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°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 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℃ 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℃), 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℃ to 2.8% at 375℃, leading to reduced resistivity (Fig. S2). In contrast, X-ray diffraction (XRD) results revealed that the film exhibited the highest crystallinity at 275℃ (Fig. S3). Additionally, post-deposition forming gas annealing was performed on the film deposited at 275℃ at the back-end-of-line (BEOL) thermal budget of 400℃ 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.

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} Aμm^{-1} on-current density, 40 cm^{2}V^{-1}s^{-1} hole mobility, and 0.9 k$\Omega\mu$m 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.

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.

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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.

References

[1] Ravsher, Taras, et al. *IEEE Transactions on Electron Devices* 70.5 (2023): 2276-2281.

[2] Sung, Ha-Jun, et al. *Advanced Science* 11.44 (2024): 2408028.

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***, **Jihoon Jeon**, 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 ALD Young Investigator Award Finalist: 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***, **Jihoon Park**, 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*; Il Hwi Lee,* SurplusGLOBAL, Inc., Republic of Korea*; Nam Young Kim,* SurplusGLOBAL Inc., 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.

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

Moderators: Dennis Hausmann, Lam Research, **Reza Jafari Jam**, AlixLabs

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 N. 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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2:15pm **AA-TuA-4 Bottom-Up Mo Fill for Metal Interconnect Applications: Selective and Superconformal Approaches**, ***David Mandia***, *Matthew Griffiths, Arya Shafiefarhood, 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.

3:15pm **AA-TuA-8 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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ALD Applications
Room Event Hall - Session AA-TuP
ALD Applications Poster Session

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°C, 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, Republic of Korea

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°C [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-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-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-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-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-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 (≥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 ≥ 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, **Seungwan Ye**, Hong Keun Chung, Jihoon Jeon,* 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, Republic of Korea

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°C). 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 Towards 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, Republic of Korea

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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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*, Jeong Hwan Han, **Seon Gu Choi**, Jae Hyeon Lee,* 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

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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. The critical AlN IL thickness is estimated to be 20 nm.

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-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-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-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-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°C, ZrC: ~3420°C, ZrN: ~2980°C), 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-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.

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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-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, Republic of 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*; Yoon Soo Hyun,* Hanyang University, Republic of 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-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, Jeong Min Yang, Dong Jun Song,* KoMiCo Ltd., 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-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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AA-TuP-76 Effect of Interfacial Layer on Ferroelectricity of $Hf_{1-x}Zr_xO_2$ 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 $Hf_{1-x}Zr_xO_2$ 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-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-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-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 HfO_2 Thin Films Produced Via Novel Catalytic Atomic Layer Deposition Process*, Sara Harris, Dane Lindblad, Aaron Wang, Arrelaine Dameron, Matthew Weimer, **Brandon Woo**,* 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 3.3×10^{-9} to 8.1×10^{-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, **Shasha Liu**,* 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-89 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.

AA-TuP-90 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 $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NCM622) cathodes to enhance the performance and durability of lithium-ion batteries.

Single-crystal $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (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.

AA-TuP-91 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 μC/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-92 Implementation of Firing Type Threshold Device Using Atomic Layer Deposited Vanadium Oxide*, **Yong Tae Kim**, Jaeyeong Heo,* Chonnam National University, Republic of Korea*; Pyeongkang Hur, Junwoo Son,* Seoul National University, Republic of Korea

In the field of semiconductors, there is an increasing demand for high-performance/low-power computing hardware. To meet this demand, researchers are currently exploring devices that simulate the human brain and deviate from the traditional von Neumann method. Specifically, phase transition metal oxide materials have been found to exhibit a rapid insulator-metal transition firing-type switching phenomenon at a certain threshold voltage depending on voltage application. This phenomenon is characterized by volatile behavior that returns to the original state when the voltage is removed, as well as a very large current change and a fast switching speed of several nanoseconds.

To develop a high-performance phase transition device, it is essential to achieve precise control over the material properties of thin films. Previous research on phase transition materials has mainly relied on PVD-based processes such as sputter. However, this approach has significant limitations when it comes to implementing a phase transition oxide on a complex 3D structure due to poor step coverage. To address this challenge, we developed an ALD-based vanadium oxide (VO_2) process technology that enables the successful formation of a VO_2 thin film through subsequent heat treatment. Furthermore, the characteristics of thin films under various heat treatment conditions were analyzed using various analysis equipment, ultimately leading to the successful implementation of an ALD-based VO_2 firing type device.

