Atomic Layer Etching
Room Tampa Bay Salons 3-4 - Session ALE-MoA
Plasma and/Energy-Enhanced ALE I

Moderators: Heeyeop Chae, Sungkyunkwan University (SKKU), **Keren J. Kanarik**, Lam Research

4:00pm **ALE-MoA-11 Atomic Layer Processing of Electronic Devices***, **Andreas Fischer**, Thorsten Lill,* Clarycon Nanotechnology Research, Inc.*; Fred Roozeboom,* University of Twente, Netherlands **INVITED**

Atomic Layer Etching (ALE) is increasingly adopted to meet atomic-scale patterning requirements in advanced semiconductor manufacturing. This work presents a comprehensive technical analysis of ALE fundamentals, process mechanisms, and performance metrics with emphasis on processing outcomes relevant to nanoscale and 3D device integration. ALE utilizes sequential, self-limiting surface reactions to achieve controlled etch-per-cycle behavior, enabling sub-nanometer material removal, excellent across-wafer uniformity, and reduced aspect-ratio dependent etching compared to reactive ion etching (RIE). Thermal and plasma-assisted ALE regimes are evaluated with respect to etch selectivity, damage mechanisms, and directionality. Thermal ALE demonstrates highly selective isotropic etching driven purely by surface chemistry, achieving minimal plasma-induced damage and enabling precise removal of oxides and high-k materials critical for advanced gate stacks and 3D architectures. Plasma-assisted ALE enables tunable anisotropy through low-energy ion activation while maintaining atomic-scale precision and improved surface smoothness relative to conventional plasma etching, supporting applications including contact hole formation, sidewall damage removal, and nanoscale pattern transfer. Process comparisons highlight ALE's superior uniformity, reduced excess-energy damage, and enhanced selectivity driven by self-limiting surface chemistry and controlled ion energies. Performance trade-offs—including throughput, precursor safety, chamber contamination, and temperature control—are analyzed to assess scalability toward high-volume manufacturing. The results demonstrate that ALE provides a robust pathway toward atomic-level etch control required for next-generation transistors, stacked memory devices, and heterogeneous material integration. Continued advances in precursor design, plasma control, and process optimization are expected to further expand ALE deployment in future semiconductor nodes.

4:30pm **ALE-MoA-13 Plasma-Enhanced Atomic Layer Etching of Mbe- and Ald-Grown Ultrathin HZO for Ferroelectric Tunnel Junctions***, **Marimuthu Rajendiran**, Nikolai Andrianov, Venkata Raveendra Nallagatla, Joaquín Miranda,* Silicon Austria Labs GmbH, Austria*; Polychronis Tsipas, Stavros Kitsios,* Institute of Nanoscience and Nanotechnology, National Center for Scientific Research "Demokritos", Greece*; Nathan Savoiad, Alexander Flasbyd,* Integrated Systems Laboratory, D-ITET, ETH Zurich, Switzerland*; Athanasios Dimoulas,* Institute of Nanoscience and Nanotechnology, National Center for Scientific Research "Demokritos", Greece*; Laura Bégon Loursd,* Integrated Systems Laboratory, D-ITET, ETH Zurich, Switzerland*; Deluca Marco,* Silicon Austria Labs GmbH, Austria

Abstract

Ferroelectric tunnel junctions (FTJs) based on $Hf_{0\cdot5}Zr_{0\cdot5}O_2$ (HZO) are promising candidates for next-generation non-volatile memory and neuromorphic computing owing to their CMOS compatibility, low power consumption, and fast switching speed. Scaling HZO to ultrathin dimensions (<4 nm) is critical to enhance FTJ performance in neuromorphic computing while maintaining robust ferroelectricity and energy efficiency. In this work, we present a systematic investigation of plasma-enhanced atomic layer etching (PE-ALE) of HZO thin films grown by molecular beam epitaxy (MBE), or by plasma-enhance atomic layer deposition (PEALD). The PEALE process employs a $Cl_2/BCl_3/Ar$ plasma chemistry at a substrate temperature of 50 °C, targeting controlled, layer-by-layer material removal. To support process development, density functional theory (DFT) and molecular dynamics (MD) simulations are used to establish a macroscopic fluid-dynamics-based framework for atomic layer etching, enabling identification of the energy window favorable for monolayer-scale removal of HZO. By tuning key process parameters such as RF power, plasma exposure time, and gas composition, an ALE window for HZO is identified. Furthermore, a comparative study between MBE- and ALD-grown HZO films highlights differences in etching behavior, including process window, surface morphology evolution, and implications for achieving ultrathin ferroelectric layers. These results provide important insights into thickness scaling strategies for ferroelectric HZO and offer a pathway to improve the FTJs device performance.

Reference

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4. Hoffmann, M.; Murdzek, J. A.; George, S. M.; Slesazeck, S.; Schroeder, U.; Mikolajick, T. *Atomic Layer Etching of Ferroelectric Hafnium Zirconium Oxide Thin Films Enables Giant Tunneling Electroresistance.* ***Appl. Phys. Lett.*****2022**, *120,* 122901.

4:45pm **ALE-MoA-14 Atomic Layer Etch Process for Nb and Ta Using CF_4/H_2 Plasma***, **Ryan Walsh**,* University of Nevada, Reno

Atomic layer etch (ALE) processes were developed for Nb and Ta on Si using a CF_4/H_2 plasma for the surface modification step and Ar^+ irradiation for the removal step. These materials are widely used in superconducting quantum device fabrication. The processes were investigated with respect to RF bias, CF_4/H_2 dose time, and Ar^+ etch time in order to identify the ALE window and saturation points. Ta and Nb yielded identical 0.23 +/- 0.01 nm/cycle etch rates for a soft-saturation process. The total cycle time was 16 sec with synergies of > 99% and 87% for Ta and Nb, respectively, and surface roughnesses were significantly reduced as compared to both the as-deposited films and an RIE process with similar chemistry. Over-saturated and under-saturated process were also investigated. A significant difference in EPC between different phases of Tantalum was also observed, suggesting crystal structure plays an important role in etch dynamics. Tantalum Nitride was also investigated due to its thin native oxide, which could help improve superconducting device performance.

To demonstrate the usability of these processes in industry, the effect of reduced purge times on ALE process performance was studied. For all processes the etch per cycle, selectivity, synergy, and surface roughness before and after were reported. A full process for Si was not studied but relevant parameters were reported. These processes are promising for real world manufacturing of devices that are sensitive to damage and require precise etch control.

5:00pm **ALE-MoA-15 Uncovering Plasma-Enhanced Atomic Layer Etching of Silicon Nitride Using Molecular Dynamics Simulations with Machine Learning Force Fields***, **Sungwon Park**, Gyeong Hwang,* University of Texas at Austin

Plasma-enhanced atomic layer etching (PEALE) enables anisotropic etching with atomic-scale precision and low roughness, yet its detailed mechanism remains unclear. Here, we present a molecular dynamics framework with machine-learning force field (MLFF) to study SiN_x PEALE driven by sequential CF_4 adsorption and Ar^+ bombardment. Multi-cycle simulations capture the evolution of the chemically modified layer and reveal descriptors that govern etch behavior.

At low Ar energy (30 eV), the modified layer gradually evolves toward a pseudo-steady state in composition and thickness. Fluorine accumulation saturates at $F/Si \approx 1.0$, while carbon remains at consistently low levels due to preferential removal as volatile C–N-containing species (e.g., NCF). Silicon desorbs mainly as SiF_x (SiF_4 dominant with substantial SiF_2), and nitrogen is removed primarily as N_2. The per-cycle N/Si removal ratio converges to ~1.3, indicating that near-stoichiometric SiN_x etching is obtained.

At higher Ar energies (50–70 eV), however, deeper fluorine penetration combined with increased nitrogen sputtering produces an under-coordinated, Si-rich surface. CF_4-derived carbon readily binds to the surface, forming a rigid SiC network within the modified layer. This suppresses SiF_x formation and increases surface roughness, ultimately leading to etch stop.

These results reveal an Ar–energy–dependent transition in carbon fate—from volatile removal to SiC formation—that determines whether SiN_x remains in a steady-etch regime or reaches etch stop. Building on this mechanistic picture, we will also discuss practical strategies to suppress SiC buildup.

5:15pm **ALE-MoA-16 Comparative Study on Atomic Layer Etching Characteristics of Conventional C_4F_8 and Low-GWP C_3F_6**, ***Dong Ki Lee**, Chul-Hee Cho, Inho Seong, Dayeon Kang, Shinjae You,* Chungnam National University, Department of Physics, Republic of Korea

Atomic Layer Etching (ALE) has emerged as a critical technology for achieving atomic-scale precision in next-generation semiconductor fabrication. However, the high Global Warming Potential (GWP) of conventional perfluorocarbon gases widely used in the process, such as C_4F_8, necessitates the urgent development of eco-friendly alternative processes. In this study, we investigate the ALE characteristics of C_3F_6, a promising low-GWP candidate, in comparison with conventional C_4F_8 on silicon oxide (SiO_2) and silicon nitride (Si_3N_4) films to evaluate its feasibility for sustainable manufacturing, targeting high-selectivity applications such as the Self-Aligned Contact (SAC) process. The etching process was performed in an Inductively Coupled Plasma (ICP) reactor, where key parameters including bias power and step times were varied to verify the self-limiting behavior essential for ALE. We primarily focused on analyzing the process windows, etch rates, and etch selectivity derived from both C_4F_8 and C_3F_6 plasmas. Furthermore, to elucidate the reaction mechanisms and difference in dissociation pathways between the two gas systems, Residual Gas Analysis (RGA) was employed to analyze the gas-phase chemistry and monitor the evolution of neutral species and reaction by-products. In this presentation, we will discuss the potential of C_3F_6 to replace C_4F_8 by presenting the comparative analysis of process feasibility and investigating the correlation between plasma species and etch characteristics, thereby providing guidelines for eco-friendly semiconductor processing.

Atomic Layer Etching
Room Tampa Bay Salons 5-9 - Session ALE-MoP
Atomic Layer Etching Poster Session

ALE-MoP-1 Low-Temperature Isotropic ALE of Oxides for 3D Nanostructures and Quantum Device Fabrication*, Maria Efthymiou Tsironi,* LBNL

Atomic layer etching (ALE) with high selectivity, low damage, and minimal thermal budget is increasingly important for advanced microelectronics and quantum devices. In this work, we present a plasma-based ALE approach for SiO_2 and Al_2O_3 that enables controlled, isotropic material removal using sequential SF_6, trimethylaluminum (TMA), and low-power Ar plasma exposures. The processes are designed to operate at room temperature or modest heating, expanding the accessible parameter space for temperature-sensitive substrates.

