MW exposures (*without* plasma generation) during the H_2O purges of each ALD cycle had no significant impact on growth. However, the same MW exposures during the TEMA-Hf purge were found to increase film thickness by ~50% and increase refractive index from 1.9 to 2.1 over the control sample. The impact during the precursor purge as opposed to H_2O purge is consistent with our previous results on TMA/H_2O Al_2O_3.[11] This work demonstrates quality ALD deposition at a temperature normally below the standard "window" for this process, allowing for a decrease in thermal budget. Additional electrical and analytical data will be presented, including density, crystallinity, stoichiometry, roughness, as well as leakage and capacitance of MOS and MIM device structures.

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11:30am **AF-WeM-15 Atomic Level Engineering of Dy-doped HfO2 Ultra-thin Films via Controlling Lateral and Vertical Mixing***, **Byung-Ha Kwak**,* Ajou University, Republic of Korea*; Ngoc Le Trinh,* Incheon National University, Viet Nam*; Bonwook Gu, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea*; Il-Kwon Oh,* Ajou University, Republic of Korea

We investigate the effects of Dy doping in HfO_2 thin films using two distinct atomic arrangement strategies: lateral mixing, known as atomic layer modulation (ALM), and vertical mixing, known as supercycle ALD. Lateral mixing can control atomic concentration by sequentially exposing two precursors (Dy and Hf) in a first-half cycle of ALD process and exposing a single reactant that reacts both precursors at the second-half cycle, determined by chemical reactivity and steric hindrance of two precursors.[1] This method allows precise controlling of atomic-level doping even in ultrathin films under 5 nm thickness. In contrast, the vertical mixing method, where a few cycles of Dy_2O_3 deposition are followed by multiple cycles of HfO_2, has limitations[2], as it requires a minimum thickness to maintain a consistent concentration across the film.

In the lateral mixing process, when both precursors were sequentially exposed for their respective saturation times, the Dy concentration in deposited films was measured to be 20.6 % when a Dy precursor was exposed first, whereas it was 12.5 % when a Hf precursor was exposed first. We elucidate growth mechanism of ultra-thin films of lateral mixing by density functional theory (DFT) and Monte-Carlo (MC) simulations with experimental observation. We observe different crystalline structures between lateral mixing and vertical mixing. In single HfO_2 and vertical mixing films, tetragonal (101) phase was observed after 600 ℃ annealing process. However, no crystalline phase was observed in lateral mixing films at the same annealing process. We also observe that both lateral mixing and vertical mixing films showed lower leakage current density than a single HfO_2 film of same thickness, which will be discussed with growth mechanism and crystalline structure. Interestingly, the lateral mixing case for Hf-precursor-exposed first exhibits leakage currents approximately 180 times lower than Dy-precursor-exposed first. We believe that these approaches will significantly advance the development of high-k materials with optimized properties, supporting the future scaling down of semiconductor devices and enhancing their performance in next-generation electronic applications.

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11:45am **AF-WeM-16 Process-Structure-Properties of Atomic Layer Deposited Niobium Nitride and Evolution of Strain with Plasma Chemistry***, **Neeraj Nepal**, Joseph C Prestigiacomo, Maria Gabriela Sales, Peter M Litwin, Vikrant J Gokhale, Virginia D Wheeler,* U.S. Naval Research Laboratory

Niobium nitride (NbN) has exceptional physical, chemical, and electrical properties that can be utilized in a range of applications such as gate metal, superconducting qubits and detectors (T_c ~9-17 K [1]), RF antennas, resonators, and Cu interconnect diffusion barriers. For all these applications, a low temperature growth process with wafer scale uniformity, conformality, and subatomic thickness control is highly desirable. Atomic layer deposition (ALD) provides a path towards integration of NbN at lower temperatures with control over the desired properties. Most reported thin plasma-enhanced ALD (PEALD) NbN films [2-3] to date are either amorphous or polycrystalline. In this talk, we report on highly oriented single phase, PEALD NbN (111) films and discuss the evolution of strain with plasma chemistry.

ALD NbN films were deposited on resistive Si and c-sapphire in a Veeco Fiji Gen2 ALD reactor using (t-butylimido)tris(diethylamido)niobium(V) (TBTDEN) and N_2/H_2 plasma precursors. Similar to previous reports [2], TBTDEN required a boost to enable growth. Growth windows and film morphological, structural, and electrical properties were optimized for TBTDEN temperature (80-100°C), TBTDEN boost (1-2s), TBTDEN pulse (1.5-2.0s), plasma pulse (20-30s), H_2/N_2 ratio (1.5-12.5), and temperature (150-400 °C). Optimum growth parameters (TBTDEN = 100°C, TBTDEN boost = 1.5s, TBTDEN pulse = 2s, and H_2/N_2 = 60/20sccm) yielded an ALD window from 250-300°C with a growth rate (GR) of ~ 0.5A/cy. While GR was almost constant for $N_2 \geq 20$ sccm, room temperature resistivity (ρ_{RT}) increased linearly with N_2 flow. High-resolution XRD scans show 1st and 2nd order (111) NbN peaks. Lattice constants obtained from XRD show that strain changes from compressive to tensile with increasing N_2 flow, in which an N_2 flow of 20 sccm provided an almost strain-free film. The compressively strained 12.6 nm thick film at 5 sccm N_2 resulted in lower ρ_{RT} (~139μΩcm) and superconducting critical temperature (T_c~12.26K). Measured T_c is similar or higher than reported T_c (12.10K) of 15nm thick ALD NbN films [3]. For an optimized 30nm thick film, carbon is below the XPS detection limit, RMS surface roughness is 0.52nm, and rocking curve FWHM is 0.69°, which is narrower than previously reported for 30 nm thick films [3]. T_c on all those films were also measured to establish process-structure-property relationships, and results will be discussed in the context of use in quantum and high temperature contact applications.

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Atomic Layer Etching
Room Samda Hall AB - Session ALE1-WeM

Plasma and/Energy-Enhanced ALE + Sustainability

Moderators: Jane P. Chang, University of California, Los Angeles, **Sung-Il Cho**, Samsung Electronics

8:00am **ALE1-WeM-1 Centering Sustainability in Future Plasma-Enhanced ALE Processes***, Nathan Marchack, Robert Bruce,* ***Eric Joseph,*** IBM Research Division, T.J. Watson Research Center **INVITED**

Recent progress in the field of artificial intelligence has also highlighted the critical role of semiconductor manufacturing in delivering the necessary compute requirements. Simultaneously, the prospect of future proliferation of such technologies presents serious ramifications for the environment. Examinations of the increases in resource consumption as both software [1] and hardware [2] advance have raised awareness of the need to consider the sustainability of future development. In this talk we will examine this idea as it pertains to plasma-enhanced atomic layer etching (PE-ALE), building off our recent work on reducing gas usage in deep Si etching. [3] We review new results studying mechanisms of halogen substitution on Si surfaces and the need for synergy between all facets of the development process, from substrate materials to gas precursor development. Adopting this focus as soon as possible will strengthen the fundamental role of atomic layer processes in enabling future technologies.

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8:30am **ALE1-WeM-3 Cryogenic Atomic Layer Etching of SiO_2 by Physisorption of HF/C_2H_5OH and Ar Plasmas***,* ***Shih-Nan Hsiao,*** *Makoto Sekine,* Nagoya University, Japan*; Yoshihide Kihara,* Tokyo Electron Miyagi Limited, Japan*; Masaru Hori,* Nagoya University, Japan

The continues reduction of the chip size and development of innovative 3D integrated device architectures have required the adoption of advanced processing methods. Plasma-assisted atomic layer etching (PE-ALE) has emerged as a promising technique for sub-nanoscale material removal in semiconductor processes due to its unique self-limiting surface reactions. Cryogenic plasma etching enabling the unique feature of physisorption of neutrals/condensed layer has been reported for ALE of dielectric materials [1]. Our recent reports indicates that the cryogenic plasma etching can significantly enhance the etching throughput of SiO_2 through the co-adsorption of H_2O/HF species using the CF_4/H_2 gases [2]. Building on this, we developed the cryogenic ALE (Cryo-ALE) process involving an HF dose for surface modification and Ar ion bombardment for SiN etching. This work extends the Cryo-ALE process to SiO_2, utilizing an HF/C_2H_5OH dose for etchant physisorption followed by an Ar ion bombardment. *In situ* monitoring techniques, including spectroscopic ellipsometry and attenuated total reflectance Fourier transformation infrared spectroscopy (ATR-FTIR), were used to analyze the surface structure and etching characteristics. The substrate temperature (T_s) was controlled from 20 to –60 °C using a coolant circulating system connect to the bottom electrode. The etched depth per cycle (EPC) of the SiO_2 after the process increased from approximately 0.28 nm/cycle to 0.79 nm/cycle as the T_s was decreased from 20 to –60 °C. (see supplemental document for details). ATR-FTIR analysis revealed that this increase in EPC correlates with an enhanced amount of surface-adsorbed HF/C_2H_5OH during the surface modification step. Conversely, the EPC vs T_s for the SiN exhibited an opposite trend, indicating that the etching selectivity between SiO_2/SiN can be effectively tuned by adjusting T_s.

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[2] S. N. Hsiao et al., Small Methods, 2400090 (2024).

[3] S. N. Hsiao et al., Chem. Mater. 36, 11042 (2024).

8:45am **ALE1-WeM-4 Cryogenic ALE of SiO_2 using CF_4 Plasma***, Madjid Adjabi, Jack Nos, Sylvain Iseni,* GREMI - CNRS/Orleans University, France*; Gilles Cunge, Martin Kogelschatz,* LTM - CNRS/Grenoble Alpes University/Grenoble-INP, France*; Philippe Lefaucheux, Loïc Becerra,* GREMI - CNRS/Orleans University, France*; Emilie Despiau-Pujo,* LTM - CNRS/Grenoble Alpes University/Grenoble-INP, France*;* ***Thomas Tillocher,*** *Rémi Dussart,* GREMI - CNRS/Orleans University, France

Cryogenic Atomic Layer Etching of SiO_2 ("Cryo-ALE") has been developed several years ago to address some limitations when it is performed at room temperature.The ALE process achieved under these last temperature conditions involves a C_4F_8 plasma in the modification step. This results in fluorocarbon deposition on the reactor walls, and eventually to process drifts, which affects reproducibility. Consequently, chamber cleaning is necessary. This can be addressed by flowing C_4F_8 in gas phase and cooling the SiO_2 substrate at cryogenic temperature. C_4F_8 molecules are physisorbed only on the cooled surface and therefore, wall pollution is greatly reduced. The thin physisorbed C_4F_8 layer is then used as a reservoir to etch around one SiO_2 monolayer in the subsequent Ar plasma of one ALE cycle.

Alternatively, a relevant approach consists in selecting a gas with a higher F/C ratio, which polymerizes much less than low F/C ratio gases such as C_4F_8. For instance, a CF_4 plasma is in etching regime at room temperature and does not promote polymer deposition on the chamber walls at room temperature too. Nevertheless, it is shown by absorption spectroscopy that the sticking coefficient of CF radicals increases dramatically when the surface is cooled at cryogenic temperature. This means that a CF_4 plasma can be used to deposit a fluorocarbon layer only on cooled surfaces, in particular SiO_2. But the chamber walls, at room temperature, are polymer-free.

Consequently, a CF_4 plasma can be used as a modification step in a SiO_2 Cryo-ALE process. It is demonstrated that repeating cycles of a CF_4 plasma step followed by an Ar plasma with low energy ion bombardment, with each cycle separated by a purge step, enables sequential etching of SiO_2 cooled at cryogenic temperature. The EPC increases as the substrate temperature decreases and reaches 0.46 nm/cycle at -130°C. This process, provided deposition during CF_4 plasma is well balanced with etching in the Ar removal step, exhibits a high synergy that can approach 100%.

Acknowledgments: The authors thank Tokyo Electron Limited for financial support and helpful discussions and acknowledge ANR, which
supports the project PSICRYO for "Understanding Plasma-Surface Interactions in CRYOgenic etching for advanced patterning applications" (No. ANR-20-CE24-0014). This work was also supported by CERTeM platform, which provides most of the equipment.

9:00am **ALE1-WeM-5 Atomic Layer Etching of Indium Oxide Thin Films via Ligand Addition and O_2 Plasma Reactions***,* ***Minchan Kim,*** *Jihyun Gwoen, Hae Lin Yang, Jin-Seong Park,* Hanyang University, Korea

The Oxide semiconductors (OSs), which utilize materials like IGZO as channel layers, have been gaining increased attention as the demand for high mobility and low off - current in semiconductor devices continues to grow.Especially, InOx is emerging as a key material for next-generation devices due to its outstanding electron mobility. Achieving these characteristics requires high-quality thin films, which can be precisely and uniformly fabricated using atomic layer deposition (ALD), a technique essential for high-mobility InOx and next-generation device applications. While ALD enables precise deposition, achieving the desired crystallinity in InOx at low thickness remains challenging due to issues like nucleation and non-uniform film growth. To address this, an etch-back process using Atomic Layer Etching (ALE) is often employed, depositing the film to the required properties before selective removal. However, in the case of InOx, the low volatility of modified byproducts like $InCl_3$ or InF_3 makes their removal chemically difficult, posing significant limitations to the applicability of ALE technique

In this study, we explored the operation of Atomic Layer Etching (ALE) for InOx by incorporating an additional hydrogen treatment modification step into the conventional ligand-based ALE process using Hacac (acetylacetone). The process was evaluated through Spectroscopic Ellipsometry (SE), X-ray Photoelectron Spectroscopy (XPS), and X-ray Diffraction (XRD) to determine whether the ALE cycles proceeded in a layer-by-layer manner driven by self-limiting reactions. The findings showed that the thickness of the indium oxide thin film could be controlled with precision, while an improvement of approximately 37% in RMS roughness was observed, indicating better film quality after the ALE process. Furthermore, XPS and XRD analysis confirmed that the bulk chemical composition remained unchanged following the hydrogen modification step, suggesting that the mechanism effectively induced reactions at the surface level. These results provide useful insights into controlling oxide semiconductor deposition and improving thin-film quality for potential device applications.

9:15am **ALE1-WeM-6 Development of a Novel Magnetically-Confined Plasma Source for Advanced Semiconductor Manufacturing***, Tae S Cho,* Wonik IPS*; Jihyun Kim,* ***Giwon Shin****, Hakmin Kim, Jeonghun Kim, Sooyoung Hwang, Jaehoon Choi,* Wonik IPS, Republic of Korea

The relentless pursuit of miniaturization in the semiconductor industry, characterized by sub-10 nm feature sizes, 3D stacked architectures, and complex gate-all-around (GAA) structures, demands increasingly sophisticated plasma processing techniques. These advanced applications require plasma sources capable of operating over a broad pressure range while providing a high radical density with minimal ion-induced damage to delicate device structures.

To address these critical requirements, we have developed a novel ignitor-free remote plasma source utilizing a magnetic core configuration. Preliminary test with argon and argon-nitrogen gas mixtures demonstrates a stable operating pressure range of 0.1 to 17 Torr and 0.1 to 4.5 Torr, respectively.

Furthermore, this source exhibits a unique capability for plasma mode transition. By adjusting the magnetic core's winding ratio, the plasma can be dynamically transitioned between voltage mode and current mode operations. This flexibility allows for optimized process control, enabling the generation of high radical density for rapid etch rates in current mode, while minimizing ion bombardment for delicate deposition processes in voltage mode. Optical emission spectroscopy (OES) measurements confirm a significant enhancement in radical density in current mode compared to voltage mode.

Based on these promising results, ongoing efforts are focused on optimizing the plasma reactor, magnetic core geometry, and radio frequency (RF) generator to further enhance the performance and versatility of this innovative plasma source for advanced semiconductor manufacturing applications.

9:30am **ALE1-WeM-7 Low-Damage Plasma Atomic Layer Etching of Silicon Dioxide and Nitride via DC Substrate Bias and Remote Inductively Coupled Plasma Source***, Hee Chul Lee,* ***HongHee Jeon****, SoWon Kim,* Tech University of Korea

Atomic Layer Etching (ALE) is an advanced etching technique consisting of two sequential steps: surface modification and removal of the modified surface. This process enables precise atomic-scale thickness control through its self-limiting characteristics, making it highly suitable for next-generation semiconductor device fabrication.