AA-TuP-93 Introducing a Surface Acoustic Wave-Based Miniaturized Aerosol Source for Controlled Liquid Precursor Delivery in ALD Processes*, **Mehrzad Roudini**, Andreas Winkler,* IFW, Germany

Atomic Layer Deposition (ALD) demands high precision in the delivery of liquid precursors to achieve uniform thin films. We present a novel miniaturized aerosol source technology, utilizing surface acoustic wave (SAW) techniques, to introduce liquid precursors efficiently and with exceptional control. In SAW aerosol generation (also known as SAW atomization), aerosols are formed by the interaction of a microscale liquid layer with an acoustic wave field on the surface of a microfluidic chip, which is the driving force of the miniature aerosol generator [1]. This integrated

system enables precise manipulation of liquid flow rates and generated droplet size, resulting in enhanced control over precursor evaporation. By fine-tuning the flow dynamics, this innovative approach promises significant improvements in process efficiency, uniformity, and scalability for industrial ALD applications. Our SAW-based aerosol source offers a compact, energy-efficient solution for next-generation ALD systems, paving the way for more reliable and cost-effective thin film deposition in diverse industrial applications.

In our recent study, we analyzed aerosol droplet characteristics using laser diffraction, a well-established optical technique for droplet size measurement (Fig. 1a). Our results revealed a clear correlation between the surface acoustic wave (SAW) wavelength, liquid flow rate, and resulting droplet size [2]. The developed SAW-based aerosol generator demonstrated the capability to operate at extremely low liquid flow rates — down to a few microliters per minute — with input powers as low as 1 W [2].

To explore its potential for aerosol-based printing, we successfully generated aerosols from a fluorescent quantum dot ink and deposited them on a SiO_2-coated Si substrate using a focusing nozzle (Fig. 1c). Moreover, we integrated the SAW aerosol source into a commercial ALD (VEECO) system using a KF-40 flange-compatible setup (Fig. 1b). In a proof-of-concept experiment, we used DI water as the precursor and achieved a conformal ZnO thin film with a thickness of 49 nm after 300 ALD cycles. These results demonstrate that SAW-based aerosol generation is a promising technique for introducing liquid precursors into the gas phase in ALD processes. Ongoing work is focused on evaluating this method with low-vapor-pressure precursors to further expand its applicability.

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AA-TuP-94 Enhancing Stability and Performance of LMBs Through Al2O3-Assisted SEI Protection on SnO2-Coated Cu Current Collectors by ALD*, Roy Byungkyu Chung,* Kyungpook national university*; **Dawon Lee**, Jiseop Byeon,* Kyungpook national university, Republic of Korea

Recent advances in rechargeable battery technology have intensified the search for next-generation systems with higher energy densities and longer cycle lives. Lithium metal batteries (LMBs) have emerged as a promising candidate, offering a substantially greater theoretical capacity than conventional lithium-ion batteries. However, practical implementation of LMBs is hampered by issues such as dendrite growth and the instability of the Li plating–stripping interface.

In our previous work, we demonstrated that depositing a thin SnO_2 layer onto Cu current collectors via atomic layer deposition (ALD) can effectively facilitate uniform Li nucleation and suppress dendrite formation, thus enhancing both the efficiency and cycle life of LMBs[1]. Nevertheless, the intrinsic volume expansion of SnO_2 during repeated charge–discharge cycles exerts mechanical stress, which may lead to cracks or ongoing solid electrolyte interphase (SEI) consumption, ultimately causing gradual capacity loss.

To address these challenges, we introduced an Al_2O_3 artificial SEI layer on top of the SnO_2-coated Cu. By depositing Al_2O_3 layers ranging from 0.5 nm to 20 nm and performing electrochemical analyses in Li metal half cells, we found that a 2 nm Al_2O_3 coating provided the highest efficiency and longest cycle life. We suggest that this performance to the Al_2O_3 film's ability to mitigate mechanical degradation while protecting the current collector from oxidation. Consequently, this study offers new insights into the design of artificial SEI layers, underscoring their critical role in achieving sustained operational reliability in LMBs.