For SiO_2, we implement a near-room-temperature ALE sequence using alternating SF_6 and Ar plasma steps. Ellipsometry measurements indicate self-limiting behavior in both half-reactions, with no measurable etching during isolated SF_6 or plasma exposures and an expected etch-per-cycle (EPC) of ~1 Å. A defined temperature and plasma-power window supports stable etching and strong selectivity to underlying Si, making the process suitable for applications where substrate preservation is critical.

We further extend this strategy to Al_2O_3 by introducing a TMA pulse following SF_6 surface fluorination. This fluorination–ligand-exchange mechanism enables isotropic removal of the modified layer, yielding an EPC of ~0.9 Å/cycle at 150 °C. The process provides reliable etching on both horizontal and vertical surfaces, demonstrating applicability to 3D structures. XPS, AFM, and SEM confirm reduced surface roughness and uniform material removal, consistent with self-limited etching.

Together, these results establish a versatile ALE platform capable of high-precision, low-temperature oxide etching. The approach offers a safer and more controllable alternative to HF-based methods and supports the fabrication of complex geometries in emerging semiconductor, superconducting, and quantum technologies.

This work is carried out through a collaboration between Lawrence Berkeley National Laboratory, the Molecular Foundry, and the University of Copenhagen as part of the NQCP program, enabling coordinated development of low-temperature ALE for next-generation nano- and quantum device fabrication.

ALE-MoP-2 Active-Learning Accelerated Atomistic Modeling of ALE Processes*, Fedor Goumans,* Software for Chemistry & Materials, Netherlands*; Nestor Aguirre,* Softare for Chemistry & Materials, Netherlands*; Nicolas Onofrio,* Software for Chemistry & Materials, Netherlands

Atomic-layer etching (ALE) demands recipe windows that remove target material while avoiding interface damage. We introduce an ML-augmented multiscale modeling pipeline for ALE that combines DFT energetics, an active-learning machine learning interatomic potential (MLIP), automated reaction discovery, and 3D kinetic Monte Carlo (kMC) growth/etch simulations to predict spatial trap-density proxies and etch-selectivity maps. A task-adapted MLIP, fine-tuned from a small DFT seed set via uncertainty-guided sampling, accelerates PES exploration and identifies candidate dissociative and adsorption channels as well as penetration of the etchant or plasma ions. Only structure with high uncertainty in energies and forces are re-computed with DFT, limiting the DFT budget while ensuring accuracy for kinetically relevant steps. The final, DFT-verified reaction network drives 3D-kMC simulations that produce rasterized maps of (near-interface) defect proxies as a function of etchant kinetic energy, flux, and surface termination. We present two ALE case studies: Ru/H and SiO2/HF etching giving insights in how the processes (energies, fluxes) can affect the resulting structures and electronic properties of the etched thin films.

ALE-MoP-3 Stabilization of Etch Rate in SiO_2 Quasi-ALE Using an O_2 Plasma*, Akimi Uchida,* *Tomoyuki Nonaka, Koshi Hanada,* Samco Inc., Japan

Fluorine-based quasi-atomic layer etching (quasi-ALE) of SiO_2 is widely used as an ALE process. However, in this process, fluorocarbon (CF) polymers deposited on the reactor chamber re-evaporate and redeposit on the wafer surface, causing the etch rate per cycle to gradually increase with increasing cycle number [1,2]. This behavior originates from the fact that, unlike ideal ALE, the modification step in quasi-ALE does not proceed in a self-limiting manner, and the etch rate depends on the thickness of the deposited film. As a result, even when cycles are repeated under identical process conditions, the etch amount per cycle cannot be maintained at a constant value. In this study, we focus on the instability of the etch amount per cycle and propose a method to stabilize it. A SiO_2 quasi-ALE process using C_4F_8/Ar gas was employed, in which modification and removal steps were alternately repeated in a cyclic manner. To remove CF polymers deposited on the reaction chamber and stabilize the etch amount per cycle, a short O_2 plasma step (several seconds) was inserted after the removal step of each cycle. The etch amount per cycle was evaluated and compared with and without the O_2 plasma step.

Without the O_2 plasma step, the etch amount per cycle increased after approximately 50 cycles, leading to a loss of linearity in the etch rate. In contrast, when the O_2 plasma step was introduced in every cycle, the etch amount per cycle remained nearly constant throughout all cycles, resulting in stable linear etching characteristics. Furthermore, the self-limiting behavior observed during the removal step exhibited similar saturation characteristics regardless of the presence or absence of the O_2 plasma step. These results demonstrate that the proposed method effectively stabilizes the etch amount per cycle in fluorine-based SiO_2 quasi-ALE processes by suppressing cycle-to-cycle variations without altering the underlying reaction mechanism.

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ALE-MoP-4 Ion-beam Atomic Layer Etching for Effective Damage Removal in Vertical GaN-Based Devices*, Sung Hyun Kim,* *Jong Soon Park, Geun Young Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

GaN is a wide-bandgap semiconductor that exhibits excellent electrical and optical properties, making it suitable for LED device. In particular, it is well-suited for light-emitting diodes due to its direct bandgap property. [1] Light-emitting devices adopt a mesa structure to expose multi-quantum well (MQW) layer composed of InGaN and GaN emitting layer. A direct plasma-based etching process is commonly used to form these structures. [2] Unfortunately, reactive ions accelerated by the combined potential of the self-bias and sheath inevitably induce structural and physical damage, which particularly lead to electrical and optical degradation of the MQW. To mitigate plasma-induced damage, wet etching techniques using KOH solutions are employed to remove the damaged GaN surface layer. [3] Subsequently, atomic layer etching (ALE) has been investigated to eliminate the remaining damage layer. However, ALE conducted in direct plasma cannot efficiently target vertical GaN structures including MQWs, because accelerated ions are incident perpendicularly to the surface. To address this issue, ALE utilizing an ion-beam source has been investigated, enabling selective targeting of MQW layers through the use of tilted ion beams.

In this study, atomic layer etching (ALE) utilizing an ion beam is introduced after RIE process to remove the damage caused by RIE in GaN-based structures, including multi-quantum well (MQW) layers composed of InGaN and GaN. X-ray photoelectron spectroscopy (XPS) analysis reveals that RIE-induced damage alters the N/Ga and Ga/In atomic ratios relative to reference data. However, after ion-beam ALE treatment following RIE, the atomic ratios return to values similar to the reference data, whereas wet etching only partially restores the atomic ratios. Consequently, ion-beam ALE is a promising approach for enhancing device performance by providing efficient surface damage removal, particularly in nanoscale vertical GaN-based devices.

References:

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ALE-MoP-5 Highly Selective Atomic Layer Etching of Mo using O_2/Cl_2 by Formation of MoO_xCl_y*, Su Jeong Yang,* *Yun Jong Jang, Geun Young Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

As demand for high-performance chips increases, not only the critical dimension (CD) of device gates but also the CD of interconnect metals is decreasing. Cu is currently used as an interconnect material with a barrier material in a damascene structure because of low resistivity. However, there is a limit in scaling down of Cu width due to the existence of barrier metal, the need for new materials to replace Cu is increasing to overcome this limitation. Molybdenum (Mo) is one of the candidates for next-generation interconnect materials, as it has lower apparent resistivity (electron mean free path × bulk resistivity; $\lambda \times \rho_0$) than Cu when the critical dimension (CD) is below 10 nm.

In this study, anisotropic atomic layer etching (ALE) of Mo was performed using O_2 and Cl_2 plasma radicals as adsorption gases to precisely control the etch depth of Mo. The etch depth per cycle (EPC) of Mo and hard mask materials such as TiN, Si_3N_4 were compared in the Mo ALE process under Cl_2 and Cl_2:O_2 conditions. The results showed that, by adding O_2 to Cl_2, even though the Mo EPC is slightly decreased, highly selective Mo etching relative to TiN could be achieved. X-ray photoelectron spectroscopy (XPS) showed the formation of volatile MoO_xCl_y on the Mo surface during ALE which can be easily removed during the desorption step.

ALE-MoP-6 Improving Optical Resonator Quality Factors in Thin-Film Lithium Niobate with Atomic Layer Etching, ***Ivy Chen***, *Selina Zhou, Alireza Marandi, Austin Minnich,* California Institute of Technology

Thin-film lithium niobate (TFLN) is a nonlinear optical integrated photonics platform of intense interest, owing to its ability to generate and manipulate electromagnetic waves from a broad range of frequencies. Currently, the performance of on-chip devices based on TFLN is limited by imperfections arising from the fabrication process. Much of these imperfections originate from the dry etch process of lithium niobate, such as sidewall surface roughness, aspect ratio dependent etching, and other geometry inhomogeneities over the chip. Atomic layer etching (ALE) could be used to overcome these difficulties and enable unprecedented device performance. Recently, we have reported isotropic and directional HBr-based ALE processes that are able to smooth sidewalls (in the isotropic case) and achieve aspect ratio independent etching (in the directional case). Here, we present results on applying our isotropic and directional ALE processes to TFLN devices, along with other post processing methods, to improve the quality factor of optical resonators. The effect of ALE and subsequent processing on the surface roughness, sidewall surface roughness, and sidewall angle of TFLN devices will also be discussed. Using isotropic and directional ALE together to smooth sidewalls and achieve aspect ratio independent etching could enable unprecedented device performance and large-scale integration of photonic circuits.

ALE-MoP-7 Recovery of Plasma-Induced Surface Damage in Gan-Based Led via Atomic Layer Etching, ***Young Woo Jeon***, *Jong Woo Hong, Geun Young Yeom,* Sungkyunkwan University, Republic of Korea

Gallium Nitride (GaN)-based devices have emerged as key components in optoelectronic and power applications because their wide direct bandgap and high energy conversion efficiency enable superior performance. Light-emitting diodes (LEDs) and power semiconductors, in particular, strongly benefit from these material properties [1]. As the critical dimensions of LED structures continue to scale down, reactive ion etching (RIE) has been widely adopted to form anisotropic profiles during device fabrication. Nevertheless, energetic ion bombardment during the RIE process introduces surface and lattice damage, which degrades both the electrical and optical characteristics of GaN devices. Conventionally, wet etching has been employed as a post-treatment to mitigate this damage; however, its effectiveness is often limited by insufficient damage removal and residual surface defects [2–3].