In this study, low-damage and high-productivity ALE process for SiO_2 and SiNx was developed using both inductively coupled Remote Plasma (RP) and DC substrate bias. The process focuses on the effective removal of interfacial defects and residual byproducts. The proposed ALE process is designed to support next-generation DRAM technologies, where precise etch control and material stability are essential.

For Direct Plasma (DP)-ALE, the process conditions were set to RF Power of 50W, process pressure of 100 mTorr with Ar, CF_4, C_4F_8, and CHF_3 discharge gases. The reactor configuration featured a 40 mm showerhead-to-substrate distance. The experiments were conducted with process parameter changes in adsorption time, desorption time, and DC substrate bias. To ensure process stability and reduce contamination, O_2 plasma cleaning was performed before and after each ALE cycle to effectively remove residues from the chamber walls. Ellipsometry was employed to measure thickness variations before and after etching, confirming fluorocarbon (FC) film deposition, with additional characterization planned using X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM).

The DP-ALE results indicated FC film deposition per cycle of 1.2 Å for SiO_2 and 2.2 Å for SiNx at an adsorption time for 3 seconds. Under conditions RF power of 50W, DC substrate bias of 90V, and a desorption time for 60 seconds, the achieved etch-per-cycle (EPC) was 0.18 nm/cycle for SiO_2 and 0.15 nm/cycle for SiNx, confirming the presence of self-limiting characteristics.

The goal of this research is to effectively apply CP(Co-plasma)-ALE including RP and DP plasma and substrate DC bias to next-generation semiconductor technologies to minimize device damage while increasing process control and reliability. And the results of a comparative study will be presented at the conference.

Atomic Layer Etching
Room Samda Hall AB - Session ALE2-WeM
ALE Applications III

Moderators: Keun Hee Bai, Samsung Electronics Co., **Younghee Lee**, Lam Research Corporation

10:45am **ALE2-WeM-12 In-Situ Observation of Surface Reaction and Advanced Process for Damage-Less Atomic Layer Etching***,* ***Takayoshi Tsutsumi,*** Nagoya University, Japan **INVITED**

11:15am **ALE2-WeM-14 Isotropic ALE of 2D Crystalline MoS_2 using SF_6:H_2 Plasma and O_2 Plasma***,* ***Sanne Deijkers****, Christian Palmer, Nick Chittock, Guillaume Krieger, Silke Peeters, Marcel Verheijen,* Eindhoven University of Technology, The Netherlands*; Harm Knoops,* Oxford Instruments Plasma Technology, Netherlands*; Erwin Kessels, Adrie Mackus,* Eindhoven University of Technology, The Netherlands

Two-dimensional crystalline MoS_2 is an emerging material for nanoelectronics, where it can be applied as a channel material in field effect transistors. MoS_2 exhibits a high carrier mobility, even at the monolayer thickness of 6.5 Å, and therefore it is expected to replace Si in the future [1]. Application of MoS_2 in nanoelectronics requires highly controlled deposition and etching processes. Currently available ALE processes either require an external step like a wet treatment [2], or are optimized for amorphous MoS_2 [3]. Here, we present a plasma-enhanced ALE process, which can etch crystalline MoS_2 in an isotropic manner.

In the ALE cycle, the crystalline ALD-grown MoS_2 film was first fluorinated and subsequently oxygenated to create volatile $Mo_xO_yF_z$ species. The fluorination step employs a plasma mixture containing SF_6 and H_2, which is believed to produce *in situ* HF, as suggested by previous studies on H_2-diluted fluorine plasmas [4,5]. F radicals, which are known to etch MoS_2 continuously [6,7], are scavenged by the hydrogen to form HF as observed in the plasma [8]. The SF_6:H_2 ratio was tuned to ensure modification occurs without continuous etching. For the oxygenation half-cycle an O_2 plasma was used, whereas O_2 gas and H_2O did not result in significant etching.

The resulting etch per cycle combining the SF_6:H_2 plasma and O_2 plasma is 0.92 ± 0.02 Å. Before ALE the crystallinity of the films was confirmed by observation of the characteristic MoS_2 peaks in Raman spectroscopy, and after ALE a decrease in these peaks is seen, verifying etching of the crystalline material. Furthermore, no F contamination was observed after ALE by x-ray photoelectron spectroscopy (XPS). However, XPS showed the presence of some oxidation of Mo and S. The isotropic nature of the ALE process was confirmed using transmission electron microscopy in 3D trenches.

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11:30am **ALE2-WeM-15 Design of Multi-Coil Single-Switch Induction Heating System with PI-Based Burst Mode Control for ALD/ALE Processes to Achieve High Efficiency and Rapid Transient Response***, **Sang-Wook Ryu,*** Dongguk University, Republic of Korea*; Jihyun Kim, Hakmin Kim,* Wonik IPS, Republic of Korea*; Tae S. Cho,* Wonik IPS*; KWANGSEON JIN,* Wonik IPS, Republic of Korea

Atomic layer deposition (ALD) and atomic layer etching (ALE) processes commonly rely on conventional resistive heating methods, which suffer from significantly low efficiency and slow transient response. To overcome these limitations, this paper proposes an induction heating system and control technique specifically tailored for ALD/ALE applications to achieve higher efficiency and faster transient response. Because ALD/ALE processes require localized temperature control, multiple coils must be employed to provide precise heating across different regions. Therefore, unlike typical multi-switch designs such as full-bridge or half-bridge topologies, which require multiple semiconductor switches per coil, the proposed system adopts a single-switch topology for each coil, thereby reducing hardware complexity while enabling fine-grained temperature control across the entire region. Because a single semiconductor switch must handle the entire load voltage and current in a single-switch topology, the proposed multi-coil single-switch design is restricted to a narrow switching frequency range to ensure system reliability while controlling the temperature. To enhance stability under this constraint, a burst-mode operation at a fixed switching frequency is introduced to facilitate near-linear temperature control, with its burst interval precisely regulated by a proportional–integral (PI) controller. A prototype of the proposed induction heating system is developed using a TI-TMS320F28335 digital signal processor (DSP). The performance of the proposed multi-coil induction heating system, integrating a PI-based burst mode for ALD/ALE applications, is validated through comparative experiments, demonstrating significantly improved efficiency and faster temperature response than conventional resistive heating.

11:45am **ALE2-WeM-16 Enhanced Plasma Ignition and Sustaining of Transformer-Coupled Plasma Source with a Secondary Coil***, Tae S Cho, **Jae Hoon Choi**, Hak Min Kim, Gi Won Shin, Soo Young Hwang, Ji Hyun Kim,* Wonik IPS, Republic of Korea

The need for miniaturization in the semiconductor industry, characterized by sub-10 nm features, 3D stacked architectures, and complex gate-all-around structures, requires increasingly sophisticated plasma processing technologies. These advanced applications require plasma radical sources such as transformer-coupled plasma (TCP) that can operate over a wide pressure range while providing high fluxes of reactive species with minimizing ion-induced damage to delicate device structures. However, ignition with electronegative gases in TCP sources requires high breakdown voltages, often requiring initial plasma generation with an inert gas such as argon, which reduces process throughput. To overcome this limitation, a secondary coil was introduced to generate the high voltage for plasma ignition. The ignition and sustain ranges in argon-nitrogen mixtures were investigated using a TCP source incorporating several ferrite cores. One of the ferrite cores integrated both primary and secondary coils, with the secondary coil terminals connected to reactors on both sides of the core. The current induced in the secondary coil generated an additional electric field between the reactors, enhancing both plasma ignition and sustaining. Experiments were performed at pressures of 0.5–2 Torr and radio frequency (RF) powers up to 3000 W at frequencies of several hundred kHz using various argon-nitrogen gas mixing ratios. The secondary coil enabled stable plasma ignition across a wider range of argon-nitrogen mixtures, eliminating the need for initial plasma generation with inert gas, unlike conventional TCP discharges. This enhanced ignition and sustain ranges provide significant advantages for precise control of process gases and short plasma on/off times in advanced manufacturing processes such as atomic layer deposition (ALD) and atomic layer etching (ALE).

Area Selective ALD
Room Tamna Hall A - Session AS1-WeM

Area Selective Deposition II

Moderators: Stacey Bent, Stanford University, **Anjana Devi**, Ruhr University Bochum

8:00am **AS1-WeM-1 Area-selective ALD of ZnS on Atomic Layer Etched (ALE) Substrates via Growth Modulation***, **Taewook Nam,*** Sejong University, Republic of Korea **INVITED**

Area-selective atomic layer deposition (AS-ALD) has become essential for advanced semiconductor manufacturing by enabling precise bottom-up material deposition and reducing process complexity. Various approaches have been developed to achieve selective deposition, including surface activation, growth inhibition using self-assembled monolayers, and growth-etch back processes. These strategies are particularly crucial for fabricating self-aligned features in advanced technology nodes, where traditional lithography and etching face increasing challenges in meeting the demands of device scaling.

Thermal atomic layer etching (ALE) is a method for thin film removal based on sequential surface modification and volatile release reactions. After thermal ALE, atomic layer deposition (ALD) may be needed to deposit another material on the etched surface. Many thermal ALE procedures are defined by sequential fluorination and ligand-exchange reactions. These reactions can leave the surface terminated with fluoride and methyl or chloride species, respectively. These terminated surfaces may inhibit ALD. Additional chemical treatment may be required to reactivate the surface for normal ALD growth.

In this study, zinc sulfide (ZnS) ALD was conducted on Al_2O_3, SiO_2, HfO_2, and native oxide on Si substrates before and after ALE. The ALE was performed at 300 °C using sequential HF and $Al(CH_3)_3$ (TMA) exposures. ZnS ALD was conducted at 300 °C using diethylzinc (DEZ) and hydrogen sulfide (H_2S) exposures. The ZnS ALD thicknesses were monitored using in situ spectroscopic ellipsometry. When ZnS ALD was performed on as-deposited Al_2O_3 ALD films, the ZnS ALD films grew immediately with no noticeable nucleation delay. In contrast, the ZnS ALD growth was completely inhibited until 50 ALD cycles after the Al_2O_3 film was etched using sequential HF and TMA exposures. Similar results were observed for the other metal oxide substrates.

Various chemical treatments were explored to reactivate the metal oxides after ALE for normal ZnS ALD. The surface species present after ALE using HF and TMA exposures are fluoride or methyl species. These species lead to a nucleation delay for ZnS ALD. These surface species can react with exposures of H_2O_2 or H_2O to add hydroxyl groups to the surface. The ZnS ALD had only a slight nucleation delay using H_2O_2 exposures after ALE. This study reveals that ZnS ALD growth occurred almost immediately after H_2O_2 reactivation of the etched Al_2O_3 substrate. Results will also be shown for different chemical treatments for the various metal oxide substrates.

8:30am **AS1-WeM-3 Passivation of Nitride Surface Using Aldehyde Inhibitor for Area Selective Atomic Layer Deposition of SiNx on Oxide Surface***, **Summal Zoha**, Ngoc Le Trinh, Bonwook Gu, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

In recent years, area-selective atomic layer deposition (AS-ALD) has emerged as a superior technique for precise and selective thin-film deposition, surpassing conventional methods. AS-ALD has demonstrated promising potential for 2D and 3D nanoscale patterning by using inhibitor molecules to tailor surface properties. This approach enables thin-film deposition exclusively on desired growth surfaces (GS) while preventing unwanted growth on non-growth surfaces (NGS). Among various inhibitors, small molecule inhibitors (SMIs) have received significant attention for their effective inhibition despite their small size. The choice of surface inhibitor is crucial in determining the selectivity between growth and non-growth surfaces, as well as the degree of surface passivation. In this study, an aldehyde-based inhibitor, trimethylhexanal (TMH), was utilized for AS-ALD to achieve selectivity between oxide and nitride surfaces. TMH displayed selective adsorption on a diluted hydrofluoric (DHF) acid-treated Si_3N_4 surface while leaving the SiO_2 surface unaffected. The DHF pretreatment facilitated favorable TMH adsorption on Si_3N_4 via interactions with NH and NH_2 surface groups, whereas the OH-terminated SiO_2 surface exhibited no TMH adsorption. Density functional theory (DFT) calculations confirmed the favorable adsorption energy of TMH on the nitride surface. To assess the blocking properties of TMH, SiN_x ALD was performed using silicon tetrachloride ($SiCl_4$) as the precursor and ammonia (NH_3) as the reactant.

The results demonstrated that SiN_x could be selectively deposited on the SiO_2 surface with no detectable growth on the TMH-treated Si_3N_4 surface. This process shows great promise for 3D patterning in silicon devices, where AS-ALD is critical to meeting the demands of miniaturization.

8:45am **AS1-WeM-4 Blocking Effects of Small Molecule Inhibitors in Atomic Layer Deposition: An Off-lattice Kinetic Monte Carlo Study***, **Zhaojie Wang**, Yanwei Wen, Rong Chen, Bin Shan,* Huazhong University of Science and Technology, China

Small molecule inhibitors (SMIs) hold great promise for their compatibility with area-selective atomic layer deposition (AS-ALD) due to their gas-phase dosing scheme. However, it is quite challenging to describe the complex steric hindrance of inhibitors in simulations. In this work, an off-lattice kinetic Monte Carlo (KMC) simulation method is developed to evaluate the performance of SMIs. The heat-driven conformation transformations are considered in our method. During our simulation, the shape of each molecule is constantly changing to describe its dynamic steric hindrance, which is achieved by constantly refreshing its conformation following the Boltzmann distribution. The results show that the saturated deposition density of long-chain thiol inhibitor 1-mercapto octane on the substrate (~1.4/nm^2) is relatively lower than ethanethiol (~2.0/nm^2) due to its larger size, and the branched isomer 2-Ethyl-1-hexanethiol has an even lower deposition density (~1.1/nm^2). When DMAI is used as an ALD precursor, 1-mercapto octane has a better blocking effect than shorter thiol inhibitors despite its lower deposition density, which emphasizes the large steric hindrance provided by the long chain. Benzene-containing inhibitors show better DMAI-blocking performance than thiols due to their stronger binding strength to the substrate. Meanwhile, the desorption of SMIs gets faster after the simulation temperature increases from 100 to 130°C, resulting in a more rapid blocking failure. This work provides a reasonable method to study the molecular steric hindrance of SMIs and can be applied to large-scale molecular screening of potential inhibitors.

9:00am **AS1-WeM-5 Controlling the Surface Chemistry of Silicon Nitride Using a Plasma Pretreatment for Area-Selective Deposition***, **Marc Merkx**, Pengmei Yu,* Eindhoven University of Technology, Netherlands*; Jhon González,* Universidad Tecnica Federico Santa Maria, Chile*; Ilker Tezsevin,* eindhoven University of Technology, Netherlands*; Rachel Nye de Casto, Dennis Hausmann,* Lam Research Corporation*; Erwin Kessels,* Eindhoven University of Technology, Netherlands*; Tania Sandoval,* Universidad tecnica Federico Santa Maria, Chile*; Adriaan Mackus,* eindhoven University of Technology, Netherlands

Selective deposition on SiO_2/SiN_x patterns, where either oxide-on-oxide or nitride-on-nitride deposition is desired, is currently considered as the “holy grail” in the field on area-selective deposition (ASD). Unlike other silicon-based materials (e.g., Si, SiO_2), SiN_x can be terminated with a large variety of surface groups e.g., (NH_2, NH, N, SiH). As a result, the surface chemistry of a SiN_x surface is very sensitive to the manner in which the layer was deposited, and to how the layer was treated after deposition. In addition, in case of air exposure, this surface chemistry becomes even more complex due to (partial) oxidation of the layer (which adds OH groups). For ASD, the surface chemistry of the SiN_x strongly affects the (selective) adsorption of the inhibitors and precursors. In this contribution, it will be discussed how plasma pretreatments can be used to control the surface chemistry of a SiN_x surface and correct for any unwanted oxidation, as well as how the obtained surface chemistries affect inhibitor adsorption on a SiN_x surface.

Three different plasma chemistries were explored: N_2, H_2, and NH_3 plasma. In-situ reflection adsorption infrared spectroscopy (RAIRS) results show that the N_2 and NH_3 plasma pretreatments were effective in removing the OH groups introduced by air exposure, whereas the H_2 plasma was insufficient and only partially removed the OH groups. The N_2 plasma was observed to result in a largely N-terminated SiN_x surface, while the NH_3 plasma resulted in a largely NH_2-terminated surface. The effect of the plasma pre-treatments on the adsorption of trimethylacetaldehyde (TMAAH) and acetylacetone (Hacac) inhibitor molecules onto the SiN_x was studied using in-situ RAIRS and density functional theory (DFT) calculations. Our results show that the SiN_x surface termination strongly affects whether and how strongly the inhibitors adsorb on the SiN_x surface. Importantly, Hacac was found to require a N-terminated SiN_x surface for adsorption, while TMAAH adsorbs most strongly on a NH_2-terminated surface. Therefore, these results demonstrate the importance of understanding and controlling the surface chemistry for ASD.