AA-TuP-95 Low-Temperature Processed Al-Doped HfO_2/IGZO Ferroelectric Thin Films for High-Performance Non-Volatile Memory Devices*, **Lee Gahong**,* Sungkyunkwan University, Republic of Korea

This study develops high-performance HfAlO (Al-doped HfO_2) thin films processed at a low annealing temperature of 350°C for non-volatile memory (NVM) applications. IGZO (Indium Gallium Zinc Oxide) was used as the channel layer, deposited via sputtering at a thickness of 20 nm on top of the HfAlO thin films, aiming to explore the potential for applications in memory technologies with thermal constraints. The atomic layer deposition (ALD) method was used to deposit Al-doped HfO_2 films with Al concentrations of 1%, 3.7%, 4.5%, 7%, and 9% mol on p-type silicon substrates. After deposition, rapid thermal annealing (RTA) was performed at 350°C for 1 or 5 minutes. Electrical characterization confirmed the activation of ferroelectricity, with 2Pr (remanent polarization) values varying depending on Al doping concentration, annealing time, and the presence of IGZO. The films with 3.7 mol% Al doped and annealed for 5 minutes exhibited the best performance, achieving 2Pr = 18.3–20 μC/cm^2 and a storage window of 0.3–3.5 V. The IGZO channel layer was sputtered onto the HfAlO films, and electrical evaluation confirmed the stability of the ferroelectric phase and excellent polarization strength. This study suggests that precise doping and low-temperature processing enable successful integration of HfAlO into high-performance, IGZO-based non-volatile memory devices, demonstrating the suitability of low-temperature treatments for memory technologies sensitive to thermal conditions.

AA-TuP-96 Effect of Proton Irradiation on the Electrical Performance on SnO_2 Thin Film Transistor with ITO Electrodes*, **Huiseung Kim**, Suhyeon* *Park, Dawon Lee, Jiseop Byeon, Jeongin Seo,* Kyungpook National University, Daegu, Republic of Korea*; Jeongtae Kim, Dong-seok Kim,* Korea Atomic Energy Research Institute, Republic of Korea*; Roy Byungkyu Chung,* Kyungpook National University, Daegu, Republic of Korea

As the aerospace industry continues to grow, there is increasing interest in the performance of electronics operating under extreme environments such as space. Among various electronics, oxide-based thin film transistors (TFTs) have emerged as essential components in various information technology applications. For aerospace use of the oxide TFTs, first and foremost, it is crucial to understand how space radiation affects the performance of TFTs. The channels of oxide TFTs are typically made from materials such as IGZO, IZO, ZnO, SnO2, etc. Numerous studies have evaluated the effects of radiation on IGZO, IZO, and ZnO-based TFTs. [1-4] However, the impact of high-energy radiation on SnO2-based TFTs remains largely unexplored.

Among various types of radiation, protons are used to comprehensively analyze the effects of space radiation because they not only constitute a significant component of the space radiation environment but also allow for precise assessment of radiation-induced damage by measuring changes in parameters such as carrier density, transconductance, and other electrical properties. [5, 6]

In this study, SnO_2 films with thicknesses of 6.5 and 20 nm thick were prepared using thermal atomic layer deposition. The 20-nm films were used for various material characterizations, while the 6.5-nm films were used for TFT fabrication. [7, 8] Both the films and devices were irradiated with a 5-MeV proton beam at fluences of 10^{11}, 10^{12}, 10^{13}, and 10^{14} cm^{-2}. Changes in the physical properties of the SnO_2 films were examined by Hall measurements and x-ray photoemission spectroscopy. For the TFTs, we used ITO (thickness = 100 nm) as the source and drain electrodes. Device performance was evaluated using a semiconductor parameter analyzer. In this presentation, we discuss a systematic investigation into the impact of proton irradiation on device performance, with particular attention to variations in the material properties.

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AA-TuP-97 Fabrication of p-type SnO Thin Films via Thermal ALD*, **Suhyeon Park**,* *Huiseung Kim, Dawon Lee, Jiseop Byeon, Jeongin Seo, Roy Byung Kyu Chung,* Kyungpook National University, Daegu, Republic of Korea

Tin oxide (SnOx) is a promising materials for oxide semiconductor devices such as thin-film transistors (TFTs), due to their tunable electronic properties derived from the multivalent nature of Sn^{2+} and Sn^{4+}. SnO_2 is a typical n-type semiconductor, while SnO shows p-type conductivity, making it suitable as a complementary material in complementary metal oxide semiconductor (CMOS) circuits. However, SnO is thermodynamically unstable and easily oxidized, requiring precise stoichiometry control and optimized deposition processes for stable p-type SnO formation.