To address this issue, atomic layer etching (ALE) was employed as a post-RIE treatment to selectively eliminate the damaged surface region in GaN-based structures, including InGaN/GaN multi-quantum well (MQW) layers. Transmission electron microscopy (TEM) images revealed that the MQW layers became indistinct after RIE, indicating structural deterioration. Although subsequent wet etching partially restored the layer contrast, TEM images showed that ALE produced much clearer interfaces, demonstrating more effective damage removal.Photoluminescence (PL) measurements indicated that RIE-induced damage increased as device dimensions decreased, but after the ALE, PL intensity was improved after ALE and became more significantly improved for smaller devices.Overall, as GaN-based LEDs continue to shrink in size, an efficient damage-recovery process becomes increasingly important. Compared with conventional wet etching, ALE offers superior surface restoration and is therefore a more suitable approach for enhancing device performance.

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ALE-MoP-8 Development Atomic Layer Etching of Ga_2O_3 Using CF_4 Plasma and $Sn(acac)_2$, *To-En Hsu, Yu-Hsuan Yu,* ***Chien-Wei Chen,*** National Center for Instrumentation Research, National Institutes of Applied Research, Taiwan

Gallium oxide (Ga_2O_3), featuring an ultra-wide bandgap and a high breakdown electric field, is regarded as a promising material for high-power semiconductor devices; however, its etching process remains challenging in terms of achieving both high precision and low plasma-induced damage. Atomic layer etching (ALE), which employs cyclic self-limiting surface reactions, provides a potential solution for realizing highly controlled and low-damage etching.

In this study, a plasma-based ALE process for Ga_2O_3 using tetrafluoromethane (CF_4) plasma and tin(II) acetylacetonate ($Sn(acac)_2$) as sequential reactants is developed. The CF_4 plasma half-reaction is first investigated to verify the surface fluorination behavior of Ga_2O_3. The CF_4 plasma is operated at a power of 30 W and a working pressure of 0.5 Torr, with a reaction time of 5 s per cycle. A total of 5 cycles (25 s) and 25 cycles (120 s) are performed to examine the evolution of surface chemical states. X-ray photoelectron spectroscopy (XPS) analysis reveals that the fluorine concentration on the surface increases with the number of plasma cycles (Figure 1). Meanwhile, the intensities of Ga and O signals decrease, indicating a signal attenuation effect caused by the formation of a fluorinated surface layer, which confirms effective surface fluorination of Ga_2O_3 by the CF_4 plasma. After confirming the surface fluorination behavior, $Sn(acac)_2$ is introduced as the second reactant to complete the full ALE process. During the full reaction cycles, the CF_4 plasma is applied at a power of 50 W with a reaction time of 10 s per cycle, while the process temperature is maintained at 450 °C. The $Sn(acac)_2$ exposure consists of a 0.1 s pulse followed by a 1 s soak, enabling the conversion of surface fluorides into volatile reaction products and their subsequent removal, thereby completing a single ALE cycle. Following the full ALE process, spectroscopic ellipsometry measurements show a continuous decrease in film thickness with increasing ALE cycle numbers, confirming effective atomic layer etching achieved by the combined CF_4 plasma and $Sn(acac)_2$ reactions (Figure 2). The average etching rate is approximately 0.105 nm per cycle.

Overall, this work demonstrates a repeatable and precisely controllable plasma-enhanced ALE process for Ga_2O_3, highlighting its potential for applications in ultra-wide bandgap semiconductor devices and advanced manufacturing technologies.

ALE-MoP-9 Thermal Atomic Layer Etching of Yttrium-Doped Hafnium Oxide Using Hydrofluoric Acid and Boron Trichloride, ***Aziz Abdulagatov***, *Andrew Cavanagh,* University of Colorado Boulder; *Florian Wunderwald, Uwe Schroeder,* NaMLab gGmbH, Germany; *Steven George,* University of Colorado Boulder

Y-doped HfO_2 (Y:HfO_2) is known to stabilize the orthorhombic/tetragonal (o/t) ferroelectric phase of HfO_2 and widen the ferroelectric thickness window. However, Y-doping in HfO_2 could also affect the thermal ALE of Y:HfO_2. In this study, Y:HfO_2 was etched using sequential exposures of hydrogen fluoride (HF) and boron trichloride (BCl_3). The initial Y:HfO_2 films with thicknesses of 10 nm were deposited on 10 nm of TiN with an underlying W layer of 30 nm. The Y:HfO_2 film thicknesses were then monitored during thermal ALE using in situ spectroscopic ellipsometry (SE) measurements.

The in situ SE measurements showed that sequential HF and BCl_3 exposures at 270 °C resulted in the linear decrease of the Y:HfO_2 thickness. The etch rate was 0.22 Å/cycle during the first 80 ALE cycles. Subsequently, there was a gradual reduction of the etch rate to ~0.15 Å/cycle over the next 60 ALE cycles (Figure 1). X-ray photoelectron spectroscopy (XPS) analysis before and after ALE showed an increase in the Y concentration from ~2 to 4 at.%. This increased Y concentration indicated preferential Hf removal during the ALE cycles. The reduced etch rate was attributed to the gradual Y accumulation on the surface. The Y buildup was consistent with thermochemical calculations that showed low favorability for BCl_3 ligand exchange with YF_3. $YF_3 + 2BCl_3(g) \rightarrow BF_3(g) + YCl_3(g)$ has an unfavorable $\Delta G(270\ °C) = +41.1$ kcal. In contrast, $HfF_4 + 4/3BCl_3(g) \rightarrow 4/3BF_3(g) + HfCl_4(g)$ has a favorable $\Delta G(270\ °C) = -10.9$ kcal.

Atomic force microscopy (AFM) measurements revealed only a minor increase in root-mean-square (RMS) roughness. The initial RMS roughness was 7.0 Å. The RMS roughness increased to only 7.7 Å after removal of 3 nm by etching. Grazing-incidence X-ray diffraction (GIXRD) analysis of the initial 10 nm Y:HfO_2 film showed only metastable o/t phases. After etching removal of 3 nm, GIXRD revealed no phase transformation and reduced peak intensity and peak broadening consistent with decreased crystallite size. In contrast, HZO ALE of a 10 nm HZO film thickness using HF and dimethylaluminum chloride (DMAC) showed transformation from predominantly o/t-phase to monoclinic phase after etching at 250 °C.

ALE-MoP-10 Thermal Gas-Phase Etching of Silicon Materials by Chlorination Using $SOCl_2$, SO_2Cl_2, and HCl, ***Troy Colleran,*** University of Colorado at Boulder

Silicon materials such as Si, Si_3N_4, SiO_2, and SiC play a critical role in the semiconductor industry. Selective etching of silicon materials while leaving nearby dielectric materials such as HfO_2 or ZrO_2 intact is a challenge in semiconductor device fabrication. In this study, the thermal etching of silicon materials by chlorination using $SOCl_2$, SO_2Cl_2, and HCl was explored using quadrupole mass spectrometry (QMS) studies on powders. The measure of etching was the appearance of SiCl4+ ion intensity during the QMS studies. Temperature ramp studies were performed to determine the onset temperature of each etching reaction.

The thermochemistry of etching silicon materials by $SOCl_2$, SO_2Cl_2, and HCl to produce $SiCl_4$ is favorable. However, reaction kinetics may dictate the feasible etching temperatures. Si chemical vapor etching (CVE) was demonstrated using $SOCl_2$, SO_2Cl_2, and HCl exposures above 200°C (Figures 1 & 2). SiO_2 CVE was achieved using SOCl2 exposure above 400°C. Si_3N_4 CVE was observed for $SOCl_2$, SO_2Cl_2, and HCl exposures above 200°C (Figure 3). SiC CVE was demonstrated for HCl exposures above 200°C (Figure 4). The SiCl4+ ion signal increased progressively at higher temperatures above the threshold temperature for all silicon materials. In contrast, there is selectivity for etching these silicon materials compared with HfO2 and ZrO2. Thermochemical calculations suggest that SO_2Cl_2 and HCl will not chlorinate either HfO_2 or ZrO_2. Etching HfO_2 and ZrO_2 using $SOCl_2$ requires temperatures above 350°C.

Etching of silicon materials by $SOCl_2$, SO_2Cl_2, and HCl required the removal of the native oxide on the initial silicon-containing powders prior to exposure to the chlorination precursors. The native oxide was removed by a 5 minute exposure to HF at 400°C. Time-resolved QMS data showed the evolution of H_2O^+ and SiF_4^+ ion signals during SiO_2 removal. The H_2O^+ ion signal decreased during the HF exposure consistent with the native oxide removal. Si, SiC, and Si_3N_4 powders that were not treated with this initial HF exposure did not produce any $SiCl_4^+$ ion signals during the $SOCl_2$, SO_2Cl2, or HCl exposure.

ALE-MoP-11 Atomic Layer Etching of Metal Oxides Using Halogen-Free Liquid Phase Organic Etchants, ***Hana Kim,*** *Hyeon Sik Cho, Hyun Ju Jung, Myeong Il Kim, Jaemin Kim, Duck Hyeon Seo, Juhwan Jeong, Sun Young Baik, Kyuho Cho,* EGTM Co. R&D Center, Republic of Korea

Atomic layer etching (ALE) of metal oxide thin films is of increasing importance for advanced device fabrication requiring precise thickness control and minimized surface damage. Most reported metal oxide ALE processes rely on halogen-based chemistries and, in many cases, metal-containing etchants to enhance surface reactivity [1-4]. In this work, we report a halogen- and metal-free ALE process for metal oxides enabled by halogen-free liquid phase organic etchants.

The ALE cycle consists of an etching step employing fully organic etchants followed by a reactive removal step that regenerates the surface for subsequent cycles (Fig. 1). The organic etching chemistry exhibits a clear saturation behavior with respect to etchant feed time, resulting in a self-limited etch-per-cycle (EPC) governed by etch-stop formation through surface reaction saturation. During sequential Etchant/Remover ALE, the etched thickness per cycle remains constant once the etchant feed time exceeds a critical window, demonstrating feed-time-limited material removal by the organic etchant (Fig. 2). This saturation behavior was consistently observed for both TiO_2 and Nb_2O_5 thin films.