9:15am **AS1-WeM-6 Area Selective Atomic Layer Deposition of Ruthenium with Pinacolborane as a Small Molecule Inhibitor***, Mikko Ritala, **Sundas Ismaeel**,* University of Helsinki, Finland

With the miniaturization of microelectronic devices, it is important to find efficient small molecule inhibitors (SMI) and processes to achieve selective growth between different materials on substrate surfaces. Ru has advantages over Cu in terms of bulk resistivity, electron mean free path (λ), processing, and electromigration which makes it a good candidate for narrow interconnect lines in the future [1, 2, 3]. Area Selective Atomic Layer Deposition (AS-ALD) of Ru would be useful in making interconnects bottom-up inside 3D features without the formation of voids. AS-ALD can also eliminate misalignment between different layers of interconnect metallization [4]. This study investigates pinacolborane as an SMI on native SiO_2, Pt, TiN, HfO_2, and ZrO_2 surfaces. After exposure to pinacolborane vapor, Ru ALD followed using bis(cyclopentadienyl)ruthenium ($RuCp_2$) and O_2 at 340°C. The results from energy dispersive X-ray spectroscopy (EDS) indicate that the Ru film growth is inhibited on TiN, HfO_2, and ZrO_2, making them non-growth surfaces (NGS) but film grows normally on native SiO_2 and Pt, making them growth surfaces (GS). The optimization of temperature and effective pinacolborane dose is essential for achieving maximum selectivity.

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9:30am **AS1-WeM-7 Inherent Area-Selective Deposition of Low-Resistivity Molybdenum Carbide Films by Thermal Atomic Layer Deposition***, Jeong Hwan Han, **Ji Sang Ahn**,* Seoul National University of Science and Technology, Republic of Korea

With the ongoing downscaling of logic and memory devices, one of the main challenges has emerged such as edge placement error issues resulting from top-down patterning. To overcome the limitations of lithography, a recent focus in bottom-up patterning is based on area-selective atomic layer deposition (AS-ALD). Numerous studies have investigated AS-ALD that employed precursor inhibitors such as SAMs or SMIs to prevent precursor adsorption in non-growth areas. However, there is an increasing need for research into inherent AS-ALD strategies, which exploit the intrinsic properties of substrates with the chemical adsorption of the precursor to enable selective adsorption at targeted surface sites. Molybdenum carbide (MoC_x) has attracted as promising materials for metallization, particularly as bottomless diffusion barriers, liners, capping layers, and interconnects, due to their high melting points, low resistivity, excellent thermal stability, and low reactivity with Cu and its area selective deposition methods have been requiring.

In this work, we developed conductive MoC_x films via thermal ALD without the use of halogen-based precursors, at the deposition temperatures of 200−300°C. This process enabled area-selective growth of MoC_x films on metallic substrates (TiN, Ru, Cu) over oxide substrates (SiO_2, Al_2O_3) by utilizing the intrinsic chemical adsorption of the precursor. We investigated the crystallinity, chemical bonding states, impurity, and resistivity of the MoC_x films, and evaluated the selectivity between substratesthrough analysis of Mo areal density and film thickness. Moreover, the selective growth of MoC_x films on metallic substrates was demonstrated on metal/dielectric patterns using auger electron spectroscopy (AES) mapping and energy-dispersive X-ray spectroscopy (EDS) analysis, indicating the feasibility of implementing this process in practical device applications. To elucidate substrate-dependent surface chemistry in MoC_x AS-ALD, density functional theory (DFT) calculations were conducted, revealing the relative adsorption energies of Mo precursor between metal and dielectric substrates. In conclusion, a newly developed inherent AS-ALD of MoC_x films presents a promising alternative to top-down processes, offering a simplified workflow and potential conducting materials for advanced metallization.

9:45am **AS1-WeM-8 Enhancing Area Selective Deposition Through Sub-saturated ALD: A Pathway to High Volume Manufacturing***, **Nupur Bihari**,* Lam Research Corporation

Area Selective Deposition is a key technique in semiconductor fabrication processes, enabling the deposition of thin films in a controlled, pattern specific manner. Achieving a high level of selectivity, i.e., no growth on "non-growth surface" and high-density continuous growth on the "growth surface" is essential for ensuring good device yield. Traditional Atomic Layer Deposition processes often face limitations in selectivity due to the inherent challenges in controlling surface chemistry and reaction kinetics.

This talk will explore an approach to enhancing area selectivity through a subsaturated ALD process. By carefully controlling the precursor selection, flux and reaction time to operate in a subsaturated regime, we can significantly reduce unwanted deposition on non-target areas while ensuring high quality film growth on desired regions. This method leverages the intrinsic self-limiting nature of ALD while mitigating issues such as precursor overexposure and undesired nucleation, resulting in improved spatial uniformity and deposition control.

The talk will present experimental results demonstrating the superior selectivity and film quality achieved with sub-saturated aluminum oxide ALD in a dielectric on dielectric (DoD) process compared to a traditional, saturated process. We will also discuss the underlying mechanistic insights, including the role of surface coverage, precursor dynamics and impact of process parameters such as temperature, dilution and pressure. Additionally, a known challenge with ASD – metrology will be discussed. Lam's successful attempts at image processing to understand large scale selectivity over an entire die will be presented. With the need to shorten the time from R&D to High Volume Manufacturing (HVM), this fast, quantitative metrology is key to rapid validation of new processes.The quick turnaround image processing method allows for testing of marginal processes enabling a larger number of experiments in a short period of time.

This work provides future directions for optimizing selectivity and process uniformity at smaller pitches across a wide range of semiconductor applications.

Area Selective ALD
Room Tamna Hall A - Session AS2-WeM
Area Selective Deposition III

Moderators: Rick Chen, Merck KGaA, Darmstadt, **John Conley**, Oregon State University

10:45am **AS2-WeM-12 Industrial ALD/ASD Perspectives: Atomic Level Process Control for Semiconductor Devices***, **HanJin Lim**,* Samsung Electronics, Republic of Korea **INVITED**

As the semiconductor devices are highly integrated and refined to feature sizes of 10 nm or less, the thickness of the functional films that affect the electrical properties of the device is also thinned to 5 nm or less. Since the role of the interface becomes dominant in such a functional thin film, engineering techniques using various interfacial layers for electrical properties are being introduced. On the other hand, in order to implement such a thin film in a 3D semiconductor structure, ALD technology is essential, and various processes and interfacial layer technology introduction cases are to be examined for phase stabilization and interface control of atomic level film quality. In addition, in order to realize high-quality and uniform film quality in a complex 3D structure, we will look at examples of innovation in ALD precursors and facility technologies and advancement of process technologies, and finally, we will look at cases of improvement in semiconductor device characteristics using selective deposition technology.

11:15am **AS2-WeM-14 Area-Selective Deposition for Dielectric Films on Metal Substrates: Coupon to Full Wafer***, **Rachel Nye de Castro**, Paul Lemaire, Alexander Fox, Joel Smith, Nupur Bihari, Bill Nunn, Kevin Mclaughlin, Dennis Hausmann,* LAM Research

Area-selective deposition (ASD) has potential to reduce reliance on costly lithography steps and improve shorting margins for small pitch sizes. ASD has been successfully demonstrated for many material sets, notably dielectric on dielectric (DoD) for fully self-aligned vias,[1] yet the demand for thicker films and new materials continues to grow to enable advanced applications. Selectively depositing a film on a surface of a different type, e.g. a dielectric film on a metal substrate, is inherently more challenging because after the first few cycles of deposition, both the growth and non-growth surfaces are the same type (dielectric in this example), resulting in similar reactivity towards ALD precursors. This work discusses the development of selective dielectric on metal (DoM) deposition from coupon-scale to full wafer patterns. We utilize inhibitor molecules to selectively block deposition on our desired non-growth surface (dielectric in this case). Numerous inhibitors are screened on both dielectric (SiO_2, SiON, SiOC, etc) and metal (W, Co, Cu, Ru, etc) surfaces using water contact angle (WCA) measurements to characterize hydrophobicity after selective inhibitor adsorption. Inhibitors with the best WCA contrast between dielectric and metal are then evaluated for blocking performance using AlO_x ALD.Ellipsometry, mass, and x-ray reflectivity measurements demonstrate several nm of AlO_x deposition on metal surfaces without any selectivity loss on dielectric. Further verification from TEM and EELS elemental analysis confirm that this selectivity is extended to patterned coupons and full wafers. We demonstrate selective AlO_x on patterned wafers with excellent selectivity (EELS, top-down SEM), which is also extended to other deposited films (e.g. SiN, MoN). These inhibitors are compatible with high volume manufacturing requirements, 3D features, and a wide range of temperatures that accommodates low thermal budget materials as well as high temperature ALD processes. This selective DoM process enables applications such as selective hard masks and etch stop layers and improved shorting margins.

References

Parsons, G. N.; Clark, R. D. *Chem. Mater.* **2020,** *32,* 4920-4953.

11:30am **AS2-WeM-15 Redox-coupled Inherently Selective Atomic Layer Deposition of SiO_2 on SiO_2/Si_3N_4 for 3D NAND structure***, **Kun Cao**, Zilian Qi, Eryan Gu, Rong Chen,* Huazhong University of Science and Technology, China

Area-selective atomic layer deposition (AS-ALD) provides a promising approach for bottom-up fabrication by enabling atomic-level control over material growth in pre-defined patterns, particularly on complex 3D architectures. In this study, a novel strategy is proposed that combines surface-state modulation via alcohols pre-treatment with oxygen partial pressure optimization to enhance selectivity between SiO_2 and Si_3N_4 surfaces. Methanol pre-treatment maintains the amination of Si_3N_4 surfaces, effectively delaying nucleation in non-growth regions, while controlling oxygen partial pressures prevent undesired oxidation of amines to hydroxyl groups. Di(isopropylamino)silane (DIPAS) is employed as a selective SiO_2 precursor, demonstrating inherent selectivity without additional surface inhibitors. The inclusion of dynamic precursors pulses in the ALD process further improved precursor transport and reaction uniformity in high-aspect-ratio 3D NAND structures. This approach achieved ~3 nm thick SiO_2 films on SiO_2 surfaces, with minimal deposition on Si_3N_4 surfaces. Uniform deposition across the top and bottom layers of high aspect ratio 3D structures is demonstrated. This approach combines methodology of surface-state engineering and dynamic precursor pulsing highlights a robust method for expanding AS-ALD applications in complex 3D nanoelectronics.

11:45am **AS2-WeM-16 Area-selective Atomic Layer Deposition of Ruthenium via Plasma Surface Modification***, In-Hwan Baek, **Dahui Jeon**,* Inha university, Republic of Korea

As semiconductor devices continue to scale down and increase in complexity, achieving both high performance and reliability has become increasingly critical. Ruthenium (Ru) has emerged as a key material for next-generation interconnects and electrode applications due to its low resistivity (~7.1 μΩ·cm), high work function (~4.7 eV), and excellent chemical stability. To fully utilize these properties, area-selective atomic layer deposition (AS-ALD) is essential for enabling Ru deposition exclusively in growth regions while inhibiting it in non-growth areas. This bottom-up patterning approach mitigates edge placement error (EPE) and enhances overall process yield.

Conventional AS-ALD techniques using self-assembled monolayers (SAMs) as surface inhibitors are inherently limited by their low thermal stability, leading to selectivity degradation over multiple cycles. As the deposition process proceeds, SAM desorption or decomposition leads to unwanted Ru nucleation in non-growth regions, compromising the selectivity of the process. Furthermore, achieving uniform SAM coverage in high-aspect-ratio structures poses additional challenges.

To overcome these limitations, we developed an atmospheric-pressure X plasma surface modification process, which introduces hydrophobic functional groups that effectively suppress Ru nucleation in non-growth areas while maintaining stability throughout multiple ALD cycles. This method demonstrated infinite selectivity, with no Ru deposition detected in non-growth regions even after 200 ALD cycles, while achieving over 30 nm of Ru film growth in targeted areas—exceeding the selectivity performance of conventional AS-ALD approaches.

Additionally, we established a substrate-dependent X plasma effect, demonstrating selective removal of hydrophobic X functional groups based on surface chemistry, which influenced Ru nucleation behavior. Furthermore, we verified that post-deposition atmospheric O_2 plasma treatment effectively eliminates residual X inhibitors from non-growth areas without compromising Ru film integrity in growth regions. These findings highlight plasma-assisted AS-ALD as a scalable, highly selective approach for advanced semiconductor integration.

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ALD Applications
Room Halla Hall AB - Session AA1-WeA

Battery Applications I

Moderators: Wei-Min Li, Jiangsu Leadmicro Nano-Equipment Technology Ltd., **Keith Wong**, Applied Materials

1:30pm **AA1-WeA-1 Atomic Layer Deposition and Molecular Layer Deposition for Li and Na Metal Anodes***, **Yang Zhao,*** University of Western Ontario, Canada

Li-metal batteries (LMBs) and Na-metal batteries (NMBs) are considered as the promising next-generation battery systems to replace conventional Li-ion batteries (LIBs) due to their high theoretical energy density [1]. For LMBs and NMBs, Li metal and Na metal are the ultimate choices for achieving high energy density due to their high specific capacity, low electrochemical potential, and light weight. However, as alkali metals, both Li and Na metal anodes suffer from serious challenges including 1) Li/Na dendrite formations and short circuits; 2) Low Coulombic efficiency and poor cycling performance; and 3) Infinite volume changes.

In this presentation, I will introduce our research that contributed to the design of artificial interfaces for Li and Na metal anode using atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques [2-3]. i) Developing ionic conductive protective layers for Li and Na metal anodes. A two-step strategy is developed to obtain the smooth and stable LiAlOx and NaAlOx artificial layer for Li and Na metal anodes by the post-lithiation process, respectively. [4]. ii) Nano-alloy structure to the nano-laminated structure for Li and Na metal anodes. Through tailoring the compositions of the hybrid interfaces, we realize the nano-alloy structure to the nano-laminated structure. [5]. iii) An organic-rich or an inorganic-rich interface? We demonstrate the controllable fabrication of the hybrid artificial SEI for Li metal anode with different organic-inorganic ratios. Three typical compositions were realized: organic-rich interface, organic-inorganic-balanced interface and inorganic-rich interface. The different organic-inorganic ratios of the hybrid interfaces result in the tuning of the mechanical properties, lithiophilicity, diffusion kinetics and Li dendrite formation of the Li metal anode [6]. iv) A new hybrid protective layer for the Na metal anode. A metal-doped hybrid polyurea (PU) film with tunable composition, sodiophilic sites and improved stiffness was fabricated by introducing Zn or Al as crosslinkers into the polymer chains and adopted as an artificial SEI for Na metal. Compared to bare Na and pure PU-coated Na, the Na metal anode coated with the metal-doped PU film exhibits significantly improved electrochemical performance [7]. All these ideas have also been further applied to solve the practical issues for different Li and Na metal battery systems.

[1] Energy Environ. Sci., 2024, 17, 442-496

[2] Chem. Soc. Rev., 2024,53, 5428-5488

[3] Chem. Soc. Rev., 2021, 50, 3889-3956

[4] Small, 2022, 18, 2203045

[5] Adv. Mater., 2023, 35, 2301414

[6] Adv. Fun. Mater., 2024, 2406426

[7] Adv. Mater., 2024, 2406837

1:45pm **AA1-WeA-2 Low Temperature Spatial Atomic Layer Deposition of LiF Films for Li-Ion Batteries**, *Joost van Himste,* SparkNano, Netherlands*; Niels Hoogendoorn,* Eindhoven University of Technology, The Netherlands*; Jamie Greer,* Air Liquide Advanced Materials, Germany*; Nicolas Blasco,* Air Liquide Advanced Materials, France*; **Paul Poodt,*** SparkNano, and Eindhoven University of Technology, Netherlands

Lithium fluoride (LiF) thin films have gained significant attention as protective/passivating layers for Li-ion battery electrodes due to their wide electrochemical stability window and excellent chemical stability. When deposited using highly conformal methods like atomic layer deposition, LiF can effectively coat the complex, porous structures of battery electrodes to improve their electrochemical performance and stability.