Previous studies have attempted to realize p-type SnO using atomic layer deposition (ALD) processes with Sn^{2+}based precursors. However, these precursors face limitations in terms of either commercial availability or cost, which hinders their practical use in research. To address this issue, we employed Tetrakis(dimethylamino)tin(IV) (TDMASn), a Sn^{4+}-based organometallic precursor, to fabricate SnOx thin films via thermal ALD.

After deposition of SnO_X films, post-annealing was carried out in a forming gas atmosphere to reduce the films to SnO. To prevent reoxidation and improve long-term stability, an Al_2O_3 capping layer was additionally deposited on the film surface. The oxidation states were analyzed using X-ray photoelectron spectroscopy (XPS), and the electrical properties were evaluated through Hall effect measurements and TFT characterizations.

This study demonstrates the feasibility of forming stable p-type SnO films using a cost-effective precursor. By applying an Al_2O_3 capping layer, we confirmed the potential to enhance the environmental stability of the SnO films. Based on these process conditions, the integration of SnO_2 and SnO is expected to contribute to the future realization of tin oxide-based CMOS technology.

AA-TuP-99 Atomic Layer Infiltration of ZnO on Polyimide Substrates for Flexible Encapsulation Hybrid Film*, Ji Ho Jeon, Jeong Hwan Han, Byung Joon Choi, Su Min Eun, Si Eun Jung, Ye Jin Jung,* Seoul National University of Science and Technology, Republic of Korea*; Kwanhyuck Yoon, Woo Yong Sung,* Samsung, Republic of Korea

Flexible electronic devices, such as OLEDs, are emerging as key components of next-generation display technology. However, their susceptibility to moisture and oxygen presents a major challenge for long-term stability. This issue is particularly critical for flexible devices, where repeated bending can cause cracks or delamination in the encapsulation layer, demanding more efficient sealing solutions. Thin film encapsulation (TFE) technology has been developed to address this concern, but achieving both high flexibility and excellent barrier properties simultaneously remains difficult. Conventional dyad-type TFE, which alternates inorganic and organic layers, improves moisture barrier performance by extending the penetration path of moisture and oxygen. However, this approach increases film thickness, reduces flexibility, and suffers from long-term stability issues due to pinholes and cracks at the interfaces. Thus, hybrid structures combining the benefits of organic and inorganic materials are sought after.

In this study, we developed an ultra-thin, highly flexible single-layer encapsulation film by infiltrating ALD ZnO into a polyimide (PI) substrate using an atomic layer infiltration (ALI) process. This method fills the free volume in the polymer with ZnO, forming a dense organic-inorganic hybrid layer. The physical and optical properties of the hybrid film were analyzed through several techniques. Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) were used to confirm the infiltration depth of ZnO into the PI substrate. The moisture barrier performance of the encapsulation film was evaluated using a Mocon to determine the water vapor transmission rate (WVTR). The results demonstrate that the PI/ZnO hybrid encapsulation film, produced using ALI technology, holds significant promise as a high-performance, single-layer encapsulation solution for flexible electronic devices.

Acknowledgement

This work was supported by National Research Foundation of Korea (NRF) grants funded by the Ministry of Education (MOE) (NRF-2021R1A6A1A03039981) and by the Technology Innovation Program (RS-2024 00467233) through the Korea Planning & Evaluation Institute of Industrial Technology(KEIT) funded by the Ministry of Trade, Industry & Energy(MOTIE, Korea).

AA-TuP-100 Effect of Different Counter Reactants on Interfacial Oxidation and Electrical Properties of HfO_2 Grown on TiN by Atomic Layer Deposition*, Aravind H. Patil, Byung Chan Lee, Seoung won Shim, Su min An, Minheyok Lee, Young-ho Kang, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

The continued miniaturization of complementary metal-oxide-semiconductor (CMOS) gate stacks requires the integration of ultra-thin, high-k dielectric materials such as HfO_2 by atomic layer deposition (ALD). During HfO_2 ALD on TiN surfaces, however, the oxidant exposure on the TiN substrate leads to the formation of TiO_2 or TiO_xN_y, which deteriorates the electrical properties. Therefore, counter reactant selection is a key parameter for minimizing the interfacial oxidation layer as well as film quality. In this study, we investigated the ALD of HfO_2 on TiN using cyclopentadienyltris(dimethylamino)hafnium ($CpHf(Nme_2)_3$) as a precursor and H_2O, H_2O_2, and O_3 as different oxidation reactants. The effect of each oxidant on the formation of the interfacial oxidation layer and film quality was investigated by employing density functional theory (DFT) calculations as well as experimental analyses. Notably, the results showed that H_2O exhibited the lowest interfacial oxidation, while containing higher carbon impurities, whereas O_3 showed better film purity, but exhibited increased interfacial oxidation thickness. H_2O_2 exhibited intermediate behavior, maintaining film purity while minimizing interfacial oxidation. These findings provide insights into reactant selection for HfO_2 ALD, which will be useful for next-generation ultra-thin high-k dielectrics.