In addition, a linear reduction in film thickness with increasing ALE cycle number was observed for TiO_2 thin films, demonstrating cycle-by-cycle controllability of material removal (Fig. 3). Similar linear etch behavior is being evaluated for Nb_2O_5 thin films under the same ALE scheme. The reactive removal step oxidatively eliminates or transforms etch-inhibiting surface species formed during the etch step; within the tested process window, the film thickness change is insensitive to the removal-step feed time, indicating that material removal is defined by the etch step rather than the regeneration step.

Unlike many reported metal oxide ALE processes that rely on halogen chemistry and/or metal-containing etchants to enhance reactivity, the present approach achieves self-limited etching through organic reaction saturation and reactive surface regeneration alone. These results demonstrate a halogen- and metal-free ALE approach for metal oxides based on organic reaction saturation, providing a controllable and damage-mitigated etching method for functional oxide materials.

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ALE-MoP-12 Reaction Mechanism of Isotropic Atomic Layer Etching of Zirconium Oxide: An *In Vacuo* X-ray Photoelectron Spectroscopy Study, ***Hye-Lee Kim,*** *Mi-Soo Kim, Eunju Ham, Sejeong Jo, Hyun-Jeong Yoo,* Sejong University, Republic of Korea*; Youn Seoung Lee,* Hanbat National University, Republic of Korea*; Sun-Jae Kim, Won-Jun Lee,* Sejong University, Republic of Korea

The advent of complex 3D semiconductor architectures, such as gate-all-around (GAA) field-effect transistors (FETs) and vertical memory structures, has increased demand for isotropic atomic layer etching (ALE) to achieve precise, damage-free patterning. The ALE process typically relies on a self-limiting cycle comprising a surface modification step followed by a subsequent removal step. However, a fundamental understanding of these half-reactions is often obscured by surface oxidation and adventitious carbon contamination that arise during air-exposed sample transfer for ex situ analysis. In this study, we present an investigation of ZrO_2 isotropic ALE using a custom-built in vacuo X-ray photoelectron spectroscopy (XPS) system. By integrating the ALE process chamber directly with the XPS analysis chamber under high vacuum, we successfully characterized the surface chemical states of each half-reaction without atmospheric artifacts. Our *in vacuo* analysis revealed distinct surface evolution during the ALE cycles that were unobservable in conventional *ex situ* measurements. During the modification step using NF_3 remote plasma, Zr–O bonds were converted to Zr–F bonds, confirming effective surface fluorination. In the subsequent removal step using dimethylaluminum chloride (DMAC), the depletion of the Zr–F signal was accompanied by the appearance of specific ligand residues derived from DMAC. This step-by-step tracking enabled us to confirm the reaction pathways via ligand exchange. Notably, the *in vacuo* capability enabled high-sensitivity detection of trace surface residues that would have been indistinguishable in ex situ analysis due to the air exposure. These findings are critical for optimizing isotropic ALE processes for next-generation high-k dielectric applications.

ALE-MoP-13 Numerical and Experimental Investigations on Tailored Waveforms, ***Sebastian Mohr,*** *Hyungseon Song,* Quantemol Ltd., UK*; Ben Harris, Daryl White, Geoff Hassall,* Oxford Instruments Plasma Technology, UK*; James Ellis,* Oxford Instruments, UK

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

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

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

This presentation will show our continued efforts to simulate industrial applications of ICPs combined with tailored waveforms to allow precise control of ion energies. The simulations are carried out with the Hybrid Plasma Equipment Model [3]. The simulated results are compared to experimental results with a focus on how the precise shape of the tailored waveform affects the ion energy distribution measured at the electrode for different pressures and ICP powers.

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ALE-MoP-14 Thermal Etch and SEM3D–Modeling Driven Profile Engineering for Metal–Gate Corner Preservation in Advanced MEOL SAC Processing*, Prabhat Kumar,* Lam Research Corporation

As middle–of–line (MEOL) scaling advances, robust source–drain (S/D) contact formation—especially in self–aligned contact (SAC) schemes—has become critical to device performance, yield, reliability, and power efficiency. At aggressively scaled nodes, small deviations in contact geometry can significantly increase resistance and leakage. A major challenge in current plasma–based etch processes is **metal–gate corner loss**, which degrades gate integrity and is expected to worsen with further CD shrink.

To address this, we developed an **innovative thermal etch process** capable of minimizing corner loss while achieving high metal gate selectivity. The method utilizes liquid precursor and HF gas delivered under vacuum in cyclical or co–flow operation. Liquid is vaporized through a heated delivery system, while HF is introduced through the gas manifold; these species react in situ to form a neutral–dominant, chemical etch pathway that selectively removes oxide without physically damaging metal gates. This enables highly selective oxide etching while preserving the sensitive gate corners that are typically eroded in ion–driven plasma processes.

Because thermal etching relies predominantly on neutral–chemistry reactions rather than directional ions, controlling the lateral component of the etch and maintaining profile fidelity are key challenges. To overcome this, we introduced a **conformal liner deposition step**, which shapes the sidewalls prior to thermal etch, followed by a **breakthrough process** that removes polymer at the etch front to enable clean thermal–oxide removal. This hybrid approach stabilizes the feature profile, suppresses lateral encroachment, and significantly reduces corner retreat.

To optimize process behavior and quantify the impact of neutral–driven reactions, we modeled the thermal etch using the **SEMulator3D (SEM3D)** profile simulator. SEM3D was calibrated to wafer data and used to capture lateral–etch tendencies, reaction penetration depth, and sensitivity to liner thickness and thermal–etch conditions. Modeling results guided the development of a combined **liner + thermal etch sequence** that minimizes lateral loss, improves uniformity, and preserves gate–corner geometry. The SEM3D–based DOE accelerated tuning of precursor flow, sticking behavior, cycle time, and breakthrough parameters, enabling precise control of the etch front.

Across customer wafers and device test structures, the integrated process demonstrated **excellent metal–gate selectivity**, near–elimination of corner loss, and strong compatibility with existing MEOL integration schemes. By coupling a novel thermal etch chemistry with physics–based profile modeling and a liner–assisted control strategy, this work provides a scalable and manufacturable solution to one of the most critical challenges in future SAC–based S/D contact formation.

ALE-MoP-15 Modelling Atomic Layer Etching of a ZnO Surface Using Thermogravimetric Analysis and Solvothermal Synthetic Methods*, Justin Moore,* *Titel Jurca,* University of Central Florida

Atomic layer deposition (ALD) is the backbone of the modern semiconductor industry, allowing for the deposition of films with atomic scale control for the creation of sub 5 nm nodes. Atomic layer etching (ALE), a relatively more recent process, has proven itself to be just as essential as its ALD counterpart, allowing for the removal of material with atomic scale precision. Despite this, ALE lacks the diversity of precursors afforded to ALD processes due in part to the challenge of modifying a surface while also ensuring the resulting reaction products are volatile and thermally stable enough to be removed cleanly. Herein we demonstrate a method to model and isolate the products of an ALE process, encompassing ZnO and a series of acetylacetonate precursors, utilizing thermogravimetric analysis (TGA) and small scale solvothermal reactions (synthesis).

Acetylacetone precursors with more electron withdrawing functionalities exhibit increased reactivity with ZnO, while acetylacetone precursors with more electron donating functionalities exhibit reduced to no reactivity with ZnO. Isolation and subsequent TGA analysis of the resulting zinc acetylacetonate complexes reveal that more fluorinated complexes are more volatile at temperatures relevant for an ALE process. This approach demonstrates a fast and efficient process to screen precursors that could effectively etch a surface to yield volatile thermally stable byproducts. This bypasses the need for an ALD/ALE reactor in the preliminary studies, and as a result expedites the discovery phase while lowering the associated costs and efforts around ALE process optimization.

ALE-MoP-16 Exploring Hydrofluorocarbons for Thermal ALE of High-k Oxides*, Michael Nolan,* Tyndall Institute, Ireland*; Rita Mullins,* Tyndall National Institute, University College Cork, Ireland

Thermal Atomic Layer Etching (ALE) has potential to deliver atomic level control over the etch of many materials and in particular for future CMOS nodes with requirements for sub-nm levels of control on complex 3D structures. It is performed using sequential surface modification followed by reaction with a second precursor to release volatile products. The self-limiting surface chemistry typical for ALD is also exploited here with the modification and therefore etch limited to only the outer surface layer. For metal oxides, typically HF is used to fluorinate the initial surface to form metal-fluoride layer (M = metal) which undergoes ligand-exchange with a precursor such as TiCl4 or SiCl4, which volatilizes the modified layer. HF is a toxic and challenging to handle chemical and other fluorides used in etch, e.g. CF4, C4F8 and NF3 are PFAS or have high global warming potential (GWP). Hydrofluorocarbons such as CH3F or CH2F2 have GWPs < 100 and are not strictly PFAS, lacking the terminal CF3 group. In this contribution we present first principles simulations of the potential for CH3F and CH2F2 to be used as alternatives to HF for ALE of high-k oxides HfO2, ZrO2 and HfZrO4. Our thermodynamic calculations show that self-limiting ALE can be preferred at temperatures relevant for CMOS processing. Detailed analysis of the interaction at the oxide surfaces, in particular the activation barriers for C-F bond break and surface fluorination show that these molecules generally have high barriers to C-F dissociation limiting their usefulness, which is shown by computed process maps. On amorphous HfO2 and HfZrO4, the hydrofluorocarbons can show low barriers to C-F bond breaking which suggests they may be useful alternatives to HF for amorphous and ternary oxide ALE.

ALE-MoP-17 Halogen-Free ALE of Copper*, Persi Panariti, Asare Dua,* ***Adam Hock***, Illinois Institute of Technology

Controlled ALE of metallic copper without surface modification has proven challenging, because copper surfaces are relatively chemically inert. But modifying the surface by oxidation (i.e., forming a CuOx surface layer) facilitates the etch step, which consists of removal of the modified layer as a volatile metal complex. Therefore, Cu oxidation is especially important for enabling ALE. We have developed a novel ALE process for Cu metal that is halogen-free and operates at temperatures less than 200°C. This poster describes our *in situ* characterization of the ALE mechanism and ALE results on Cu thin films.