Several combinations of Li precursors and co-reactants for LiF deposition have been explored in the literature. However, these processes often require high deposition temperatures and yield films with notable contamination from oxygen (O), carbon (C), or silicon (Si). Furthermore, the low volatility and reactivity of many Li precursors, combined with the use of greenhouse gas- and PFAS-based or otherwise hazardous co-reactants (e.g., SF_6, CF_4, or HF), pose challenges to the applicability, sustainability, and scalability of reported ALD processes.

To address these limitations, we present a newly developed plasma-enhanced spatial ALD process employing a novel Li precursor named LIFA (Air Liquide Advanced Materials). This approach eliminates the need for greenhouse gas-, or otherwise hazardous co-reactants. Pure LiF films have been successfully deposited at temperatures ranging from 100°C to 200°C, making the process compatible with deposition on Lithium metal anodes. The films exhibit a growth per cycle of 0.04–0.05 nm/cycle and a refractive index of 1.36–1.39 at 633 nm. Characterization via XPS, XRD, and SEM confirms that the films are polycrystalline, highly pure, free of C and O contamination, and stable in ambient conditions.

These LiF films demonstrate excellent conformality on porous substrates and have been applied to various anode and cathode materials, including graphite, silicon, and LMNO, where they have shown significant improvements in electrochemical performance. Additionally, we outline our approach to scaling up the process for industrial-scale manufacturing using high-speed, atmospheric-pressure roll-to-roll spatial ALD. The combination of this sustainable and efficient LiF deposition process with high-speed spatial ALD presents a promising avenue for the mass production of high-performance Li-ion batteries.

2:00pm **AA1-WeA-3 Advancing Nickel-Rich Layered Oxide Cathodes via Atomic-Scale Synthesis and Surface Engineering***, **Jin Xie,*** ShanghaiTech University, China

Nickel-rich layered oxides ($LiNi_xCo_yMn_{1-x-y}O_2$, NCM) offer high energy density for lithium-ion batteries, yet challenges in synthesis control, structural stability, and interfacial compatibility limit their performance. This work integrates two strategies focused on atomic layer deposition (ALD) to overcome these obstacles and enable next-generation cathode materials.

First, we improve the mechanical stability of layered oxides through surface atomic coatings and controlled nucleation during high-temperature solid-state synthesis. Solid-state synthesis of layered oxides requires precise control over nucleation and grain growth. We demonstrate that an Al_2O_3 coating, which transforms into lithium aluminate during synthesis, acts as a low-interfacial-energy nucleation template. This approach promotes rapid and uniform nucleation at reduced temperatures, as evidenced by solid-state NMR and in situ synchrotron XRD. The resulting Ni-rich cathodes feature densely packed, fine primary particles, enhancing mechanical strength and structural integrity, as confirmed by in situ compression tests.

Second, we improve the surface stability of layered oxides through surface coatings that suppress surface decomposition during high-temperature solid-state synthesis. High temperatures are necessary for forming well-ordered layered structures but can lead to Li/Ni mixing and rock-salt phase formation. By applying a conformal oxygen-affine coating, we stabilize the surface layered structure during high-temperature lithiation. This prevents surface decomposition, preserves lithium-ion pathways, and reduces phase separation during cycling. The optimized cathodes exhibit excellent rate capability and cycle stability.

By leveraging intermediate phases, conformal coatings, and doping strategies, we address synthesis challenges in Ni-rich cathodes. Coupled with advanced characterization, our work paves the way for high-energy, high-power, and mechanically robust battery materials—bridging fundamental insights with industrial-scale production for improved lithium-ion batteries.

References:

1. Promotion of the nucleation of ultrafine Ni-rich layered oxide primary particles by an atomic layer-deposited thin film for enhanced mechanical stability. Nano Lett. 2023, 23, 5770-5778.

2. Pinning the surface layered oxide structure in high temperature calcination using conformal atomic layer deposition coating for fast charging cathode. Adv. Funct. Mater. ASAP, 2423888.

2:15pm **AA1-WeA-4 Unveiling the Unconventional ALD Chemistry of Trimethylaluminum (TMA) on Battery Materials**, ***Donghyeon Kang**, Kyobin Park, Jeffrey Elam,* Argonne National Laboratory

Trimethylaluminum (TMA) is a cornerstone precursor in atomic layer deposition (ALD), widely employed for depositing aluminum-based coatings. It reacts with H_2O, HF-pyridine, and H_2S to generate Al_2O_3, AlF_3, and Al_2S_3 by ALD, respectively, following well-established ALD mechanisms. These processes enable ultra-thin Al-based coatings on various substrates, particularly energy storage materials such as battery cathodes, anodes, and solid electrolytes.

Our research explores the unconventional ALD chemistry of TMA on reactive metal substrates, solid-state electrolytes, and battery cathode materials. Notably, on Li-metal anodes, TMA deviates from conventional ALD pathways, forming a carbon composite layer instead of the expected Al_2O_3. This unexpected behavior stems from the inherent reactivity between TMA and Li metal, challenging established ALD paradigms. Additionally, we reveal TMA's interactions with Li-based impurities on solid-state electrolytes and battery cathode surfaces, leading to the formation of protective coatings with beneficial properties. Despite TMA's extensive use, these reactions have remained largely unexplored.

In this presentation, we will unveil our findings using in situ quartz crystal microbalance (QCM), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), Raman spectroscopy, and *ab initio* calculations. Furthermore, we will discuss the implications of these discoveries for battery material surface treatments, highlighting their potential for scalable industrial applications.

2:30pm **AA1-WeA-5 Novel Li-Precursor for Interface Engineering in Li-Ion Batteries***, **Meike Pieters**, Cristian van Helvoirt, Lina Bartel, Niels Hoogendoorn, Mariadriana Creatore,* Eindhoven University of Technology, The Netherlands

Ultra-thin coatings (< 5 nm) on Li-ion battery (LiB) electrodes are essential to reduce interface degradation reactions, and improve the performance and lifetime of next-generation LiBs. ALD is a precise and scalable technique to apply these coatings conformally on 3D electrodes. So far, LiO^tBu has been widely adopted as Li-precursor, but it requires a high source temperature (130-180°C). Out of the few other known Li-precursors, only LiHMDS can be used at lower source temperature (60-90°C), but it can lead to Si impurities, which we reported in recent work [1].

Here we address the application of the novel Li-precursor *Lider* developed by Air Liquide, for a wide range of materials, of interest in the field of LiBs: Li_2CO_3, Li_3PO_4, and LiF. *Lider* is Si-free and can be used at a low source temperature of 85°C, but it does not react with H_2O. An O_2 plasma (O_2*) as co-reactant leads to saturation behavior with a GPC of 0.25 Å at 150°C, but the GPC decreases with increasing temperature. XPS and XRD demonstrate that Li_2CO_3 is grown with a (002) orientation, and that the film density of 2.0 g/cm^3 is close to the theoretical density of Li_2CO_3 (2.1 g/cm^3). This suggests that LiOH reacts to Li_2CO_3 during the deposition, presumably due to CO_2 formed in the O_2* step, and not upon air exposure, since the films are air-stable. O_3 as co-reactant results in a higher GPC of 0.35 Å. The film density decreases upon air exposure, and XRD shows no diffraction peaks, which could be due to incorporation of (air sensitive) Li_2O and/or LiOH, which suppresses the Li_2CO_3 crystallinity [2]. This comparison suggests that O_3 may be preferred over O_2* as co-reactant when C incorporation is undesired, e.g. in Li-containing ternary oxides.

The O_2* and O_3-based *Lider* processes are combined with TMPO to grow LiPO. The film composition depends on the co-reactant: O_2* results in a more Li-rich film than O_3. Interestingly, no C impurities were observed in both films. We hypothesize that carbonates are abstracted from the film as CO_2 when exposed to TMPO, similar to the reaction occurring during TMA exposure [3].

Finally, LiF is grown with SF_6* as co-reactant. The GPC is 0.3 Å at 150°C but LiF can be grown at temperatures as low as 50°C, which makes this process compatible with Li metal. XPS shows a Li:F ratio of ~0.8 and low bulk C levels of ~1 at.%. The films are crystalline with a preferred (100) orientation.

Given the range of chemistries attainable by the usage of *Lider*, this contribution will also address applications of the above-mentioned materials in LiBs.

[1] Pieters et al., J. Phys. Chem. C 2024, 128

[2] Hornsveld et al., RSC Adv. 2017, 7

[3] Young et al., J. Phys. Chem. C 2019, 123

2:45pm **AA1-WeA-6 Oxidative Molecular Layer Deposition of Polypyrrole on High Surface Area Powder Substrates for Li-ion Battery Applications***, **Brandon Woo**, Jaime DuMont, Markus Groner, Casey Christopher, Drew Lewis, Jessica Burger, Greg Pach, Wyatt Blevins,* Forge Nano*; Malachi Noked, Ortal Shalev,* Bar Ilan University, Israel*; Arrelaine Dameron,* Forge Nano

Oxidative molecular layer deposition (oMLD) of conjugated polymer films offers a unique solution to many of the interfacial material challenges present in Li-ion batteries. Polypyrrole encapsulated Si anode materials, for example, has the potential to alleviate the volume change of Si, improve the material conductivity, and enhance cyclic stability. Versus solution-based polymerization processes, oMLD can enable molecular-level control of polymer thickness through layer-by-layer growth via sequential surface reactions of monomer(s) and oxidant(s).[1] [2] [3]

In this talk, we demonstrate the successful transfer of the $SbCl_5$/pyrrole oMLD process from wafers to high surface area powder batches, both in fluidized bed and rotary bed particle-ALD reactors with particle diameters as small as 50 nm. The surface area of these powders is thousands of times larger than that of silicon wafers. The scale up to high surface area powders was achieved via controlled high volume precursor delivery, good powder mixing, monitoring of the process with in-situ mass spectroscopy and various external analysis techniques. LECO carbon and nitrogen analysis confirmed an inverse relationship between temperature and purge times with the growth per cycle. ICP-OES allowed for the tracking of both Cl and Sb impurities. Raman spectroscopy confirmed the presence of signature polypyrrole vibrational modes such as the C=C backbone stretching and C-H in plane deformation. TEM analysis confirmed the particles were conformally and uniformly encapsulated. This work represents a significant advancement of the oMLD process in generating new-composite materials for various energy related applications.

[1] Kim, et. Al. Journal of Vacuum Science & Technology A 40, 063401 (2022)

[2] Wyatt, et. Al. ACS Applied Polymer Materials 2022 4 (8), 6156-6168 (2022)

[3] Wyatt, et. Al. Chem. Mater. 35, 1, 154–162 (2023)

3:00pm **AA1-WeA-7 Taming Lithium Nucleation and Growth on Cu Current Collector by Electrochemical Activation of ZnF_2 Layer***, **Viet Phuong Nguyen**, Jae-Hyun Kim, Seung-Mo Lee,* Korea Institute of Machinery & Materials (KIMM), Republic of Korea

Lithium-metal anodes are essential for the advancement of next-generation batteries. However, their practical use is largely hindered by the uncontrollable growth of dendrites and intricate problems associated with fabricating anodes that meet capacity requirements. Here, we demonstrate that an ultrathin ZnF_2 layer uniformly deposited by atomic layer deposition on the copper foil could produce a novel and efficient current collector to address these challenges. We observed that ZnF_2 can be transformed into LiZn alloy and LiF salt in one step by simple electrochemical activation. The resulting LiZn alloy exhibited high lithiophilicity, which reduces overpotential and promotes uniform lithium nucleation, while the LiF salt enhanced the solid electrolyte interphase, ensuring uniform lithium growth. This synergistic effect led to a dendrite-free, densely packed lithium anode with an extended lifespan, achieving over 900 h in symmetric cells at a high current density of 3 mA cm^{-2} and a high cut-off capacity of 3 mAh cm^{-2}. Furthermore, full cells utilizing our lithium anode (Li capacity of 6 mAh cm^{-2}) paired with $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ cathodes (mass loading of 11.5 mg cm^{-2}) demonstrated drastically improved rate capability and excellent cycling stability. Our approach holds great promise for developing safer and more efficient lithium-metal-based batteries for future energy storage solutions.

3:15pm **AA1-WeA-8 Atomic Layer Deposition of Aluminum Phosphorus Oxynitride and Its Application as Passivation Layers on Aluminum Metal Anode***, **Jian Liu**, Li Tao,* University of British Columbia, Canada

Aqueous aluminum (Al) batteries are attractive energy storage technology due to the theoretical capacity of Al, low reduction potential, low cost, and environmental friendliness. However, the practical application of aqueous Al batteries has been hindered by aggressive parasitic reactions, such as hydrogen evolution and Al corrosion, at the Al and aqueous electrolyte interface. This work developed aluminum phosphorus oxynitride (AlPON), a hypothetical Al-ion conductor, by plasma-enhanced atomic layer deposition (PEALD) and successfully applied it to suppress side reactions at the Al and electrolyte interface. The PEALD of AlPON was performed in a temperature range of 120-200 ºC using trimethylaluminum, water, a new P-N-containing precursor, and plasma oxygen as precursors. The growth rate and composition of AlPON showed a strong dependence on the deposition temperature, and the growth mechanism of AlPON was proposed. Electrochemical evaluation using Tafel curves and electrochemical impedance spectroscopy in the Al|Al symmetric cells revealed that the AlPON coating significantly reduced the self-corrosion of the Al metal anode and improved its (electro-)chemical stability in the aqueous electrolyte. Last, this work demonstrated that the PEALD receipt could be extended to deposit other metal phosphorus oxynitrides, a new group of inorganic materials by ALD.

ALD Applications
Room Halla Hall AB - Session AA2-WeA

Battery Applications II

Moderators: Il-Kwon Oh, Ajou University, **Junjie Zhao**, Zhejiang University

4:00pm **AA2-WeA-11 Novel Atomic and Molecular Layer Deposition Processes for Robust Battery Interfaces***, **Xiangbo Meng**, Kevin Velasquez Carballo, Kang Lu, Aiying Shao,* University of Arkansas

Adopting lithium metal (Li) as anodes and nickel (Ni)-rich lithium nickel manganese cobalt oxides ($LiNi_xMn_yCo_zO_2$, NMCs, x ≥ 0.6, x + y + z = 1) as cathodes, the resultant Li||NMC lithium metal batteries (LMBs) could be twice higher in energy (up to 500 Wh/kg) but 50% lower in cost ($100/kWh) than that of LIBs, holding great promise to replace LIBs for the applications of portable electronics, electric vehicles, and aircrafts. Unfortunately, such a compelling technology has been hindered from commercialization due to some serious interfacial issues related to the Li anodes and NMC cathodes. Aimed at addressing these challenges, we recently have developed a series of novel coatings via atomic and molecular layer deposition (ALD and MLD). ALD and MLD share several unique merits but are complementary in their target materials. They have emerged as two new techniques of interface engineering of rechargeable batteries in the past decade.[1-5] They both could deposit conformal and uniform coatings over complex shapes of different substrates, operate at low process temperature, and accurately control coating thickness. Through adopting different precursors, ALD exclusively deposits inorganic films while MLD specially grows organic or hybrid films. For the issues of Li anodes and NMC cathodes, we particularly designed function-oriented coatings via ALD and MLD. Using our ALD and MLD processes, very encouragingly, both the surface-coated Li anodes and NMC cathodes have exhibited remarkable improvements in their electrochemical performance. Our studies have further shown that the combination of these coatings can synergistically maximize their benefits to achieve higher performance of Li||NMC LMBs, enabling a cell capacity fading 10 times slower than that of bare Li||NMC cells and a capacityretention improvement over 60%after 500 charge/discharge cycles. In this talk, we will introduce these novel coatings and their compelling effects. Particularly, we would like to explain the underlying mechanisms related to their benefits. Thus, our studies have not only opened new areas of surface coatings but also demonstrated their technical feasibility for developing high-performance LMBs.

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1. *Adv. Mater.* **2012,** 24, (27), 3589-3615.
1. *Energy Storage Materials* **2020,** 30, 296-328.
1. *J. Mater. Chem. A* **2017,** 5, 10127-10149.
1. *J. Mater. Chem. A* **2017,** 5, (35), 18326-18378.
1. *J. Mater. Res.* **2021,** 36, 2-25.