ALD Applications
Room Halla Hall - 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.

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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_3O_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_3O_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 BC - Session AA2-WeM

Display Applications

Moderators: Fan Yang, Huazhong University of Science and Technology, **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 - Session AA3-WeM
Other Energy Applications

Moderators: Rong Chen, Huazhong University of Science and Technology, **Hyeontag Jeon**, Hanyang University

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, **Joshua Sraku Adu,*** Korea Research Institute of Chemical Technology (KRICT), Republic of Korea

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 Applications
Room Halla Hall - 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 ALD Young Investigator Award Finalist: 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 ALD Young Investigator Award Finalist: 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.

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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)

ALD Applications
Room Halla Hall - Session AA2-WeA

Battery Applications II

Moderators: Il-Kwon Oh, Ajou University, **Junjie Zhao**, Zhejiang University

4:15pm **AA2-WeA-12 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.

[1] Gölert et al, 2017, https://doi.org/10.1016/j.nanoen.2017.01.054

[2] Sallaz et al, 2024, https://doi.org/10.1021/acselectrochem.4c00022

4:30pm **AA2-WeA-13 Enabling Uniform Lithiation in Solid-State Synthesis by Preventing Pre-Matured Surface Grain Coarsening Through Grain Boundary Engineering**, ***Yifan Wu**, Jin Xie,* ShanghaiTech University, China

Solid-state reactions are a foundational and widely used method for synthesizing inorganic solid materials, especially metal oxide ceramics. In typical processes, solid precursors are mixed and heated to high temperatures to induce heterogeneous reactions forming new phases. However, solid-state diffusion-driven phase transitions at elevated temperatures often introduce structural inhomogeneity. For example, Li-ion battery cathodes such as $LiTMO_2$ (TM = Ni, Mn, Co) are commonly produced via high-temperature reactions involving $TM(OH)_2$ precursors and lithium sources (e.g., LiOH) in oxidative atmospheres. This complicated non-equilibrium reaction also suffers inherent heterogeneity arises from insufficient solid state lithium diffusion.

While previous studies emphasize optimizing lithium diffusion and particle growth, the intrinsic heterogeneity in solid-state calcination calls for more advanced control strategies. In this work, we found that early-stage formation and coalescence of primary layered particles on polycrystalline $Ni_{0.9}Co_{0.05}Mn_{0.05}(OH)_2$ ($NCM(OH)_2$) hinder lithium diffusion, resulting in structural non-uniformity and reduced electrochemical performance. To overcome this, we developed a conformal WO_3 coating via atomic layer deposition (ALD), which effectively regulated lithium transport and suppressed particle coarsening at grain boundaries during calcination. In situ high-temperature X-ray diffraction (XRD) revealed that the WO_3 layer shifted the early-stage reaction from growth-dominated to nucleation-dominated, thus maintained the grain boundary integrity and improved reaction homogeneity. Scanning transmission electron microscopy (STEM) analysis confirmed that rocksalt phases and voids formed in the uncoated product which is signatures of poor lithium diffusion, and they were absent in the WO_3-coated product. As a result, the modified cathode delivered significantly improved performance (92.9% capacity retention after 200 cycles, vs. 78.7% for the pristine sample) under 2.8V-4.4V charging/discharging cycles.

This work advances the understanding of early-stage solid-state reactions and provides a pathway to achieve homogeneity in high temperature solid-state reactions for next-generation cathode materials through grain-boundaries engineering by ALD technique.

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, **Han-Bo-Ram Lee**, Incheon National University

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 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.

4:30pm **AA3-WeA-13 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.

4:45pm **AA3-WeA-14 Closing Remarks and Awards***,*

ALD Applications
Room Tamna Hall BC - 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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4:45pm **AA4-WeA-14 Closing Remarks and Awards in Tamna Hall A***,*

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