Atomic Layer Etching
Room Tampa Bay Salons 3-4 - Session ALE1-TuM
Wet ALE and ALE Modeling

Moderators: Jeffrey W. Elam, Argonne National Laboratory, **Geun Young Yeom**, Sungkyunkwan University

8:00am **ALE1-TuM-1 A Dry-Wet Quasi-ALE Approach for Transition Metals: Tungsten as a Model System*, Cinzia Chan,*** KU Leuven and Imec, Italy*; Jean-Francois de Marneffe,* IMEC Belgium*; Christopher Gort,* TU Darmstadt, Germany*; Jill Serron,* IMEC Belgium*; Marta Agati,* IMEC Belgium, Italy*; Felix Seidel,* IMEC Belgium*; Jan P. Hofmann,* TU Darmstadt, Germany*; Stefan De Gendt,* KU Leuven and Imec, Belgium*; Dennis H. van Dorp,* IMEC Belgium, Netherlands **INVITED**

We demonstrate a hybrid dry-wet quasi-atomic layer etching (Q-ALE) process using tungsten as a model case, combining a self-limiting O_2 plasma oxidation (modification) step with a wet-chemical oxide removal step in 1 M HCl. In the study of the modification step, O_2 plasma oxidation was selected for its self-limiting behavior and benchmarked against wet oxidation, which instead produces highly soluble oxides in aqueous solution. The removal step was quantified by ICP-MS, revealing an initially high etch rate that decreases and stabilizes to a background value. This behavior is attributed to the rapid dissolution of plasma-generated bulk WO_3, followed by progressively slower removal as the interface approaches a suboxide-rich layer, and finally a steady-state regime governed by continuous re-oxidation and metal dissolution. Although the background etch rate is very slow (0.03 Å·min^{-1}), in Q-ALE operation the removal step is intentionally stopped before reaching this background regime, enabling controlled and selective material removal. These findings are further supported by post operando XPS, TEM and conductive AFM analyses. The dry-wet Q-ALE sequence was demonstrated on both PVD blanket and ALD-patterned tungsten wafers using existing 300-mm fab tools, achieving ~8 Å per cycle. These results highlight lab-to-fab scalability. More broadly, the combined dry-wet ALE framework provides a versatile platform for layer-by-layer etching of technologically important materials, particularly where purely wet oxidation is not self-limiting (or is chemically challenging), while wet removal offers strong oxide-to-metal selectivity.

8:30am **ALE1-TuM-3 Smooth Post-etch Morphology in Ligand Assisted Molybdenum Wet Atomic Layer Etch*, Tulashi Dahal*,** *Trace Hurd, Antonio Rotondaro,* Tokyo Electron America Inc.,

Molybdenum (Mo) has gained significant attention from semiconductor industries for its applications on logic BEOL, buried power rails, and 3 D NAND. Some of these applications require partial etch back of Mo where post-etch morphology is critical to device performance. Wet atomic layer etching offers material removal with Angstrom-level precision at or near room temperature and at ambient pressure by utilizing two sequential self-limiting steps. In the first step, the Mo surface is exposed to an oxidizing solution to form self-limiting surface passivation. In the second step, the modified Mo surface is selectively removed via dissolution in suitable chemistry. Etching of polycrystalline Mo is susceptible to surface roughness increase and uncontrolled etch rate due to solubilization of modified surface products in oxidizing solutions. Here, we present a novel method for controlled Mo etch with improved post-etch surface morphology via ligand assisted surface modification of metallic Mo in aqueous oxidizing solution. A ligand binds with the metal center to form a complex surface product that is insoluble in an aqueous oxidizing solution, preventing the continuous Mo background etch, and resulting in preserved post-etch surface smoothness.

Cyclic etch experiments were carried out by dipping Mo coupons in an oxidizing solution with varying ligand concentration followed by selective removal of modified layer in a low concentration dissolution chemistry. Mo etch rate decreases with increasing ligand concentration. The etch rate, however, can be enhanced via surface oxidation at an elevated temperature (Fig. 1). For the same ligand concentrations, Mo etch rate can be greatly improved by tuning the oxidizer concentration (Fig. 2). A significant enhancement in Mo etch rate [from ~0.12 nm/cycle with p% oxidizer +250 mM ligand to ~0.43 nm/cycle in 5p% oxidizer+250 mM ligand] with increased oxidizer concentrations suggests the formation of thicker surface oxide as surface passivation. For higher oxidizer concentration, Mo ER is independent of ligand concentrations under study (Fig. 2). The measured RMS roughness [~ (0.63±0.04) nm] of the post-etch Mo coupon with higher ligand concentration is the same as RMS roughness of [~ (0.62±0.03) nm] of the reference coupon (Fig. 3). We attribute the preserved morphology in post-etch Mo coupon with higher ligand concentration to the suppression of continuous Mo etch due to the formation of a stable metal complex that is insoluble in oxidizing solution. The ability to remove Mo at a substantial rate with atomic-level precision and preserved surface morphology in post-etch coupons using less harsh oxidizer and ligand in an aqueous solution near room temperature may provide a cost-effective alternative solution to recess Mo in the industrial scale.

8:45am **ALE1-TuM-4 The Effect of the Angle of Incidence of Ions on Atomic Layer Etching*, Joseph Vella,*** TEL Technology Center America*; David Graves,* Princeton University

Plasma assisted atomic-layer etching (ALE) processing techniques have seen widespread usage in the semiconductor manufacturing industry. In its simplest form, an ALE process consists of two steps: a chemical modification step and a removal step. The removal step is often performed by exposing the substrate to a chemically inert plasma (such as an argon plasma) where energetic ions remove the modified surface. In much of the literature, it is assumed that a majority of the ions are hitting the surface at normal incidence, although there are some published results that examine the effect of the ion angle of incidence on ALE behavior. A fundamental understanding of any effect of the ion angle of incidence with in ALE processes is relevant to etching features into patterned surface (especially for high-aspect ratio features). In this work we utilize both classical molecular dynamics (MD) simulations and a reduced order model[1] (ROM) to build this understanding. We focus on the relatively simple case of silicon (Si) ALE by exposure to chlorine gas (Cl_2) and argon ions (Ar^+). We show how the angle of incidence of Ar^+ ions affects the etch per cycle (EPC), etch product distribution, and etch product selectivity.

References

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

9:00am **ALE1-TuM-5 Ab Initio Modeling of Atomistic Diffusion of Halogen Species at the Etching Front*, Sangheon Lee,*** Ewha Womans University, Republic of Korea

Halogen atoms play key roles in etching processes for semiconducters. Flourocarbon or hydrofluorocarbon gases are commonly used for reactive-ion etching processes. When treated with plasma, these gases decompose and radicals migrate to the etching front. Halogen gases like Cl_2 are often used to treat metal or dielectric surfaces to form halogenated surfaces for atomic layer etching processes. Despite the well-established fact that etching does not proceed without halogen species, detailed surface reaction mechanisms involving halogens are rarely revealed. In this presentation, I will discuss mechanisms of halogen-mediated ethcing processes, focusing on atomistic diffusion of halogen species at dielectric and metal etching fronts. This work is based on state-of-the-art ab initio calculations combined with recent experimental results from my academic colleagues.

9:15am **ALE1-TuM-6 Quantum Chemistry Calculation for Predicting Salt By-Products in ALE Processes*, Yuri Barsukov,*** Lam Research Corp.*; Mingmei Wang, Thorsten Lill,* Lam Research Corporation

It is well established that during the thermal and plasma-assisted atomic layer etching of silicon nitride – a process widely used in the semiconductor industry – the main solid by-product is ammonia fluorosilicate (AFS) salt, if the feed gas contains both hydrogen and fluorine. In fact, such chemistries initially convert silicon nitride into AFS salt, which subsequently decomposes into gaseous by-products. During high-aspect ratio etching, the formation of AFS significantly affects the overall process performance by influencing critical characteristics such as etch rate, selectivity, and feature shape distortion, which are vital for semiconductor manufacturing.

Despite this, the thermodynamic properties of AFS – such as its decomposition temperature and the dependence of this temperature on pressure – have not been reliably determined. To address this gap, we performed calculations of standard Gibbs free energies for various crystalline structures of AFS using density functional theory (DFT). The distinctive feature of AFS is that this ionic salt decomposes and sublimates through distortion of ionic bonds, bypassing the liquid state; therefore, DFT level of approach is required to accurately describe such complex chemical bond transformations. The calculations show that the AFS decomposition temperature varies in a wide range depending on its crystal structure and decreases significantly with increasing water content, in agreement with our previous publication [1].

In addition, our simulations show that similar ionic salts with the similar properties – such as NH_4F, NH_5F_2, $(NH_4)_2SiF_6 \cdot NH_4F$, NH_4BCl_3F, $(NH_4)_2TiF_6$, and $(NO)_2SiF_6$ – can also form during etching. These compounds can be classified into reactive and unreactive salts. The simulations predict that some of these salts are stable only at temperatures below 0 °C. Given that low-temperature etching is an increasingly important direction in the semiconductor industry, such salts may play a more significant role in future etching processes.

[1] T. Lill *et al.*, “Low-temperature etching of silicon oxide and silicon nitride with hydrogen fluoride,” *Journal of Vacuum Science & Technology A*, vol. 42, no. 6, p. 063006, Dec. 2024, doi: 10.1116/6.0004019.

9:30am **ALE1-TuM-7 Influence of Oxide Phase and Surface Facet on Atomic Layer Etching of High-k Metal Oxides***, **Michael Nolan**,* Tyndall Institute, Ireland*; Rita Mullins,* Tyndall National Institute, University College Cork, Ireland

Thermal Atomic Layer Etching (ALE) is of significant interest for its potential to deliver atomic level control over the etch of many materials, in particular in semiconductor device processing for use in future CMOS nodes with requirements for sub-nm levels of control on complex structures. It is performed using sequential surface modification and volatile release reactions with relevant precursors. For metal oxides, HF is the most widely used modifier. It fluorinates the initial surface to form a metal fluoride layer, leaving the remainder of the film unmodified. The modified, non-volatile layer undergoes ligand-exchange with a second precursors of which TiCl4 and SiCl4 are widely used. This volatilizes the MF4 layer releasing product species. The question of the role of the phase and surface facets in a deposited high-k metal oxide film on thermal ALE has received insufficient attention to date but can be readily addressed with first principles atomistic simulations. In this contribution we use density functional theory simulations to explore the effect of the phase and surfaces of HfO2 and ZrO2 on the HF modification half-cycle of ALE. The models used in this study representing polycrystalline materials are the low energy (111) and (001) surface facets of monoclinic, orthorhombic and tetragonal HfO2 and ZrO2. Our thermodynamic analysis shows that for polycrystalline HfO2 and ZrO2, the HF pulse reacts in a self-limiting manner, and is favoured at temperatures typical of CMOS processing. The upper temperature limit is highly sensitive to the phase and surface of both oxides. Models of HF coverage are used to compute calculated theoretical etch rates for the different oxide phases and surface facets and these show a strong dependence on both the crystal phase and the surface so that if different phases and facets are present in a deposited high-k oxide, an uneven etch profile with increased roughness will be seen. The origin of this dependence arises from the stability, geometry and surface atomic coordination environments in the metal oxides.