4:15pm **AA2-WeA-12 Atomic Layer Deposition of Al_2O_3 and ZrO_2 Coatings on Single-Crystal NCM Cathodes: A Parametric Study for Enhanced Lithium-Ion Battery Performance***, **Sung Eun Jo**, Wooseong Kim, Hyongjune Kim,* Pohang University of Science and Technology (POSTECH), Republic of Korea*; Jungwoo Park,* POSCO Holdings, Republic of Korea*; Jihwan An,* Pohang University of Science and Technology (POSTECH), Republic of Korea

Atomic Layer Deposition (ALD) has emerged as a powerful technique for surface modification of battery materials, offering unparalleled control over coating thickness and conformality at the atomic scale. This study investigates the application of ALD-deposited Al_2O_3 and ZrO_2 coatings on single-crystal $LiNi_{0\cdot6}Mn_{0\cdot2}Co_{0\cdot2}O_2$ (NCM622) cathodes to enhance the performance and durability of lithium-ion batteries.

Single-crystal $LiNi_{0\cdot6}Mn_{0\cdot2}Co_{0\cdot2}O_2$ (NCM622) cathodes have garnered significant attention due to their superior structural stability and reduced surface area compared to their polycrystalline counterparts. These characteristics contribute to improved cycling performance and reduced side reactions with the electrolyte. However, single-crystal NCM materials still face challenges, particularly at high voltages and during long-term cycling, necessitating surface modification strategies to mitigate these issues.

This study investigates the application of Atomic Layer Deposition (ALD) to deposit ultrathin Al_2O_3 and ZrO_2 coatings on single-crystal NCM622 cathodes, aiming to address their inherent limitations while preserving their advantages. We systematically explored coating thicknesses of 10, 30, and 100 nm for both materials.

Electrochemical performance of bare, Al_2O_3-coated (10 and 30 ALD cycles), and ZrO_2-coated (10 cycles) single-crystal NCM622 cathodes, focusing on capacity retention, degradation rates, and the impact of coating thickness. While Al_2O_3 coatings showed poor longevity, retention stability diminishes with increasing thickness due to kinetic limitations. In contrast, ZrO_2 coatings at 10 cycles offer a balanced approach, combining moderate capacity retention with robust degradation resistance (after 30cycles, 3.4% increase). Optimizing ALD cycles for minimal thickness (≤10 cycles) is critical for maximizing the performance of NCM cathodes.

4:30pm **AA2-WeA-13 Role of the Precursor'S Stability for ALD Lithium-Containing Films***, **Nicolas Massoni**, Manon Letiche, Sylvain Poulet,* CEA/LETI-University Grenoble Alpes, France*; Katharina Märker, Pierre-Alain Bayle,* CEA-University Grenoble Alps, IRIG, France*; Névine Rochat,* CEA/LETI-University Grenoble Alpes, France*; Olivier Hernandez,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, France*; Messaoud Bedjaoui,* CEA/LETI-University Grenoble Alpes, France

Lithium-based layers play key roles in developing nanostructured energy storage systems. As such, ultrathin lithium phosphorous oxynitride LiPON deposited by Atomic Layers Deposition is incorporated as solid-electrolyte for on-chip microsupercapacitors [1-2]. In this way, fundamental understanding of precursors chemistry and stability could be beneficial to control thermal ALD process. In this work, we will focus on the use of Lithium hexamethyldisilazide (LiHMDS) and Diethylphosphoramidate (DEPA) precursors. Both precursors are maintained in canisters at 90°C (DEPA) and 70°C (LiHMDS). Their ageing time in the canisters was considered. New and aged precursors were characterized by Thermogravimetry (TGA), infrared spectroscopy (FTIR), Powder X-Ray Diffraction (PXRD), Nuclear Magnetic Resonance (NMR) and Pyrolysis coupled with Gas Chromatography Mass Spectrometry (PY-GCMS). The growth per cycle, stoichiometry and ionic conductivity of LiPON films were followed.

It was found that new and aged LiHMDS kept the same thermal behavior and the same structure, till 200 days of use. Hence, there was no proof of significate degradation of LiHMDS with storage duration. On the contrary, new and aged DEPA showed differences. The TGA curves progressively changed from one steep mass loss at 220°C to two partial mass losses occurring between 200°C and 320°C. FTIR spectra showed that the amine group of the aged DEPA disappeared after 60 days of storage. NMR data confirmed a deep modification of the $P-N-H_2$ chain. A possible polymerization of DEPA monomers might take place. Furthermore, yellow spots were observed in the inner bottom of the DEPA's storage canister. A SEM/EDX analysis revealed deposits enriched with phosphorous. These first measurements pointed out that DEPA has degraded in the canister. The PY-GCMS data confirmed a congruent total evaporation for new DEPA, contrary to new LiHMDS. Its vapor was made of two third of gaseous LiHMDS and one third by a lighter unknown compound.

Shortly, a mass spectrometer will be plugged to the reactor to complete the study by the understanding of the LiPON growth mechanism.

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4:45pm **AA2-WeA-14 Closing Remarks and Awards in Tamna Hall A**,

ALD Applications
Room Tamna Hall A - Session AA3-WeA

Emerging Applications

Moderators: Bong Jin Kuh, Samsung Electronics, **Markku Leskelä**, University of Helsinki, Finland

4:00pm **AA3-WeA-11 Atomic Layer Deposition for Self-Healing Stone Cultural Heritage Preservation***, Ancy Mini Vibin Lal Nayakom Mini, Gabriele Botta, Mato Knez, **Aranzazu Sierra Fernández**,* CIC nanoGUNE, Spain

The preservation of stone cultural heritage (CH) materials faces growing challenges due to environmental stressors exacerbated by climate change. Fluctuating humidity, temperature variations, and air pollutants accelerate ageing and erosion, compromising the structural integrity of historical materials. To address these issues, we develop advanced self-healing coatings designed to repair microdamage and enhance the durability of stone substrates. Inspired by the autonomous repair mechanisms observed in ancient Roman concrete, our research seeks to translate this phenomenon into protective coatings. Using Atomic Layer Deposition (ALD), we create structured nanofilms capable of mimicking self-healing properties, significantly improving the long-term preservation of stone substrates.

A key aspect of this research is the functionalization of the stone surface to optimize coating deposition, ensure homogeneity, and improve chemical adhesion. Refining pre-treatment methodologies enhances the chemical affinity and uniformity of the coatings, maximizing their stability and self-healing efficiency. The ALD process provides nanoscale metal oxide films, which, upon exposure to environmental humidity and atmospheric CO_2, initiate mineral nucleation and growth. This controlled mineralization autonomously seals microcracks before they propagate, reinforcing the mechanical stability and durability of treated stone substrates.

To assess self-healing performance, we employ nano- and microindentation techniques to monitor changes in hardness and elastic modulus across different scales, providing quantitative insights into mechanical recovery. Additionally, high-resolution Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) and Transmission Electron Microscopy (TEM) characterize the mineral phases responsible for self-healing, offering a detailed understanding of the microstructural evolution within damaged regions. These findings highlight the potential of self-healing coatings to preserve the mechanical integrity of stone substrates, offering a promising solution for sustainable CH conservation.

By emulating historical self-repair mechanisms, our coating system establishes a foundation for resilient and proactive heritage protection strategies. This research not only advances CH preservation technology but also contributes to innovative materials that extend the lifespan of cultural heritage assets.

The projects supporting these results received funding from a “la Caixa” Foundation fellowship (LCF/BQ/PI23/11970025) and the project ASSIST (PID2023-147532OA-I00) from MICIU/AEI/10.13039/501100011033.

4:15pm **AA3-WeA-12 Harnessing Atomic and Molecular Layer Deposition for Advanced Membrane Technologies in Water Treatment*, Eran Edri,*** Ben Gurion University Be’er Sheva, Israel

Advanced membrane technologies are essential for addressing pressing global water treatment challenges, including water softening, selective desalination, and biofouling mitigation. This work explores how atomic layer deposition (ALD) and molecular layer deposition (MLD) can enhance membrane performance and stability across diverse applications while preserving water permeability. We first investigated the ion selectivity of commercial thin-film composite nanofiltration (NF) membranes by applying ethylene glycol–aluminum (EG-alucone) coatings via MLD. Systematic variation in the number of deposition cycles allowed the active layer to be successively infiltrated, inflated, and coated with an alucone film. These structural and charge modifications significantly improved sodium selectivity over divalent cations, reducing water hardness in synthetic and natural brackish water samples with minimal permeability loss. This study demonstrates how MLD coatings, precisely tuned to target dielectric, steric, and electrostatic ion-exclusion mechanisms, can enable the rational design of NF membranes for enhanced selectivity. In a second application, MLD was extended to develop monovalent-selective cation exchange membranes (MVS-CEMs) critical for energy-efficient electrodialysis. By precisely controlling the thickness of ultrathin alucone layers on CEMs, high monovalent selectivity was achieved without adding significant transport resistance. This approach overcame the conventional trade-off between selectivity and resistance, advancing cost-effective brackish water desalination technologies that retain essential nutrients. Finally, ALD was employed to mitigate biofouling in reverse osmosis (RO) membranes by applying uniform aluminum oxide (Al_2O_3) coatings. Optimization of the coating thickness significantly enhanced ozone resistance, enabling ozone-based disinfection to prevent biofilm formation during extended flow-cell experiments. The protective Al_2O_3 barrier mitigated biofouling while maintaining the desalination performance of the underlying RO membranes.

These studies underscore the transformative potential of ALD and MLD in tailoring membrane surfaces for application-specific selectivity, chemical stability, and energy efficiency. This work paves the way for sustainable and versatile water treatment technologies, demonstrating how precise nanoscale surface engineering can address critical challenges in global water management.

4:30pm **AA3-WeA-13 Surface Modification of Additive Manufacturing Feedstocks***, Chris Gump, Brandon Castro, Joeseph Gauspohl,* Forge Nano*; Anthony Manerbino, Jeremy Iten,* Elementum3D*; Guillermo Rojas, Casey Christopher, Markus Groner, Dane Lindblad, Brandon Woo,* ***Arrelaine Dameron,*** Forge Nano

Additive Manufacturing (AM), also called 3D printing, constructs objects from a digital model, typically by depositing and solidifying material layer by layer. AM processes that utilize powder feedstocks include laser powder bed fusion and binder jetting. AM can manufacture objects with intricate internal structures and/or small features that cannot be easily or economically fabricated by top-down machining methods or when these machining tools are not available. However, the number of alloys that can be printed successfully with superior mechanical properties by AM is limited. Possible reasons include 1) the crystal structure/internal stresses of the as-printed part leads to adverse mechanical properties, 2) the feedstock powders do not flow well and are difficult to print uniformly leading to part defects, or 3) high reflectivity of the feedstock preventing effective absorption of input energy, 4) the powder is sensitive to ambient air and has a limited shelf life or powder degradation leads to chemical inclusions and defects. These material deficiencies can be mitigated by nanoscale surface coatings that are chemically precise and uniformly distributed. We demonstrate ALD Al_2O_3, SiO_2 and Y_2O_3 coatings on AlSi10Mg, Ti64, and SiC powders at gram and kg scale. ICP, LECO, and STEM imaging and elemental mapping demonstrated successful surface modification. These coatings increased feedstock oxidation resistance by acting as a moisture and oxygen barriers, and increased powder flowability, demonstrated by a reduction in Hall Flow time. 3D printed cubes and bars from each material were tested ‘as printed’ and after hot isostatic pressing. Parts using the ALD-coated material had the highest density, yield stress, and UTS, while also having the lowest surface roughness.

4:45pm **AA3-WeA-14 Closing Remarks and Awards***,*

ALD Applications
Room Tamna Hall B - Session AA4-WeA
Medical Applications

Moderators: Junsoo Kim, SK Hynix, **Se-Hun Kwan**, Pusan National University

4:00pm **AA4-WeA-11 Room-Temperature Atmospheric Pressure ALD for Pharmaceutical Powder Coating: Tailoring Surface Properties and Controlling Drug Release***, Viet Phuong Cao, Kim Hue Dinh, Phi Huu Bui, Truong Duc Dinh, Quoc Viet Hoang, Diem Quyen Nguyen, Tuan Hiep Tran,* ***Hao Van Bui,*** Phenikaa University, Viet Nam

The pharmaceutical industry faces persistent challenges in optimizing drug delivery systems, including achieving controlled release, improving drug dispersion in liquid formulations, and enhancing the bioavailability of poorly soluble drugs. Current strategies often involve complex processes that can compromise the stability of active pharmaceutical ingredients (APIs). To address these challenges, we have developed a novel coating process using atmospheric pressure atomic layer deposition (AP-ALD) at room temperature in a fluidized bed reactor. This scalable and chemically benign method tailors the surface properties of pharmaceutical powders. Specifically, we demonstrate that AP-ALD coatings can: (1) prolong the dissolution of pharmaceuticals by up to eightfold for extended-release applications, as demonstrated with metformin and atenolol; (2) prevent sedimentation of hydrophilic drugs, enabling long-term dispersion in liquid formulations, as shown with diclofenac; and (3) enhance the dissolution rate of poorly soluble drugs, improving their bioavailability, as demonstrated with gliclazide. Our findings reveal the transformative potential of AP-ALD in pharmaceutical manufacturing, offering precise control over surface interactions while preserving the chemical integrity of APIs and paving the way for advanced drug delivery systems.

4:15pm **AA4-WeA-12 Atomic Layer Deposition for Medical Applications***,* ***J. Ruud van Ommen****, Alina Y. Rwei, Antonia G. Denkova, Volkert van Steijn,* Delft University of Technology, Netherlands

While nanotechnology could play an enormous role in the medical field, it is not straightforward to make nanostructured materials for pharma and medical devices in a scalable manner. We will show that ALD can be used to make nanostructured materials for several health applications in a scalable way.

Modifying the surface of grains of powder – as used, for example, in dry powder inhalers for treating respiratory diseases – can increase the powder flowability while also adding a controlled release functionality. In this way, the powder is used more effectively, and the side effects on the patient can be reduced significantly [1,2].

In targeted radionuclide therapy a major hurdle is the dependence on a very limited number of nuclear reactors worldwide to produce these radioisotopes. ALD can provide a way to prepare radionuclide generators, that can be placed in hospitals, providing on-site and on-demand supply. By modifying sorbent particles for isotope separation by ALD, we have made the first step towards 99Mo/99mTc radionuclide generators [3]. By using Lu ALD on nanoparticles, we have taken a step in producing 177 Lu radionuclides [4].

We also apply ALD to substrates other than powders. Polydimethylsiloxane (PDMS) is a widely used material for lab-on-a-chip and organ-on-a-chip devices. It is very versatile, but the drawback is its low stability, especially when in contact with organic solvents. We will show that modifying the surface with ceramic oxide using ALD is a way to get much more durable microfluidic devices, usable for a range of health applications [5,6].

Summarizing, we can conclude that making nanostructured materials using ALD has a range of applications in the medical field. The combination of nanoprecision and scalability gives it a lot of potential.

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4:30pm **AA4-WeA-13 Recent Advances in Multifunctional Antibacterial Neural Interfacing Electrodes Manufactured via Atomic Layer Deposition and Hierarchical Surface Restructuring***, **Shahram Armini,*** Pulse Technologies*; Henna Khosla,* Villanova University*; Wesley Seche,* Pulse Technologies*; Daniel Ammerman,* Rowan University*; Matthew Maniscalco, Alexander Blagojevic, Pouya Tavousi,* University of Connecticut*; Sahar Elyahoodayan,* University of Southern California*; Gregory A. Caputo, Jeffrey Hettinger,* Rowan University*; Sina Shahbazmohamadi,* University of Connecticut*; Gang Feng,* Villanova University

The long-term performance of neural interfacing electrodes is critically dependent on their electrochemical stability and resistance to post-implantation infections. Surgical site infections remain a major challenge, often leading to device failure and increased patient risk. While conventional strategies rely on systemic antibiotics, the rise of antimicrobial resistance necessitates alternative, device-integrated solutions. This work highlights recent advancements in the development of multifunctional antibacterial neural electrodes utilizing hierarchical surface restructuring and atomic layer deposition (ALD). Femtosecond laser-induced surface restructuring significantly increases electrode surface area, leading to enhanced charge storage capacity and reduced impedance. ALD is then employed to deposit ultra-thin conformal metal oxide coatings, such as copper oxide and zinc oxide, to impart antibacterial functionality. The combination of structural and chemical modifications enables these electrodes to achieve unprecedented electrochemical performance while effectively inhibiting bacterial growth. A detailed evaluation of the electrochemical properties, including charge injection capacity, impedance, and specific capacitance, is presented alongside antibacterial performance studies against Escherichia coli and Staphylococcus aureus. Results demonstrate that the engineered electrodes maintain high electrochemical stability while exhibiting strong bactericidal effects, making them promising candidates for next-generation neural interfacing applications.

4:45pm **AA4-WeA-14 Closing Remarks and Awards in Tamna Hall A***,*

ALD Fundamentals
Room Tamna Hall B - Session AF-WeA

Material Growth II

Moderators: Ageeth Bol, University of Michigan, Ann Arbor, **Erwin Kessels**, Eindhoven University of Technology, Netherlands

1:30pm **AF-WeA-1 ALD of Nitride Semiconductors***, **Henrik Pedersen,*** Linköping University, Sweden **INVITED**

The group 13 nitrides, AlN, GaN, InN and their alloys, is an important class of semiconductors, forming the backbone for technologies such as light emitting diodes (LEDs) and high electron mobility transistors (HEMTs). Chemical vapor deposition (CVD) at high temperatures, 800-1200 °C, is the typical way of depositing these materials. But CVD of indium nitride (InN) is severely limited by the low thermal stability of the material,[1] and can thus only tolerate relatively low deposition temperature. As ALD is intrinsically low temperature, it is a logical path for InN films and has been demonstrated to deposit epitaxial InN films with excellent crystalline quality.[2,3] The two chemically and structurally closely related materials aluminium nitride (AlN) and gallium nitride (GaN) has been deposited by both plasma and thermal ALD, with ammonia (NH_3) as nitrogen precursor in thermal processes.

In this talk I will describe ALD of these semiconducting nitrides, with focus on the fundamental understanding of the ALD chemistry. ALD has been shown to be an enabler for the metastable InN and $In_xGa_{1-x}N$ with x close to 0.5.[4] By combining quantum-chemical density functional theory (DFT) calculations[5] and *in-situ* techniques such as mass spectroscopy[6], we can present a detailed surface chemical model for the ALD processes. I will also present results from our efforts understand the surface chemistry by *in operando* ambient pressure XPS. Finally, I will discuss limitations to thermal ALD of these nitrides and why plasma activation seems to be needed.

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2:00pm **AF-WeA-3 Towards Two New Atomic Layer Deposition Processes for the Distinct Synthesis of Coo or Co_3O_4 Thin Films***, **Olivier Debieu,*** CIRIMAT, Université de Toulouse (CNRS / INP / UT3), Ensiacet, France*; Getaneh Diress Gesesse, Julien Cardin, Bilal Bawab, Christophe Labbe, Cédric Frilay, Sylvain Duprey,* CIMAP, ENSICAEN, UNICAEN, CEA, CNRS UMR5262, France*; Jean-François Lohier,* CRISMAT, ENSICAEN, UNICAEN, CNRS UMR6508, France

Rock salt CoO and spinel Co_3O_4 are two p-type semiconductors (SCs) with a wide range of promising applications, used alone or assembled with other n-type SCs as active material in gas sensors, or as electrode in photoelectrocatalysis (PEC) as in the present project [1,2]. Based on the application conditions, *i.e.* the (photo)electrochemical conditions, metastable CoO thin films with the lowest Co^{2+} oxidation state can be more suitable than the most stable Co_3O_4 with Co^{3+} and Co^{2+}·oxidation states. Depending on the growth method, the two phases are not necessarily achievable or may coexist at the nanograins scale. Atomic layer deposition (ALD is a versatile deposition technique that allows fine control of the composition, crystalline structure and morphology of conform layers, making it then highly suitable for the targeted applications.

The present study focuses on the optimization of two new ALD recipes and annealing conditions by the substrate temperature, gas flows, and oxidizing reactant and proper annealing atmosphere to synthesis either CoO or Co_3O_4 films on Si wafer using CoAMD as precursor. To establish the relationships between these parameters and the structural and optical properties of the films, GI-XRD, XRR, FTIR, UV-Vis-NIR, and ellipsometry (SE) analysis were used. We found comparable thicknesses by XRR and by SE that were useful to select the best growth rate conditions. Comparable crystallographic compositions revealed by GI-XRD and FTIR were found to change with the ALD parameters. Interestingly, the normal incidence in FTIR measurement can act as a filter to analyze only Co_3O_4 IR-features. We found optical dispersion curves of CoO and Co_3O_4 layers, rare in the literature, modeled by standard critical point models, and 6-Lorentzian models corresponding to the six optical transitions in the 0.5-5 eV spectral range of SE measurements, respectively, providing information on the density. Two optimal synthesis routes have been thus developed at lowest thermal budget.

Following the successful synthesis of the two Co-oxide allotropes, we will assemble them on our previously prepared Nb-doped TiO_2 films[3] to form a p-n photoelectrodes (in oxidation or reduction conditions). Electrical characterizations at nanoscale using conductive AFM[4] will be performed to assess carrier transport properties before PEC activity measurement.

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2:15pm **AF-WeA-4 High-Quality ALD-Ru Process Using Thermally Stable ALD Ru Precursor*, Hideaki Nakatsubo,*** TANAKA PRECIOUS METAL TECHNOLOGIES Co., Ltd. / UNIST, Japan*; Jeongha Kim, Soo-Hyun Kim,* UNIST, Korea (Democratic People's Republic of)

Ruthenium (Ru) is expected to be a promising alternative material for copper (Cu), due its better scaling performance resulting from a shorter electron mean free path and possibility of the barrierless interconnectes scheme. Until now, many atomic layer deposition (ALD) processes have been developed to achieve a high-quality Ru film with a low resistivity as possible (bulk resistivity of Ru: 7.4 μΩ･cm), but many reported values have not yet achieved the desired low resistivity one. In this study, a novel Ru precursor, trimethylenemethane (p-methylisopropyl benzene) ruthenium [Ru(TMM)(p-cymene)], was synthesized and investigated for a high-quality ALD-Ru process. Since this precursor has a thermal stability up to 400 ℃, one can adopt a high process temperature for ALD, giving a lower resistivity than those obtained many previous ALD processes typically performed lower than 300 ℃ due to the poor thermal stability of Ru precursors. For developing ALD-Ru process, O2 was used as a reactant, and substrates used included SiO2, TiN, and Ru. The ALD-Ru process nicely shows a typical self-limiting behavior of ideal ALD with a growth per cycle (GPC) of ~1.28Åon TiN and a negligible incubation cycle at the deposition temperature of 300 oC. Interestingly, on SiO2, there was no Ru deposition even after 1000 cycles. The resistivity decreased with increasing process temperature, reaching ~14 μΩ･cm at 300℃ and ~11 μΩ･cm at 375℃, comparatively lower than those of previously reported Ru ALD processes. Annealing the Ru film in H2 gas further reduced resistivity to 8.65 μΩ･cm at 700℃, close to the bulk Ru resistivity. XRD and SEM analysis showed increased grains size and improved crystallinity with annealing, resulting in the decrease in the resistivity. In conclusion, the present study demonstrates high-performance and versatile ALD-Ru process with a very low resistivity, high GPC, and extremely high selectivity can be achieved using a newly synthesized Ru precursor.

2:30pm **AF-WeA-5 The Development of Ultralow-Dielectric Constant Boron Nitride Film by Novel Plasma Atomic Layer Deposition*, Kazuki Goto,*** *Yoshihiro Kato, Shuichiro Sakai, Hiroki Murakami, Yamato Tonegawa,* Tokyo Electron Technology Solutions Ltd, Japan

The miniaturization of electronic devices has intensified challenges related to electrical signal propagation delays, primarily due to increased wiring resistance and capacitance. As a response, there is a rising demand for low dielectric constant (low k) materials to enhance device performance. Silicon oxide-based dielectrics (SiCOH) are conventionally known as a low k material. However, the thermal and mechanical stability of these materials are significantly compromised due to their low film density. In this context, boron nitride (BN) films have emerged as promising candidates due to their low dielectric constant and high stability [1]. Hexagonal BN (*h*BN) is characterized by its layered structure and wide band gap (5.2 – 5.9 eV), and it is expected to exhibit low k values, particularly along the c-axis [2].

In this study, we explored the film formation process of *h*BN using a borazine-based precursor with N_2 and NH_3 plasma to achieve high-quality BN films with low k, high density, and high conformality. Deposition was conducted at 400 ℃ on a 300 mm Si substrate, resulting in an ideal *h*BN layered structure clearly revealed by cross-section TEM (Fig. 1a). It was possible to deposit even thicker layers while maintaining the *h*BN structure. Moreover, we have successfully deposited conformal *h*BN on a trench pattern for the first time (Fig. 1b), expanding the applicability and versatility of *h*BN. C-V measurements indicated a low k value of <3 for our *h*BN. Analysis through XPS and IR spectroscopy confirmed a stoichiometric BN composition containing a significant amount of B-N sp^2 bonds. By applying additional plasma treatments, we observed a reduction in k value along with increased density due to the promotion of sp^2 B-N bonding. The resulting *h*BN films exhibited a low k value at higher density than can be achieved with Si-based films (Fig. 2).

This methodology also facilitated control over the crystalline orientation of *h*BN. We found certain processing conditions led to the deposition of both less and highly ordered *h*BN. C-V measurements across varying oriented films demonstrated a decrease in k values correlating with order, while I-V measurements confirmed that order in crystallinity contributed to the reduction of leakage current. We established a relationship between the crystallinity of *h*BN, the k value, and leakage current. This research created high quality conformal *h*BN, demonstrating significant potential for practical applications as low dielectric constant films for high-performance semiconductor devices.

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2:45pm **AF-WeA-6 Thermal Atomic Layer Deposition of InN using Hot-wire-activated NH_3 and Hydrazine Reactants*, Bonwook Gu,*** *Kwangyong An, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

Indium nitride (InN) possesses high electron mobility, approximately 3000–4000 cm^2/V·s) and a low bandgap (~0.7 eV), making it an ideal material for high-speed transistors and RF devices that require low-power, high-performance operation. Additionally, InN exhibits excellent infrared absorption properties, enabling its applications in infrared detectors, high-efficiency solar cells, and optical sensors. Recently, as device sizes have decreased and structures become more complex, research on atomic layer deposition (ALD) for fabricating InN thin films has gained significant momentum. However, previous InN ALD research has primarily focused on plasma-enhanced processes, which pose challenges such as (1) difficulty in achieving uniform film deposition on three-dimensional structures with high aspect ratios and (2) potential substrate damage due to high-energy plasma exposure. To address these limitations, we explored the feasibility of thermal ALD for InN deposition. Thermal ALD for InN is challenging due to the high deposition temperatures required, low reactivity of reactants, and the tendency of indium compounds to oxidize easily, leading to poor film quality and low deposition efficiency. In this research, we employed hydrazine and hot-wire-activated NH_3 as reactants for thermal InN ALD. We conducted a comparative study using trimethylindium (TMI) and InPALA as In precursors. The physical and chemical properties of the deposited InN thin films were characterized using X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscopy (FE-SEM), Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD).

3:00pm **AF-WeA-7 Electron-Enhanced ALD and CVD of Titanium-, Silicon- and Tungsten-Containing Films at Low Temperatures Using Metal Precursors with Various Reactive Background Gases***, Zachary C. Sobell,* ***Andrew S. Cavanagh****, Steven M. George,* University of Colorado at Boulder

Electron-enhanced atomic layer deposition (EE-ALD) (Figure 1a) and electron-enhanced chemical vapor deposition (EE-CVD) (Figure 1b) can be employed for the low temperature deposition of thin films using metal precursors with various reactive background gases (RBGs).EE-CVD expands on the previous report of TiN EE-ALD using alternating $Ti(N(CH_3)_2)_4$ (tetrakisdimethylamino titanium (TDMAT)) and electron beam exposures with NH_3 RBG.During EE-CVD, the electron beam and the RBG are present continuously.Together with the RBG and electron beam incident on the surface, the metal precursor is pulsed into the vacuum chamber to control the film growth.

In this work, the metal precursors were TDMAT, Si_2H_6, and $W(CO)_6$.The RBGs were O_2, NH_3, CH_4, and H_2.The studies demonstrated TiO_2 EE-ALD and SiN, SiO_2, SiC_x, Si, W_2N, WO_3, and WC_x EE-CVD. To illustrate EE-ALD, TiO_2 EE-ALD was performed at T < 80 °C using alternating TDMAT and electron beam exposures together with O_2 RBG.The growth rate for the TiO_2 EE-ALD was ~0.7 Å/cycle.The TiO_2 EE-ALD films were nearly stoichiometric, displayed crystallinity, and were smooth as measured by atomic force microscopy (AFM).

To illustrate EE-CVD, SiC_x EE-CVD was performed at T < 100 °C using repeating Si_2H_6 pulses with continuous electron beam and CH_4 RBG exposures.XPS revealed a 1:1 Si:C stoichiometry for a CH_4 RBG pressure of

0.45 mTorr and C-rich films for higher CH_4 RBG pressures.The SiC EE-ALD growth rate was ~0.4 Å per Si_2H_6 pulse.The stoichiometric SiC EE-CVD films were smooth as measured by AFM.

W_2N EE-CVD was also performed at T < 120 °C using repeating $W(CO)_6$ pulses with continuous electron beam and NH_3 RBG exposures (Figure 2a).The W_2N EE-CVD growth rate was ~0.17 Å per $W(CO)_6$ pulse.The W_2N films had a resistivity of ~450 μΩ-cm.The W_2N EE-CVD films also displayed crystallinity and high purity (Figure 2b).This work shows that EE-ALD and EE-CVD with various RBGs can deposit a broad range of materials at low temperatures including oxides, nitrides and carbides.

3:15pm **AF-WeA-8 Low-Temperature Atomic Layer Deposition of (00l)-Oriented Elemental Bismuth***, **Amin Bahrami**, Jorge Luis Vazquez-Arce, Alessio Amoroso, Nicolas Perez,* Leibniz Institute for Solid State and Materials Research, Germany*; Jaroslav Charvot,* University of Pardubice, Czechia*; Dominik Naglav-Hansen,* Ruhr-University Bochum, Germany*; Panpan Zhao, Jun Yang, Sebastian Lehmann, Angelika Wrzesińska-Lashkova,* Leibniz Institute for Solid State and Materials Research, Germany*; Fabian Pieck, Ralf Tonner-Zech,* Leipzig University, Germany*; Filip Bureš,* University of Pardubice, Czechia*; Annalisa Acquesta,* University of Napoli Federico II, Italy*; Yana Vaynzof, Anjana Devi, Kornelius Nielsch,* Leibniz Institute for Solid State and Materials Research, Germany

This study presents the first successful demonstration of growing elemental bismuth (Bi) thin films via thermal atomic layer deposition (ALD) using Bi(NMe2)3 as the precursor and Sb(SiMe3)3 as the co-reactant. The films were deposited at a relatively low temperature of 100 °C, with a growth per cycle (GPC) of 0.31-0.34 Å/cycle. Island formation marked the initial growth stages, with surface coverage reaching around 80% after 1000 cycles and full coverage between 2000 and 2500 cycles. Morphological analysis revealed that the Bi grains expanded and became more defined as the number of ALD cycles increased. This coalescence is further supported by X-ray diffraction (XRD) patterns, which show a preferential shift in growth orientation from the (012) plane to the (003) plane as the film thickness increases. X-ray photoemission spectroscopy (XPS) confirmed the presence of metallic Bi with minimal surface oxidation. Temperature-dependent sheet resistance measurements highlight the semimetallic nature of Bi, with a room temperature resistivity of ≈200 μΩcm for the 2500 cycles Bi. Temperature-dependent sheet resistance was also associated with a transition in carrier-type dominance from electrons at higher temperatures to holes at lower temperatures.

ALD for Manufacturing
Room Samda Hall AB - Session AM1-WeA

ALD Equipment I

Moderators: Eun-Hyoung Cho, 2D Device TU(SAIT)/Samsung Electronics, **Woo Jae Lee**, KNU

1:30pm **AM1-WeA-1 Spatial Atomic Layer Deposition of Cu-Based Thin Films***, **David Muñoz-Rojas**,* CNRS, France **INVITED**

Spatial Atomic Layer Deposition (SALD) is an emerging variant of ALD that enables rapid processing, even at atmospheric pressure, while retaining the key advantages of ALD: precise nanometer-scale thickness control, high-quality films at low temperatures, and exceptional conformality. These features make SALD particularly well-suited for high-throughput, cost-effective applications, such as next-generation photovoltaics, LEDs, and packaging.