9:45am **ALE1-TuM-8 Modeling SiO_2 Atomic Layer Etching Using HF/NH_3 Co-Dosing***, **Philipp Haslhofer**, Tobias Reiter,* TU Wien, Austria*; Alexander Toifl, Andreas Hössinger,* Silvaco Europe Ltd., UK*; Lado Filipovic,* TU Wien, Austria

Atomic Layer Etching (ALE) is a key process for achieving conformal and selective material removal in advanced semiconductor manufacturing, particularly for high-aspect-ratio (HAR) structures in 3D memory and logic devices. Owing to its self-limiting nature, ALE enables uniform etching over extended process times. However, predictive modeling of feature-scale behavior remains challenging due to the interplay of surface modification, diffusion, and volatile etching mechanisms.

In this work, we present a feature-scale simulation framework for cyclic ALE of SiO_2 using HF/NH_3 co-dosing in a chemical-oxide-removal (COR) process. The model is implemented in the in-house process simulator ViennaPS [1] and couples geometry-agnostic Monte Carlo ray tracing for gas-phase transport with a level-set method for surface evolution. During reactant pulses, precursor transport is modeled to be ballistic with cosine angular distributions, appropriate for plasma-less processes. Local surface fluxes obtained from ray tracing are converted into surface concentrations that drive surface reactions. Formation of ammonium fluorosilicate (AFS) is described using a parallel-resistance approach, enabling simultaneous treatment of surface-limited reactions and precursor diffusion-limited reactions through the modified layer. In addition, direct volatile etching of SiO_2 by HF is incorporated via a thickness-dependent coverage function which activates under the conditions of incomplete AFS surface coverage.

Model parameters are calibrated against experimentally reported low-pressure-TEOS thickness data by Hagimoto et al. [2] for planar substrates over a range of precursor pulse times. The calibrated model is subsequently applied to HAR trench structures with aspect ratios up to 20 to investigate the influence of precursor partial pressures and sticking coefficients on etch profiles. The simulations reveal transitions from stoichiometry-limited surface modification to diffusion-limited growth regimes, as well as the emergence of inverse aspect-ratio-dependent etching under asymmetric HF/NH_3 sticking conditions, highlighting the sensitivity of ALE conformality to surface kinetics. To address the computational cost of simulating large numbers of ALE cycles, we introduce a cycle-skipping strategy in which surface concentrations are recalculated only after several cycles of constant-rate surface propagation. Comparison to gauge simulations, where surface concentrations are reevaluated for each ALE cycle, reveals that up to five cycles can be omitted while maintaining maximum profile deviations below 1% along the surface, corresponding to a significant reduction in computational cost.

Overall, the presented framework provides a physically motivated and geometry-agnostic approach for predictive ALE modeling in HAR structures capturing different reaction pathways and offers insight into the process windows governing conformality, selectivity, and throughput in HAR applications.

Atomic Layer Etching
Room Tampa Bay Salons 3-4 - Session ALE2-TuM

Thermal and Gas-Phase ALE

Moderators: Anil Mane, Argonne National Laboratory, **Fred Roozeboom**, University of Twente

10:45am **ALE2-TuM-12 In Situ ALE/ALD Surface Engineering for Reduced Dielectric Loss in Superconducting Quantum Circuits***, **Neha Mahuli**,* Amazon **INVITED**

Coherence in superconducting quantum circuits is predominantly limited by loss from imperfect surfaces and interfaces, yet atomic layer deposition (ALD) and atomic layer etching (ALE) remain relatively unexplored. In this talk, we present ALD and ALE as a surface-engineering platform for superconducting quantum devices, highlighting performance gains and future opportunities. We describe a post-fabrication, in situ surface treatment integrating ALE and ALD to reduce dielectric loss in aluminum (Al)–based coplanar waveguide (CPW) resonators and transmon qubits on silicon substrates. The process involves conformal removal of native aluminum oxide using thermal ALE at 300°C (trimethylaluminum (TMA) and Hydrogen fluoride(HF)–pyridine chemistry), followed by controlled regrowth of a thin Al2O3 layer using ALD at the same temperature. Surface characterization indicates reduced organic contamination, formation of a thinner Al-rich oxide, and effective cleaning of patterned structures, including metal sidewalls. Applying this treatment to CPW resonators reduces two-level system (TLS) loss at single-photon power by a factor of two. Similarly, for Al transmon qubits, the combined ALE+ALD process increases the mean quality factor by a similar factor, with select devices exceeding 9 x 10^6 million and energy relaxation times above 0.4 ms. Finally, we outline ongoing efforts and some initial results to disentangle the roles of etching and encapsulation, including different ALE chemistries (thermal vs plasma), and in situ ALD of alternative low-loss dielectric capping layers, underscoring the potential of ALD/ALE for surface control in superconducting quantum hardware.

11:15am **ALE2-TuM-14 Fluorine-Free Thermal Atomic Layer Etching of ZrO_2 Using $H_2O/SOCl_2$ Chemistry for Damage-Free Etch-Back of High-k Dielectrics***, **Gyeong Min Jeong**, Jihoon Shin, Jin-Seong Park,* Hanyang University, Republic of Korea

As semiconductor devices continue to scale down, precise dimensional control of individual device components has become increasingly critical. In this context, atomic-scale processing techniques have emerged as key enablers for next-generation semiconductor manufacturing. Among them, thermal atomic layer etching (ALE) has attracted attention as a surface-reaction-driven process capable of removing materials with atomic-layer precision through sequential surface modification and material removal steps. Compared to conventional plasma-based etching, thermal ALE minimizes sputtering-induced damage and effectively suppresses surface roughening. High-k dielectric materials are widely employed as replacements for Si-based insulators in advanced semiconductor devices, enabling sufficient capacitance retention even at deeply scaled technology nodes. However, the dielectric properties of high-k oxides are strongly correlated with their crystalline phases, and achieving ultrathin crystalline films with well-controlled thickness remains challenging. An etch-back approach, in which sufficiently thick crystalline films are first deposited and subsequently thinned while preserving crystallinity, is therefore required.

Thermal ALE is well suited for this purpose due to its inherently low-damage characteristics. Most reported thermal ALE processes for high-k materials normally use fluorine-based sources. From this point of view, we propose a novel thermal ALE process for zirconium dioxide (ZrO_2) that does not use the fluorination agent. ZrO_2 films were etched using alternating exposures of H_2O (water) and $SOCl_2$ (thionyl chloride), achieving a self-limiting etch rate of approximately 0.07 Å per cycle. chlorine residues were not detected within the ZrO_2 layer after etching. Surface hydroxylation induced by H_2O exposure forms a reactive termination that facilitates subsequent reactions with $SOCl_2$, enabling continuous and controlled etching. The proposed reaction mechanism is further supported by density functional theory (DFT) calculations. This fluorine-free thermal ALE approach provides precise, damage-free thickness control while preserving the crystalline properties of high-k dielectrics, offering a promising alternative to conventional fluorine-based etching processes for advanced semiconductor manufacturing.

11:30am **ALE2-TuM-15 Thermal Atomic Layer Etching by Halogenation and Ligand-Addition Using N-Heterocyclic Carbenes*, Aziz Abdulagatov,*** University of Colorado Boulder*; Charles Dezelah, Matthew Surman,* ASM Microchemistry Ltd., Finland*; Steven George,* University of Colorado Boulder

N-heterocyclic carbenes (NHCs) are strong electron pair donors and can bind to metal centers by ligand-addition.In this study, etching of Al_2O_3 was demonstrated using halogenation with hydrofluoric acid (HF) followed by ligand-addition using NHCs.The NHC sources were 1,3-dimethylimidazolium-2-carboxylate ($IMeCO_2$) or 1,3-di-tert-butylimidazol-2-ylidene (ItBu) (**Figure 1**).The thermal ALE of Au and Co was also demonstrated using hydrochloric acid (HCl) together with $IMeCO_2$ or ItBu.The studies were conducted using in situ quartz crystal microbalance (QCM) measurements.

Al_2O_3 thermal ALE was achieved using sequential HF and $IMeCO_2$ or ItBu exposures at temperatures from 230 to 290 °C.QCM profiles showed a self-limiting mass gain during fluorination and a self-limiting mass loss during the NHC ligand-addition step (**Figure 2a**).The mass change per cycle yielded an etch rate of 3.3 Å per cycle at 290 °C. The spontaneous etching of Al_2O_3 films was also observed during exposure to 2,2-difluoro-1,3-dimethylimidazolidine (DFI) (**Figure 1**).DFI provides both fluorination and ligand-addition by the NHC remaining after fluorination.DFI leads to continuous Al_2O_3 spontaneous etching at 200 to 270 °C.

The NHCs were also effective for Au and Co thermal ALE.Sequential exposures of HCl and $IMeCO_2$ or ItBu led to a linear mass decrease with the number of ALE cycles. The maximum Au mass change yielded an etch rate of 0.83 Å per cycle at 250 °C using HCl and $IMeCO_2$ (**Figure 2b**). For Co, the maximum etch rate was 3.0 Å per cycle at 290 °C using HCl and ItBu. These ALE processes are believed to proceed through the formation of volatile metal chloride–carbene adducts.The cycle times during Au and Co ALE were much shorter than earlier cycle times for Au and Co ALE measured using phosphines for ligand-addition.