A key strength of SALD, especially when utilizing close-proximity deposition heads, lies in its versatility. The design of these deposition heads can be easily customized, and since the process takes place in open air, no deposition chamber is required, further simplifying scalability.

To fully leverage the benefits of SALD, however, new processes must be developed to deposit functional materials with optimized properties using mild conditions and stable precursors. In this talk, I will introduce our close-proximity SALD approach and highlight our recent work in developing innovative SALD processes. Specifically, I will present a novel SALD method for depositing Cu_2O thin films with record-high transport properties, achieved despite low-temperature processing. I will also explore the critical role of precursors and process conditions in determining the final film properties. Lastly, I will demonstrate that, even in an open-air environment, it is possible to selectively deposit Cu, Cu_2O, or CuO from the same precursor simply by adjusting the coreactant.

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2:00pm **AM1-WeA-3 Visualization of Precursor Transport in Vapor Deposition Systems: Measurements and Simulations***, **James Maslar**, Vladimir Khromchenko, Berc Kalanyan,* NIST-Gaithersburg

Advanced models for semiconductor fabrication unit processes are needed for improved process control, defect reduction, and ultimately yield improvement. Development of such models is limited by a general lack of non-proprietary process data. The goal of this work is to aid in vapor deposition process model development by 1) generating measurement data sets and 2) evaluating the utility of these data sets by using them to validate simulations of precursor flow in our ALD chambers. Central to achieving this goal is absorption imaging of precursor flow as a function of process conditions, e.g., gas flow rate, chamber pressure, and temperature. Two precursors were selected for investigation: molybdenum pentachloride ($MoCl_5$) and tetrakis(dimethylamido)titanium (TDMAT). $MoCl_5$ flow was visualized at about 100 images per second in the ultraviolet-visible spectral region using a 7.1-megapixel complementary metal oxide semiconductor camera and a light emitting diode source. TDMAT flow was visualized at about 30 images per second in the mid-infrared spectral region using an uncooled microbolometer thermal imaging camera and a blackbody source. Simulations of flow in this chamber were performed using a commercial computational fluid dynamics (CFD) package. CFD simulations of low-volatility precursors in a carrier gas are simplified since the precursor is dilute and the gas properties are that of the carrier gas, properties that are well known for typical deposition conditions. Simulations were validated using the time-dependent, pathlength-integrated precursor concentration obtained from the absorption imaging measurements and the time-dependent total pressure measured at selected locations in the deposition system. In this talk, aspects of both the measurements and simulations will be discussed, including the choice of parameters included in the data set.

2:15pm **AM1-WeA-4 Atomic Layer Deposition on Highly Cohesive Granular Material in Fluidized Beds***, **Rens Kamphorst**,* Delft University of Technology, Netherlands*; Kaiqiao Wu,* Delft University of Technology, China*; Saeed Saedy, Gabrie M.H. Meesters, J. Ruud van Ommen,* Delft University of Technology, Netherlands

Atomic layer deposition (ALD) on granular materials is gaining increasing attention due to its potential applications in pharmaceuticals, nano-catalysts, and colloidal stabilization. Powders with smaller particle sizes have higher specific surface areas, which can be utilized, however, they pose significant challenges for processing, especially when particle sizes are <30µm. At these scales, van der Waals forces dominate making particles cohesive. In conventional fluidized beds, ALD is challenged by precursor gas escaping via cracks in the powder bed, having little interaction with the particles. Furthermore, particle clusters appear frequently, resulting in parts of individual particles being inaccessible to be coated, leading to non-uniform deposition. These complications necessitate dedicated systems that can overcome the inherent cohesiveness of such powders.

In our work, we set out to coat cohesive particles in an ALD fluidized bed reactor. We employed X-ray imaging to evaluate methods for improving fluidization of cohesive powders, including mechanical vibration, pulsed flow, and mechanical agitation. These methods are designed to break up structures within the powder, improving gas-solid interaction.

Our findings demonstrate that assistance methods initiate smooth fluidization, significantly enhancing gas-solid contact. We visualize the dynamics within powder beds subjected to various assistance methods and propose scalable methods to fluidize cohesive powders in order to perform ALD. We also show successful deposition of SiO_2 layers on otherwise un-fluidizable particles. These results open pathways for functionalizing fine powders for advanced technological applications.

2:30pm **AM1-WeA-5 From the Research Lab to the Fab: Comparison of Vapor Generation by Bubbler and Direct Liquid Injection Vapor Delivery Systems***, **David Curran**,* 5910 Rice Creek Parkway Suite 300

As the semiconductor industry is moving to smaller nodes, the need for high-quality and high-throughput vapor delivery is paramount. As the geometry and structures of the depositions evolve, research institutions and chemical manufacturers are developing new precursors offering superior reaction mechanisms for selective surface depositions and other difficult reactions. Initial testing of these precursors in chemical vapor deposition or atomic layer deposition processes are typically conducted by supplying the vapor by means of a bubbler or a flow over vessel. Bubblers in conjunction with a downstream ALD valve can be a straightforward solution; however mass delivery accuracy, adjustability and stability are known issues, which can create thin film irregularity and wafer-to-wafer variability. Additionally, if precursors are thermally sensitive, there can be issues with the liquid decaying in the heated ampoule over time leading to long deposition times and/or wasted material. To meet the industry needs, a solution is needed to improve vapor delivery to scale up from development to production.

Direct liquid injection (DLI) vaporizing systems present an attractive solution to the scale-up problem. DLI systems allow the throughput of the vapor delivery system to be increased by generating nanometer to micron sized droplets of the precursors, improving the heat transfer to the liquid. Coupled with a liquid flow controller, DLI systems can provide fast, high-throughput, consistent, known concentrations of vapor to deposition chambers.

The work presented in this presentation will directly compare the vapor concentration and quality delivered by a bubbler and a DLI vaporizer for several difficult to vaporize precursors. To compare the delivery systems, a method using Fourier Transform Infrared (FTIR) spectroscopy to conduct real-time measurement of vapor concentration and droplet content of the vapor stream will be employed. This presentation will briefly detail hardware and experimental setup used, key control criteria, and advantages and disadvantages will be discussed.

2:45pm **AM1-WeA-6 Advancing Fast Spatial Atomic Layer Deposition: Optimizing Precursor Control and Atmospheric Effects for Functional Oxide Thin Films***, **Viet Huong Nguyen**,* Faculty of Materials Science and Engineering, Phenikaa University, Hanoi 12116, Viet Nam., Viet Nam

Spatial atomic layer deposition (SALD) has emerged as a powerful technique to achieve high deposition rates while maintaining the atomic precision of conventional ALD. However, challenges persist in controlling unwanted chemical vapor deposition (CVD) contributions and optimizing process parameters for large-scale applications. In this work, a comprehensive study on enhancing control in SALD by tuning precursor diffusion, injection head geometry, and deposition conditions will be presented. Using a combination of experimental data and computational modeling, we elucidate the critical role of precursor exposure and deposition gap on growth kinetics, leveraging insights from ZnO and SnO_2 thin films.[1] A refined injection head design is proposed to mitigate CVD-related issues while maximizing throughput. Furthermore, we investigate the impact of atmospheric pressure on the electrical properties of metal oxide semiconductors,[2–4] and suggest a few strategies to enhance control over growth and functionality for optoelectronic and energy applications.[5]

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3:00pm **AM1-WeA-7 High Deposition Rate TiO PEALD Process for Semiconductor Industry***, **Sungbae Kim**, Yeahyun Gu, Hyunchul Kim, Hyungjoo Shin,* ASM, Republic of Korea

TiO thin films are increasingly used in the semiconductor industry due to their excellent physical and chemical properties. Due to their high etching selectivity for the Si base materials and pattern fidelity, they have been mainly used for patterning applications such as hard-mask and spacers. Recently, however, due to the material's unique optical property (High Refractive Index (R.I.) value >2.3 at 633nm), the application area has been expanded to others such as ARL (Anti-Reflection Layer) and CIS (CMOS Image Sensor) Meta-lens. As such applications often requires a thicker material than patterning films, a higher deposition rate is accordingly desirable for commercially viable productivity.

In this paper, a new process sequence was developed to increase the deposition rate while keeping the most of benefits of PEALD including film quality, uniformity, and gap fill capability. The thin film properties were characterized and compared with those of the conventional ALD process. TDMAT was used as the Ti precursor. O2 plasma was used as the reactant to grow TiO. 27.12MHz-rf source was used to generate a CCP in a commercial PEALD chamber by ASM (QCM TiO XS).

In the case of conventional ALD, there is a limitation in terms of the deposition rate even with the increasing supply of precursor due to the nature of self-limiting reaction phenomenon in PEALD. To overcome this self-limiting reaction, a low-power pulsed-plasma CVD step was introduced in a typical PEALD process cycle. (Figure1.) The new process sequence promotes the film growth by balancing the conformal deposition and the surface treatment. By this means, the new deposition rate increased to 0.94Å/sec by nearly three times compared to conventional ALD (0.34Å/sec). The results of the film deposited on a 12-inch bare Si wafer by the new process shows both uniformity and R.I. are at similar levels as the ones with conventional slow PEALD. In addition, we confirmed the step coverage is more than 80% in the pattern of open CD 90nm with aspect ratio of 3. XPS analysis also shows that the impurity concentrations of 'C' and 'N' were as low as below 2%, which is comparable to conventional PEALD process.

The high deposition rate TiO PEALD process is expected to be applicable to any new emerging applications which requires TiO's PEALD quality yet with higher deposition rate. The ASM's hardware technology enables this new process sequence for a novel PEALD.

3:15pm **AM1-WeA-8 Spatial ALD Deposited Functional Layers for Large-Area Inverted Perovskite Solar Modules***, **Xuewei Jiang**,* Huazhong University of Science and Technology, China*; Fan Yang,* Luoyu Road 1037, Wuhan, China*; Bin Shan, Rong Chen,* Huazhong University of Science and Technology, China

Perovskite solar cells (PSCs) are a promising candidate for large-scale commercialization, with efficiency and scalability as key factors. However, fabrication of large-area functional thin films including electron transport layers (ETLs), hole transport layers (HTLs) as well transparent conductive electrode, becomes one of the biggest obstacles for the commercial PSCs applications. This study explores low temperature SALD deposited SnO_2 ETL and aluminum-doped zinc oxide (AZO) as transparent conductive oxide electrodes to improve the performance of PSCs modules. By controlling oxygen vacancies through precursor reactivity, we achieved a high mobility of 19.4 $cm^2/V \cdot s$ in SnO_2 ETL (deposited at 100 ℃) and ultra low sheet resistance to 3.6 Ω/sq for AZO electrode, surpassing commercial FTO (8 Ω/sq). Additionally, textured AZO electrodes, exhibited excellent optical properties with a haze of over 55% and an average transmittance of approximately 90%. Due to the advantages of SALD, the thin films demonstrated good uniformity with only 2.8% nonuniformity in film thickness and 4.6% in sheet resistance over a 400 cm^2 area. For the 400 cm^2 PSMs with AZO electrodes achieve a PCE of 20.5% and retain 87% of their initial efficiency after 600 hours of continuous illumination. This exceptional performance stems from the excellent uniformity and mobility of the SALD-deposited SnO_2 ETL and AZO elelctrode, highlighting the potential of SALD in future PSM fabrication.

References

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ALD for Manufacturing
Room Samda Hall AB - Session AM2-WeA

ALD Equipment II

Moderators: Tae Wook Nam, Sejong University, **Bonggeun Shong**, Hongik University

4:00pm **AM2-WeA-11 Spatial Atomic Layer Deposition of Nanolaminate Barrier Coatings Enables Sustainable Packaging***, **Denys Vidish**,* University of Waterloo, Canada*; Soumyadeep Saha, Louis Delumeau, Tristan Grovu,* Nfinite Nanotechnology Inc., Canada*; Kevin Musselman,* University of Waterloo, Canada

Plastic waste poses a worldwide challenge because of its detrimental effects on the environment, society, and economy. Flexible packaging materials are being used with different types of single-use plastics. To address their harmful impact on the environment, the packaging industry has been trying to move towards compostable polymer materials such as polylactic acid (PLA). However, these compostable polymers don't provide a sufficient gas-diffusion barrier to protect the product from water vapor and oxygen. For that reason, applying vapor-barrier coatings onto packaging materials is necessary to protect the product. However, most traditional barrier coatings don't perform well on PLA and/or compromise the composability of the packaging. In this work, we introduce nanolaminate barrier coatings for flexible, sustainable packaging materials that are based on alternating nanoscale layers of aluminum oxide (Al_2O_3) and zinc oxide (ZnO). These nanolaminates were deposited using an atmospheric-pressure spatial atomic layer deposition (AP-SALD) system, which is a scalable technique that is compatible with roll-to-roll manufacturing. We show that the water-vapor transmission rate (WVTR) and oxygen-transmission rate (OTR) of PLA and PET films are significantly improved after coating them with nanolaminates and that the performance of the nanolaminates is superior to single-layer barrier coatings. We note that the thickness of nanolaminate layers directly correlates with the improvement in barrier performance until an optimal value is reached. Moreover, we demonstrate that the nanolaminates are much more resistant to cracking under stress than single-layer coatings. They maintain their barrier properties (low WVTR and OTR) after bending and Gelbo flex tests, which is crucial for flexible packaging materials. As a result, we demonstrate nanolaminate coatings deposited via AP-SALD that are very promising for improving the barrier properties of biodegradable materials for the flexible packaging industry.

4:15pm **AM2-WeA-12 Advancing Atomic Layer Processing for Next Generation Devices: Atlant 3d'S Direct Atomic Layer Processing (Dalp™)***, **Mira Baraket**,* ATLANT 3D Nanosystems, Denmark

As the demand for miniaturized and complex devices accelerates across industries, innovative and precise atomic layer advanced manufacturing techniques have become critical. ATLANT 3D's proprietary Direct Atomic Layer Processing (DALP™) technology is redefining thin-film processing by enabling spatially localized, atomically precise material growth with unmatched flexibility. Building upon Atomic Layer Deposition, DALP™ confines gas flows to a micrometer-scale area using advanced microreactors, enabling deposition of diverse materials on complex geometries and substrates with exceptional thickness control and conformality on complex structures.

DALP™ technology tackles key challenges in accelerating innovation within thin-film manufacturing. It enables rapid prototyping by allowing localized, multi-thickness depositions of diverse materials on a single wafer, significantly cutting prototyping timelines from months to hours compared to conventional methods.These capabilities have been demonstrated across diverse applications, including optics and photonics, MEMS, RF electronics, emerging memory technologies, advanced packaging, and energy storage.

This talk will explore ATLANT 3D's advancements in DALP™ technology, focusing on expanded material compatibility, enhanced resolution, and new opportunities it creates for thin-film processing. We will demonstrate how DALP™ technology drives innovation by enabling the fabrication of complete, functional devices. Through case studies, we will highlight how our advanced processing technique have been used to produce components and electronic devices. These examples illustrate how ATLANT 3D's platform not only improves material deposition processes but also revolutionizes prototyping and manufacturing, empowering industries to achieve faster and more efficient innovation.