11:45am **ALE2-TuM-16 Influence of Fluorination and Oxygenation Sources on the Thermal Atomic Layer Etching of MoS_2*, Spencer P. Smith*,** *Jacob A. Tenorio, Icelene Leong, John D. Hues, Steven M. Hues, Elton Graugnard,* Boise State University

Atomic layer etching (ALE) has proven to be a transformative technique for atomic scale processing of two-dimensional (2D) materials, including molybdenum disulfide (MoS_2), a promising material in the semiconductor industry because of its high mobility in its monolayer form. Precise etching of MoS_2 films can offer a route to desired electrical and optical properties through controlling film thickness. Previous research reported MoF_6 and H_2O as precursors for thermal ALE of MoS_2. Here, we report on progress with alternative fluorination and oxygenation sources and assess their effectiveness of thermal ALE of MoS_2. Oxygen sources include H_2O and O_3, and fluorine sources include HF/Pyridine and MoF_6. Etch rates, uniformity, and surface chemistry following ALE were characterized through spectroscopic ellipsometry, atomic force microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. The results of ALE of amorphous MoS_2 with HF indicated that there were no signs of etching with H_2O at 200 °C or 300 °C. ALE with HF and O_3 produced a mass loss per cycle of 25 ng/cm^2 at 200 °C and an etch per cycle (EPC) of 0.4 Å, similar to prior results of 0.5 Å/cyc with MoF_6 and H_2O. However, MoF_6 with O_3 at 200 °C on amorphous MoS_2 films exhibited non-self-limiting etch behavior with a mass loss per cycle of 126 ng/cm^2. Lowering the temperature to 150 °C resulted in self-limiting ALE with a mass loss per cycle of 63 ng/cm^2. Although surface oxygen concentrations increased from etching, surface morphology showed little change on amorphous films. Results for application of these chemistries to crystalline MoS_2 films will be discussed. This research further broadens the capabilities of atomic layer etching for precise processing of 2D materials.

Atomic Layer Etching
Room Tampa Bay Salons 3-4 - Session ALE1-TuA
Plasma and Energy-enhanced ALE II

Moderators: Harm C.M. Knoops, Oxford Instruments Plasma Technology, Netherlands, **Nicolas Posséme**, CEA-Leti

1:30pm **ALE1-TuA-1 Etch Characteristics of Iridium with Atomic Layer Etching Technique***, **Wendy Yan**,* IBM Research **INVITED**

Iridium (Ir) is a promising replacement for copper (Cu) in next-generation interconnects, yet its plasma etching is limited by low-volatility reaction products. This work investigates Ir plasma atomic layer etching (ALE) using Cl/O$_2$ and CF$_4$/O$_2$ chemistries. The ALE sequence employs oxygen-assisted halogenation for surface modification, followed by low-energy ion activation to enable directional desorption of Ir-containing byproducts.

Etching mechanisms are examined using X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and transmission electron microscopy (TEM). XPS identifies Ir–Cl, Ir–F, and Ir–O bonding states, TOF-SIMS quantifies modified layer thickness and molecular distribution, and TEM probes small critical-dimension feature profiles and sidewall chemical composition. Correlating these surface and structural analyses with etch-per-cycle, profile anisotropy, line-edge roughness, and hardmask selectivity enables a better understanding of Ir ALE characteristics and guides the optimization of Ir interconnect pattern fidelity and dimensional control.

2:00pm **ALE1-TuA-3 Selectivity, Surface Roughness and Residue of Plasma-Based Atomic Layer Etching of Metals and Dielectric Materials for Semiconductor Devices***, **Heeyeop CHAE**,* Sungkyunkwan University (SKKU), Republic of Korea

The critical dimensions of semiconductor devices continue to shrink, reaching nanometer and even angstrom scales in both 2D and 3D structures. Consequently, the demand for atomic-scale precision in etching processes is rapidly increasing. This talk will present various examples of plasma-based atomic layer etching (ALE) with emphasis on etch selectivity, surface roughness, and residue control for both metal and dielectric materials. Materials discussed include silicon nitride, titanium nitride, zirconium oxide, silicon oxide, aluminum oxide, hafnium oxide, molybdenum, ruthenium, and tantalum nitride. Typical ALE processes consist of two sequential steps: surface modification and material removal. Surface modification is achieved through various reaction pathways, including fluorocarbon film deposition, surface fluorination, chlorination, and oxidation using plasma-generated radicals. In the subsequent removal step, the modified layers are eliminated through mechanisms such as ion bombardment, thermal desorption, ligand exchange, ligand volatilization, or halogenation. This talk will also address key characteristics of plasma-based ALE processes, including etching selectivity, surface roughness, and residual surface contamination.

2:15pm **ALE1-TuA-4 Directional Atomic Layer Etching of MgO-Doped Lithium Niobate Using Br-Based Plasma***, **Ivy Chen**,* California Institute of Technology*; Frank Greer,* Jet Propulsion Laboratory (NASA/JPL)*; Austin Minnich,* California Institute of Technology

Lithium niobate (LiNbO$_3$, LN) is a nonlinear optical material of high interest for integrated photonics with applications ranging from optical communications to quantum information processing. The performance of on-chip devices based on thin-film lithium niobate (TFLN) is presently limited by fabrication imperfections such as sidewall surface roughness and geometry inhomogeneities over the chip. Atomic layer etching (ALE) could potentially be used to overcome these difficulties. Although an isotropic ALE process for LN has been reported, performing LN fabrication completely with ALE faces several challenges, including the lack of a directional ALE process for pattern transfer and the redeposition of involatile compounds. We report a directional ALE process for LN consisting of sequential exposures of HBr/BCl$_3$/Ar plasma for surface modification and Ar plasma for removal. The HBr chemistry is found to decrease redeposition compared to F- and Cl-based plasmas, which we attribute to the higher vapor pressures of Br-based products. A grating pattern etched entirely by the process (total etch depth of 220 nm) exhibits no aspect ratio dependent etching (ARDE) down to the smallest tested gap of 150 nm, in contrast to ion milling in which ARDE manifests even at 300 nm gaps for the same etch depth. The HBr plasma chemistry is also found to support an isotropic process consisting of sequential exposures of H$_2$ plasma and HBr/BCl$_3$/Ar plasma. These processes could be used together to perform the complete fabrication process for TFLN devices, eliminating imperfections arising from ion milling.

2:30pm **ALE1-TuA-5 Examining AlGaN Atomic Layer Etch per Cycle Uniformity and Repeatability by Cross-Referencing In-Situ Etch Depth Monitoring with Electrical Characterisation***, **Ben Jones**, Matthew Loveday, Sung-Jin Cho, Andrew Newton,* Oxford Instruments Plasma Technology, UK

Atomic layer etching (ALE) of AlGaN is well suited to the critical gate recess step of AlGaN/GaN normally-off metal insulator semiconductor-high electron mobility transistors (MIS-HEMT) [1]. A two-dimensional electron gas (2DEG) forms at the AlGaN–GaN interface (**Fig. 1**) enabling the mobility and carrier density required for high–performance power devices. As shown in **Fig. 2**, 2DEG mobility directly governs device efficiency [2]. Its formation depends strongly on AlGaN film properties and thickness. Precise control of the AlGaN gate–recess thickness is essential for engineering threshold voltage (V_{TH}) and blocking capability, ideally ~5 nm thickness [3]. Low–damage processing is necessary to minimise interface traps, leakage, and electric–field crowding [4].

Using a reflectance-based endpoint technique, sub-5 nm AlGaN films have been etched with Cl$_2$/BCl$_3$ ALE. **Fig. 3** plots dose time vs etch–per–cycle (EPC) for 30 - 120 ms doses, with a clear EPC jump at 40 ms and plateauing thereafter, indicating saturation. Process repeatability is demonstrated in **Fig. 4**: across 11 runs, EPC ranged from 0.79–0.88 nm/cycle. The normal distribution of this data set is plotted in **Fig. 5**, indicating run-to-run EPC uniformity of 5.4 %. However, reflectance end pointing only measures the targeted point and gives no cross–wafer EPC uniformity. Such uniformity is difficult to measure on <10 nm AlGaN due to surface roughness, ellipsometry limits, and FIB/SEM damage. We aim to infer etched film uniformity by correlating reflectance–measured AlGaN thickness with sheet resistance obtained via Hg–probe analysis. **Fig. 6** shows in–situ thickness measurements for targeted 5 nm and 0 nm endpoints, illustrating the strength of the technique: the ALE sequence stops automatically when the desired thickness is reached [5]. **Fig. 7** displays raw reflectance data; the initial smooth region occurs before the “turning point,” after which true thickness is extracted, shown by the stepped profile. Accurate end thickness does not require knowledge of the initial AlGaN thickness.

In this submission we will quantify EPC uniformity across Ø150 mm AlGaN–GaN substrates by combining in–situ reflectance thickness measurement with local Hg–probe C–V/I–V sheet–resistance mapping. We will also electrically characterise surface roughness of sub–5 nm AlGaN films produced by ALE and ICP etching. Finally, we will expand the current dataset to show how etch–process parameters influence run–to–run uniformity across multiple AlGaN–GaN wafers.

2:45pm **ALE1-TuA-6 Atomic Layer Etching Techniques for Sidewall Surface Damage Removal in GaN-Based LEDs***, Chan Ho Kim, Sung Hyun Kim, Young Woo Jeon, Jong Woo Hong, Jong Soon Park, **Geun Young Yeom**,* Sungkyunkwan University, Republic of Korea **INVITED**

As the GaN light emitting diode (LED) device technology is developed from conventional LED to micro LED, the lateral dimension of LED devices is decreased, and the ratio of sidewall area relative to overall device area is increased. Especially, as the GaN LED device size decreases below 5 microns, the performance and reliability of GaN devices are significantly degraded. One of the reasons for the degradation of the micro LED device is the damage from the sidewall due to the ion bombardment during the reactive ion etching (RIE).Ion bombardment during the RIE can lead to various issues such as surface composition changes, surface defects, surface contamination, and increased leakage current.

In this study, we focused on the etching of GaN LED devices with a multi quantum well (MQW) layer, which is composed of multiple InGaN and GaN layers. A mesa structure of GaN LED device consisted of p-GaN/MQW/n-GaN/undoped-GaN layer on sapphire wafers (or silicon wafers) was etched using BCl$_3$/Cl$_2$/Ar RIE, and the sidewall damage remaining after the RIE was removed using wet etching and/or ALE methods using conventional ICP etch system and an ion beam-based etch system. The effect of wet etching of damaged GaN LED sidewall using a KOH-based solution was compared with the sidewall damage removal using ALE methods. The effect of ion beam-based ALE on the removal of sidewall damage for vertical GaN LED devices will be also discussed. The results showed that, the wet etching improved the sidewall stress or defects due to the damage by RIE, however, the optimized ALE processes removed the sidewall stress and defects on MQW layers of patterned GaN structure almost completely. This indicates that, as GaN-based devices decrease in size, the effectiveness of ALE increases, making ALE more effective than wet etching for removing sidewall etch damage for next-generation device fabrication.