4:30pm **AM2-WeA-13 Analysis of Controllable Coil Patterns to Improve Temperature Uniformity of Inducted-Heated Susceptor***, **Jihyun Kim**, Hakmin Kim, Kwangson Jin, Tae S. Cho,* Wonik IPS, Republic of Korea

To uniform the temperature of wafers and to get higher temperature faster and more efficiently is desired in the semiconductor manufacturing processes such as metalorganic chemical vapor deposition (MOCVD) growth system[1)]. Induction heating is an alternative technology that provides fast and high temperature heating. In the process of induction heating, the susceptor remains free of physical contact with the work coil or inductor. Nevertheless, the temperature distribution of the wafer on the susceptor is uneven and challenging to manage with a single coil induction heating method, owing to the skin effect of the induced current in the susceptor[2)]. The temperature uniformity of induced-heat susceptor was hence investigated with various working coil patterns for induction heating system by ANSYS Maxwell 3D modelling and simulating. The working coil could be divided into a number of multi-turns or multi-layer coils or multi-zone. Then the material of susceptor was graphite with 5mm of thickness and 300mm of diameter. A travelling wave magnetic field was used to induce eddy current in the graphite susceptor. In order to generate the temperature uniformity of graphite susceptor, the phase angle between the currents differ by $\pi/2$ or $\pi/4$, the input current changes from 10A to 30A, and the input frequency varies from 20kHz to 60kHz. The simulation results showed that the temperature distribution of the susceptor was still not uniform with the single layer and multi-layer with the single zone due to the skin effect and heat conductor in the conventional susceptor. However, the temperature uniformity of the susceptor can be greatly improved by dividing several zones of the coil with different input currents and phases with same frequency. That is the temperature uniformity is improved with the multi-zone with multi-layer coil when the currents and phases of each zone are different. Higher temperature and faster heating rate can be obtained by increasing heating frequency and input current, but the lower and higher frequency can bring worse temperature uniformity. The higher magnetic field over the wafer that can affect to the semiconductor process can also be induced with increasing higher frequency and input current. Therefore, selecting the appropriate frequency and input current for the semiconductor manufacturing processes is essential. To enhance the uniformity of temperature in the graphite susceptor to the desired level, it is necessary to identify the appropriate number of coils turns and input current for each zone, as well as the phase difference between the applied currents.

4:45pm **AM2-WeA-14 Closing Remarks and Awards in Tamna Hall A***,*

Area Selective ALD
Room Tamna Hall A - Session AS-WeA

Area Selective Deposition IV

Moderators: Benjamin Greenberg, Naval Research Laboratory, **Michael Nolan**, University College Cork

1:30pm **AS-WeA-1 Polypeptoid Brushes as Growth-Promoting Monolayers: Advancing Area-Selective Deposition for EUV Lithography***, Beihang Yu,* Lawrence Berkeley National Laboratory*; Maggy Harake, Yujin Lee, Stacey Bent,* Stanford University*; **Ricardo Ruiz**,* Lawrence Berkeley National Laboratory **INVITED**

In extreme ultraviolet (EUV) lithography, minimizing edge placement error (EPE) is critical for achieving smaller and denser features. Multiple lithographic exposures and etching steps contribute to EPE, limiting the precision of pattern transfer. Area-selective deposition (ASD) has emerged as a promising technique to mitigate these issues by selectively promoting and blocking material growth on specific regions. While recent efforts to advance ASD have focused on studying and improving the use of monolayers to block or inhibit growth in undesired regions, the use of monolayers to promote material growth in targeted regions remains relatively underexplored, particularly for metal oxide deposition at EUV-relevant dimensions.

We present a novel approach using sequence-defined polypeptoids (N-substituted glycines) as monolayer growth promoters in ASD. Our method demonstrates that polypeptoid brushes significantly enhance nucleation and growth of aluminum oxide (Al_2O_3) during vapor phase infiltration (VPI), a process akin to atomic layer deposition (ALD). By employing polystyrene brushes as blocking agents, we achieve selective deposition of Al_2O_3 exclusively in polypeptoid-modified regions. This innovative technique accelerates the deposition rate to ~5 Å per cycle, a fivefold increase over traditional ALD (~1 Å per cycle). The resulting Al_2O_3 hard mask enables high etching selectivity (up to 8:1) when transferred onto a silicon substrate using reactive ion etching (RIE).

Furthermore, we showcase the versatility of polypeptoids by tailoring their chemical composition, allowing fine-tuned control over VPI interactions. This adaptability provides a flexible method to optimize growth rates and selectivity across diverse substrates. Our work not only highlights the potential of monolayers as growth promoters but also offers new possibilities for enhancing ASD processes and reducing EPE in EUV lithography. These advancements have significant implications for the future of semiconductor patterning, potentially enabling the continued scaling of integrated circuits.

2:00pm **AS-WeA-3 Area Selective Deposition of $SiAlO_x$ Films for Self-Aligned Dielectric-on-Dielectric Application**, ***Eryan Gu**, Wang Li, Kun Cao, Rong Chen,* Huazhong University of Science and Technology, China

Area selective deposition (ASD) is a high-precision atomic-level manufacturing technology that enables the development of bottom-up manufacturing methods in the future semiconductor field. As the feature size decreases, the parasitic capacitance increases, and the RC delay limits the propagation speed of the signal, while increasing the power consumption of the chip. This study investigates the $SiAlO_x$ film via atomic layer deposition (ALD) process, focusing on the catalytic reaction mechanisms of various aluminum precursors on silicon. Trimethylaluminum (TMA) molecules, which are highly reactive, easily interact with Bis(ethylmethylamino)silane (BEMAS), resulting in relative lower k value. In contrast, dimethyl isopropylaluminum (DMAI) molecules exhibit lower reactivity, resulting in a slower catalytic reaction rate. Additionally, n-octadecanethiol (ODT) is used to inhibit nucleation on the metal surface, and the interaction between aluminum and silicon precursors and ODT is studied. The high catalytic activity of TMA on BEMAS will decrease selectivity, while the DMAI system can achieve high selectivity with 10nm on growth area of SiO_2 with minimal growth on non-growth area of Cu. This approach not only reduces the k value further but also offers a promising pathway for advancing semiconductor nodes.

References

1. Effect of Al precursor's properties on interactions with self-assembled monolayers for area selective deposition. Eryan Gu, Jin Yan, Boxuan Li, Huilong Zhou, Zhuhui Lu, Yanwei Wen, Kun Cao, Rong Chen, J. Vac. Sci. Technol. A 42, 062403 (2024)

2:15pm **AS-WeA-4 Control of Three-Color Area-Selective Deposition of PEDOT Conjugated Polymer on SiN vs SiO2 and Si-H by Adjustment of Pre-Treatment Sequence**, ***Jeremy Thelven**, Nicholas Carroll, Gregory Parsons,* North Carolina State University

Most research in area-selective deposition (ASD) focuses on deposition of one material on a growth surface while avoiding deposition on a non-growth surface. However, for many steps in manufacturing, the exposed surface is "multi-color", consisting of three or more materials. This means that any desired ASD process must be tuned to deposit on more than one growth surface while simultaneously inhibiting deposition on more than one non-growth surface.

To analyze "three-color" ASD, we studied ASD of poly(3,4-ethylenedioxythiophene) (PEDOT) conjugated polymer by molecular layer deposition (MLD) and CVD using ethylene-dioxythiophene monomer and $SbCl_5$ as reactants for oxidative polymerization.[1–2]As a three-color substrate, we use blanket samples of silicon nitride, silicon dioxide, and silicon.Initially, we treat all three surfaces with dilute HF solution producing Si-NH, Si-OH, and Si-H surface termination, respectively.As shown in Figure 1, PEDOT CVD at 150℃ results in "inherent" selectivity of more than 30 nm on SiN and SiO_2, with no substantial deposition on Si-H. This selectivity has been ascribed to Si-H reacting with the $SbCl_5$ oxidant, preventing subsequent monomer oxidation on that surface.

To control selectivity, three surface treatments were explored: 1) one cycle of MoF_6/N_2 gas for 1s/30s, respectively, at 250℃; 2) N,N-dimethylamino-trimethylsilane (DMATMS) vapor for 15 s at 250℃; and 3) DMATMS for 15 s at 250℃ followed by liquid water for 15 minutes at room temperature. Figure 1 shows the resulting PEDOT thickness (from ellipsometry) vs deposition time. The MoF_6 vapor had minimal influence on growth on SiN but converted the SiO_2 from growth to non-growth, due to conversion of reactive Si-OH to non-reactive Si-F, while simultaneously converting the Si-H from non-growth to growth, ascribed to the presence of some Mo on the Si-H. Additional control was achieved using DMATMS and liquid water. The DMATMS vapor inhibited deposition on Si-OH but had no effect on Si-H, and minimal effect on SiN, consistent with DMATMS reacting preferentially to consume Si-OH groups to produce a hydrophobic $Si(CH_3)_3$ surface. After DMATMS, we find that exposure to liquid water selectively "actives" the Si-H via surface oxidation, with little change to the DMATMS-modified SiO_2, allowing ASD on SiN and Si-H regions vs SiO_2.

Overall, these results demonstrate the concept of selectivity control for ASD of one material on "multi-color" substrates, thereby providing insight into means to adjust selectivity for a variety of future applications.

1. Kim, J.-S. et al., *Chem. Mater.* **2021**, 33, 23, 9221-9239
2. Carroll, N. M. et al., *Chem. Mater.* **2024**, 36, 8, 3655-3665

2:30pm **AS-WeA-5 Annealing PEDOT Thin Films to Generate a Selectively Deposited Etching Hard Mask Layer**, ***Nicholas Carroll**, Carwynn Rivera, Man Hou Vong, Hannah Margavio,* North Carolina State University*; Hwan Oh,* Brookhaven National Laboratory*; Gregory Parsons,* North Carolina State University

As feature sizes in contemporary device architectures aggressively shrink, enhanced understanding of area-selective deposition (ASD) is critical to support advanced patterning and feature alignment. In recent years, new strategies have been developed for ASD of poly(3,4-ethylenedioxythiophene) (PEDOT) conjugated polymer by molecular layer deposition (MLD) and chemical vapor deposition (CVD) on SiO_2 vs. Si-H,[1] orthogonal ASD of W and PEDOT,[2] and inverted "dual-tone" ASD of PEDOT on Si-OH vs. SiO_2-TMS.[3]

Hard masks for etching are a key application for ASD materials. However, conjugated polymers are expected to etch quickly during plasma exposure. In this work, we describe the effect of post-deposition annealing on the etch rate of PEDOT during O_2 plasma and demonstrate means to "reactivate" the film to convert it from non-etching to etching. In their as-deposited form, the materials etch readily, as expected. As shown in Figure 1(a), the etch rate decreases by 50% upon annealing at 250 °C and decreases to near zero after heating to 350 °C. XPS analysis in Figure 1(b) shows an increase in the concentration of the Sb oxidant after annealing. Also, Figure 1(c-e) shows HAADF STEM images and an EDS elemental map of a film after annealing 350 °C. The EDS indicates that upon annealing, Sb segregates to the film surface. We hypothesize that this Sb layer contributes to the observed reduction in etch rate. This is consistent with XPS after etching in Figure 1(f) showing Sb present in the film.

Interestingly, we find that after treating the annealed PEDOT in deionized liquid H_2O at 80 °C for 10 minutes, the films readily etch in O_2 plasma, as indicated by XPS in Figure 1(g). The ability to enable plasma etching resistance for a selectively deposited conjugated polymer film opens innovative avenues and strategies for protecting surfaces during plasma deposition or selective etching steps. These findings bolster the significance and versatility of ASD for modern manufacturing methodologies.

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

[2] H. Oh et al., *Chem. Mater.* **35**, 11 (2023).

[3] N. Carroll et al., *Chem. Mater.* **36**, 8 (2024).

2:45pm **AS-WeA-6 Ring-Opening Enhanced Etching of Cyclosiloxanes for Area-Selective MLD of SiOC(H) Thin Films**, ***Xiaocheng Huang**, Weiwei Du, Yuanhao Shen, Pengzhe Cai, Delong Liu, Junjie Zhao,* Zhejiang University, China

As the feature sizes of semiconductor devices continue to shrink, edge placement errors caused by the overlay variations in lithography will lead to dramatically increased failure probability and durability issues. Area selective deposition (ASD), a technique that enables precise deposition on specific material surface, is promising for the fabrication of fully self-aligned vias (FSAV) for solving above challenges. ASD processes relying on inherent surface differences circumvents additional processing steps for surface pre-functionalization. However, these methods often suffer from a loss of selectivity after extended number of deposition cycles due to inevitable nucleation on the non-growth surface. Here, we report a novel ASD strategy for SiOC(H) thin film based on etching enhancement achieved through selective ring-opening of cyclosiloxane precursor. *In-situ* DRIFT spectra reveal ring-opening of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V_3D_3) precursor on cobalt oxide surfaces. Furthermore, we demonstrate that ring-opening promotes the plasma etching rate. Based on these findings, we developed an etching-enhanced ASD which integrates molecular layer deposition and plasma etching in A-B-C supercycles. We obtained an exceptionally high area selectivity for SiOC(H) thin films on Co/SiO_2 patterns even after extended number of cycles. Cross-section TEM and high-resolution EDX mapping images confirm negligible nucleation on the CoO_x surface. Our work pioneers the exploration of precursor isomerization for etching-enhanced ASD and offers a new strategy for self-aligned SiOC(H) patterns.

3:00pm **AS-WeA-7 Area-Selective Molecular Layer Deposition of Polymer Thin Films for Contact Hole/Trench Shrinking***, **Pengzhe Cai**, Junjie Zhao,* Zhejiang University, China

With the rapid advancement of integrated circuit technology nodes, the demand for critical size shrinking in nano-fabrication has been growing. The traditional lithography-etching method struggles to achieve the desired pitch size while maintaining cost efficiency. Contact hole/trench shrinking is a post-processing step applied before or after etching transfer, enabling patterns that exceed the lithographic resolution limit. However, when used in back-end-of-line fabrication, contact hole/trench shrinking faces the limitations of conventional wet chemistry, which restricts its full potential. Here, we report an area-selective deposition (ASD) method for contact hole/trench shrinking. We developed a plasma-enhanced initiated molecular layer deposition (PEiMLD) process that selectively grows polymer thin films onto previously defined photoresist patterns. In this all-dry PEiMLD process, remote plasma activation on the polymer backbones of the photoresist initiates radical polymerization, grafting molecular layers to the photoresist. In contrast, common dielectric surfaces (e.g. SiO_2) are inert to such activation and thus maintained as non-growth surfaces. Thereby, we achieved an area selectivity as high as 95% on PMMA/SiO_2 substrates and demonstrated contact hole/trench shrinking by reducing the trench diameter from 126 nm to 24 nm. Moreover, attributing to the versatile options of monomers for radical polymerization, this PEiMLD method can also be applied to interfacial engineering, enabling potential applications beyond contact hole/trench shrinking. Our method paves the way for alternative nanofabrication strategies that are promising for reducing the demand for lithography and lowering manufacturing costs.

3:15pm **AS-WeA-8 Catalytic Oxygen Dissociation for Area-Selective HfO_2 Deposition on Cobalt through Selective PMMA Etching***, **Enzo Novoselic**, Christophe Vallée, Natalya Tokranova,* University at Albany-SUNY

Area-selective deposition (ASD) of thin films is critical for advanced semiconductor manufacturing, yet conventional methods often suffer from "mushrooming" defects due to poor selectivity at feature edges and lateral expansion of the isotropic growth. This work presents an alternative approach to ASD on cobalt (Co) substrates while avoiding mushrooming, leveraging catalytic dissociation for both polymer etching and selective deposition. The use of selective catalytic dissociation has been demonstrated for the etching and deposition steps. As an example, Zhang et al. [1] demonstrated selective etching on Pt/Ru/Cu/Ti, while Joseph et al. [2] demonstrated selective deposition on Pt. In this work, a polymethyl methacrylate (PMMA) material is non-selectively deposited on all exposed surfaces (Co and silicon). Through catalytic O_2 dissociation, PMMA atop Co is selectively etched in an atomic layer deposition (ALD) tool, while PMMA on silicon remains intact. Subsequently, the ALD step is performed in the same chamber at the same surface temperature, and under catalytic conditions, enabling selective growth on Co while suppressing nucleation on PMMA. Finally, PMMA is stripped, yielding structures exclusively on Co with sub-nanometer precision and vertical sidewalls.

We expect to show results demonstrating that the catalytic processes achieve near-complete selectivity and eliminate lateral overgrowth, addressing the mushrooming effect common in ASD. The use of catalytic dissociation for both etching and deposition steps simplifies integration into existing fabrication workflows. This approach offers a scalable pathway for advanced node patterning, particularly in back-end-of-line (BEOL) metallization and gate oxide applications where material selectivity and feature definition are paramount.

[1] Zhang, C.; Leskelä, M.; Ritala, M. Self-Aligned Thin-Film Patterning by Area-Selective Etching of Polymers. Coatings 2021, 11, 1124. https://doi.org/10.3390/coatings11091124

[2] Joseph A. Singh, Nick F. W. Thissen, Woo-Hee Kim, Hannah Johnson, Wilhelmus M. M. Kessels, Ageeth A. Bol, Stacey F. Bent, and Adriaan J. M. Mackus. Chemistry of Materials 2018 30 (3), 663-670. https://doi.org/10.1021/acs.chemmater.7b03818

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