Atomic Layer Etching
Room Tampa Bay Salons 3-4 - Session ALE2-TuA
ALD+ALE and Selective ALE

Moderators: Jean-François de Marneffe, IMEC, **Austin Minnich**, Caltech

4:00pm **ALE2-TuA-11 Self-Limiting Oxidation State Control of MoOx Thin Films Using Integrated ALD and ALE***, **Woojin Jeon**, Chaeyeong Hwang,* Kyung Hee University, Republic of Korea*; Christophe Vallée,* University at Albany-SUNY **INVITED**

Atomic layer etching (ALE)has evolved beyond its intrinsic advantage of precise thickness controllability, and low-damage etching, with increasing research focused onadvanced process applicationssuch as the crystallization of ultrathin films as well as the realization ofgate-all-around (GAA)andthree-dimensional (3D) integrationstructures through integration withatomic layer deposition (ALD)andarea selective deposition (ASD).

In this talk, we present our research results oncontrolling the oxidation state of deposited thin films through the integration of ALD and ALE processes. Molybdenum dioxide (MoO_2) has attracted significant attention as a high-work-function electrode material for next-generation metal-insulator-metal (MIM) capacitors, particularly for stabilizing the rutile phase of TiO_2 with a dielectric constant of 150. However, typical ALD process only allows the most stable oxidation state of MoO3, resulting in stoichiometric variations in high-aspect-ratio structures and morphology degradation during reduction have limited its practical applications. To address these issues, we introduce an approach which combines ALD of MoO_a ($2 < a < 3$) followed by ALE of MoO_3 using H_2O. The process selectively removes MoO_3through etching, leveraging the self-limiting nature of both reactions to achieve precise atomic-scale control over oxidation states without morphology degradation. MoO_2 films deposited using this method exhibit enhanced electrical performance, including a higher dielectric constant and reduced leakage current when employed as bottom electrodes in TiO_2-base MIM capacitors.

4:30pm **ALE2-TuA-13 Selective Etching of Molybdenum and Tungsten Oxides Based on Their Oxidation States Using $SOCl_2$ and SO_2Cl_2***, **Troy Colleran**,* University of Colorado at Boulder

Molybdenum, tungsten, and their oxides have important applications in microelectronics processing. This investigation explored the spontaneous etching of MoO2, MoO3, WO2, and WO3 by thionyl chloride (SOCl2) and sulfuryl chloride (SO2Cl2). The studies were conducted at 200°C using quadrupole mass spectrometry (QMS) and in situ Auger electron spectroscopy (AES). The QMS studies revealed selectivity between the +4 and +6 oxidation states of the metal oxides using SOCl2 and SO2Cl2 as the etchants. The in situ AES experiments demonstrated the removal of native oxide on both W and Mo thin films using SOCl2.

SOCl2 etched MoO3 and WO3 in the +6 oxidation state and produced MoO2Cl2 and WO2Cl2 and WOCl4, respectively. These volatile Mo and W oxychloride etching products were verified by QMS using their isotopic signatures (Figures 1 & 2). In contrast, SOCl2 did not etch the +4 oxidation state in MoO2. However, SOCl2 did etch WO2. SO2Cl2 displayed nearly opposite behavior. SO2Cl2 etched the +4 oxidation state in MoO2, but did not etch the +6 oxidation state in MoO3. SO2Cl2 also did not etch either WO2 or WO3. The lack of etching of WO2 by SO2Cl2 and the etching of WO2 by SOCl2 was attributed to the oxidation and disproportionation of WO2 to WO3.

In situ AES studies were used to evaluate the ability of SOCl2 to remove native oxide from Mo and W surfaces. After SOCl2 exposure at 250°C, the atomic percentage of oxygen on the metal films dropped from 59% on Mo and 53% on W before SOCl2 exposure to <2% on both films after SOCl2 exposure (Figures 3 and 4). SOCl2 has the potential to remove oxides on conductive Mo and W lines in BEOL interconnects. Oxidation and subsequent volatilization of the formed oxide also is a method for the thermal atomic layer etching (ALE) of Mo and W metals.

4:45pm **ALE2-TuA-14 High-Density Silicon Lines Patterning with Atomic Layer Etch Pitch Splitting (APS™) Technology***, **Amin Karimi**, Robin Athle, Reza Jafari Jam, Alfred Ahlström Andersson, Svetlana Ivanova, Kishwar Sultana, Asif Muhammad, Mostafa Torbati, Hesamedin Safavi,* AlixLabs A.B., Sweden*; Fred Roozeboom,* University of Twente, Netherlands*; Dmitry Suyatin, Jonas Sundqvist,* AlixLabs A.B., Sweden

Dense silicon line fabrication is a central process in modern electronics manufacturing, enabling key device and interconnect structures such as FinFETs, gate-all-around FETs (GAA-FETs), gate electrodes, and metal interconnects.These features appear across multiple integrated-circuit layers, from front-end devices to back-end of line metallization layers (M0–M6), and are essential for logic and memory technologies. As device scaling continues, the ability to pattern denser line arrays with tighter pitch and smaller critical dimensions (CDs) has driven innovation. To meet scaling demands, advances in lithography and patterning have included deep ultra violet (DUV) immersion lithography, nanoimprint lithography (NIL), and low- and high-NA extreme ultraviolet (EUV) lithography. In parallel, multipatterning schemes such as SADP, SAQP, LELE, and SALELE have been developed to extend resolution limits. However, each approach has limitations. Immersion lithography faces fundamental resolution constraints, NIL suffers from defectivity and throughput challenges, and EUV adoption is hindered by very high capital and infrastructure and energy costs. Multipatterning further increases process complexity through repeated deposition, lithography, cleaning, and etching steps, leading to cumulative yield loss and stricter process control chalenges. As patterns reach a 24nm pitch and below, the high-aspect-ratio mandrils used to form silicon fins and nanosheets become prone to mechanical bending or collapse during the multiple deposition and etching cycles required by SAQP.

In this work, we present Atomic Layer Etch Pitch Splitting (APS™) patterning technology developed at AlixLabs(1-4) that simplifies dense line fabrication while extending the resolution of conventional lithography. The method is based on atomic layer etching (ALE) and serves as a more sustainable alternative to conventional multipatterning. It enables significant pitch reduction with a single processing step, reducing the need for EUV at certain technology nodes. In this way, patterns defined at 14/12 nm using immersion lithography can be scaled to effective dimensions corresponding to 7/6 nm and beyond, without EUV, lowering complexity and cost. The technique operates on patterns with arbitrary topology, including straight and inclined features, enabling orientation-independent line splitting. We demonstrate silicon dense line arrays with CDs of 10 nm and half-pitch of 10 nm. The process is repeatable, allowing multiple successive splitting steps equivalent to SAQP. Our single-step patterning process alternative, APS™, reduces yield variation and eliminates intermediate metrology needs.

1. Khan Md S. A., et al. US10930515 B2, Feb. 23, 2021, priority date March 14, 2017.

2. Khan Md S. A., et al. US11424130 B2, Aug. 23, 2022.

3. Khan Md S. A., et al., US20250259851 A1, Aug. 14, 2025.

4. Sundqvist J., et al. 13429, p. 134, SPIE, Apr. 22, 2025.

5:00pm **ALE2-TuA-15 Direct Atomic Layer Processing (DALP®): Extending ALD and ALE to Spatially Localized Multi-Material Integration***, **Mira Baraket**,* ATLANT 3D Nanosystems, Denmark

The development of next-generation electronic and functional devices increasingly depends on the ability to integrate complex material heterostructures with nanoscale precision. However, conventional thin-film deposition and patterning workflows—while offering excellent uniformity and material quality—remain inherently rigid, limiting spatial selectivity, multi-material integration, three-dimensional thickness control, and rapid experimentation within a single process flow.

ATLANT 3D introduces **Direct Atomic Layer Processing (DALP®)**, a nanofabrication technology that enables digitally controlled, spatially localized deposition of multiple materials with atomic-scale precision. DALP combines the strengths of atomic layer deposition with direct-write spatial control, allowing different materials to be sequentially deposited at defined locations without intermediate lithography or masking steps. This capability enables the fabrication of complex material stacks, heterostructures, interfaces, and thickness gradients within a unified and repeatable workflow.

This presentation describes the DALP process architecture and its application across both combinatorial materials discovery and targeted device manufacturing. By enabling programmable material placement, precise thickness engineering, and high process repeatability within a single platform, DALP accelerates materials exploration while directly producing device-ready structures compatible with manufacturing environments. Representative examples demonstrate multi-material nanoscale structures for advanced semiconductor and functional material applications, where precise interface control, spatial selectivity, and scalability are critical.

DALP significantly expands the accessible design space for atomic-scale fabrication and provides a direct pathway from materials discovery to manufacturable, device-ready architectures.

5:15pm **ALE2-TuA-16 Atomic Layer Etching of Titanium Nitride with O_3 and $NbCl_5$**, ***Juha Ojala***, *Mykhailo Chundak, Anton Vihervaara, Mikko Ritala,* University of Helsinki, Finland

Titanium nitride is an essential material in the semiconductor industry, used as a gate metal and as electrode material in various devices, and as a diffusion barrier in metal interconnects. Future device architectures require materials to be formed into smaller and increasingly complex features, which drives the need for new deposition and etching processes. Thermal atomic layer etching, as an isotropic and conformal process is ideal for thinning and patterning films in high aspect ratio and non-line-of-sight structures. In some cases, ALE can also result in smoothing of the film surface, which could be used for interfacial engineering to improve device performance.

We present a new thermal atomic layer etching process for TiN based on oxidation of the TiN surface with O_3, and removal of the oxidized surface layer with $NbCl_5$. The process was studied at 200–350 °C and EPC values of 0.5–4.5 Å were observed. At 200–300 °C an Arrhenius type temperature dependence of the EPC was seen. Roughnesses of the films were studied using atomic force microscopy and it was found that at 200 °C the etching resulted in smoothing of the TiN surface from 0.7 to 0.6 nm RMS. The surface roughness was quite low even after etching at higher temperatures, as etching at 250–350 °C resulted in only slight roughening to about 0.9 nm RMS. Resistivities of the films were also measured, and it was found that the resistivity stayed comparable to the unetched film to a thickness of 4.5 nm. XPS measurements showed the presence of slight niobium oxide residue on the surface of partially etched TiN, but after full etching of the TiN film, no residues of the etchants could be seen.

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