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.

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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-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-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 $TiCl_4$ or $SiCl_4$, which volatilizes the modified layer. HF is a toxic and challenging to handle chemical and other fluorides used in etch, e.g. CF_4, C_4F_8 and NF_3 are PFAS or have high global warming potential (GWP). Hydrofluorocarbons such as CH_3F or CH_2F_2 have GWPs < 100 and are not strictly PFAS, lacking the terminal CF_3 group. In this contribution we present first principles simulations of the potential for CH_3F and CH_2F_2 to be used as alternatives to HF for ALE of high-k oxides HfO_2, ZrO_2 and $HfZrO_4$. 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 HfO_2 and $HfZrO_4$, 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 CuO_x 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.

ALE-MoP-18 Atomic Layer Etching Enabling Nano-Scale Semiconductor Manufacturing*, **Danbi Yoo**, Paul Plate,* SENTECH Instruments GmbH, Germany

Atomic layer etching (ALE) is a novel etching technique that flips the concept of atomic layer deposition (ALD)enabling atomic-level control of material removal and opening new possibilities in semiconductor manufacturing. Unlike conventional etching methods, ALE removes material in a highly controlled, layer-by-layer manner, with etch rates in the sub-nm range. This approach delivers exceptional precision, repeatability, and selectivity, facilitating the fabrication of increasingly complex nanoscale structures and devices. In particular its different modes of isotropic and anisotropic etching modes enable the fabrication of novel devices such as gate-all-around (GAA) transistors.As devices continue to shrink, pushing the boundaries of Moore's Law, the demand for smaller, more powerful, and energy-efficient devices has driven the need for new atomic-scale etch processes. ALE is and will continue to play a crucial role in the miniaturization of semiconductor devices for the future. This capability is especially critical as the demand for sub-10 nm devices is increasing.SENTECH has over thirty years of experience in developing and manufacturing plasma process systems and thin-film metrology tools for the R&D and industrial production communities. Our flexible, modular and robust systems focus on thin-film deposition, dry-etching, and characterization in semiconductor technology, microsystems technology, photovoltaics, nanotechnology, and materials research. SENTECH's systems are particularly capable for ALE applications due to their ability to independently tune high ion energy distribution while preserving a low and narrow ion energy distribution, enabling exceptional process control, selectivity, and atomic-scale etch precision.Within the scope of this work, we will showcase the fabrication of GaN-based high-electron-mobility transistors (HEMTs) in normally-on operation mode [1,2]. ALE was the key factor for manufacturing the device, enabling precise material removal, low surface roughness and damage. Furthermore, we will discuss ALE processes for oxide-based materials such as SiO_2 [3] and Al_2O_3, all of which are widely used as passivating layers or gate oxides, respectively. This will give a new perspective on processing these well-known materials, demonstrating the strength of ALE processing as a pivotal technology for the continued advancement of plasma processing.

In-situ monitoring is a cornerstone for the time-effective development of many types of processes. In particular, we will focus on ellipsometry due to its non-invasive nature and high precision in the sub-nm range, making it a highly suitable technique for thin-film characterization in ALE processes. This work will elaborate on the potential of in-situ ellipsometry for understanding surface reactions during the ALE process, process setup and process monitoring.

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Author Index

Bold page numbers indicate presenter

— A —
Abdulagatov, Aziz: ALE-MoP-9, **2**
Aguirre, Nestor: ALE-MoP-2, 1
— B —
Baik, Sun Young: ALE-MoP-11, 3
— C —
Cavanagh, Andrew: ALE-MoP-9, 2
Chen, Chien-Wei: ALE-MoP-8, **2**
Chen, Ivy: ALE-MoP-6, **2**
Cho, Hyeon Sik: ALE-MoP-11, 3
Cho, Kyuho: ALE-MoP-11, 3
Colleran, Troy: ALE-MoP-10, **3**
— D —
Dua, Asare: ALE-MoP-17, 4
— E —
Efthymiou Tsironi, Maria: ALE-MoP-1, **1**
Ellis, James: ALE-MoP-13, 3
— G —
George, Steven: ALE-MoP-9, 2
Goumans, Fedor: ALE-MoP-2, **1**
— H —
Hanada, Koshi: ALE-MoP-3, 1
Harris, Ben: ALE-MoP-13, 3
Hassall, Geoff: ALE-MoP-13, 3
Hock, Adam: ALE-MoP-17, **4**
Hong, Jong Woo: ALE-MoP-7, 2
Hsu, To-En: ALE-MoP-8, 2
— J —
Jang, Yun Jong: ALE-MoP-5, 1
Jeon, Young Woo: ALE-MoP-7, **2**
Jeong, Juhwan: ALE-MoP-11, 3
Jung, Hyun Ju: ALE-MoP-11, 3
Jurca, Titel: ALE-MoP-15, 3
— K —
Kim, Hana: ALE-MoP-11, **3**
Kim, Jaemin: ALE-MoP-11, 3
Kim, Myeong Il: ALE-MoP-11, 3
Kim, Sung Hyun: ALE-MoP-4, **1**
— M —
Marandi, Alireza: ALE-MoP-6, 2
Minnich, Austin: ALE-MoP-6, 2
Mohr, Sebastian: ALE-MoP-13, **3**
Moore, Justin: ALE-MoP-15, **3**
Mullins, Rita: ALE-MoP-16, 4
— N —
Nolan, Michael: ALE-MoP-16, **4**
Nonaka, Tomoyuki: ALE-MoP-3, 1
— O —
Onofrio, Nicolas: ALE-MoP-2, 1
— P —
Panariti, Persi: ALE-MoP-17, 4
Park, Jong Soon: ALE-MoP-4, 1
Plate, Paul: ALE-MoP-18, 4
— S —
Schroeder, Uwe: ALE-MoP-9, 2
Seo, Duck Hyeon: ALE-MoP-11, 3
Song, Hyungseon: ALE-MoP-13, 3
— U —
Uchida, Akimi: ALE-MoP-3, **1**
— W —
White, Daryl: ALE-MoP-13, 3
Wunderwald, Florian: ALE-MoP-9, 2
— Y —
Yang, Su Jeong: ALE-MoP-5, **1**
Yeom, Geun Young: ALE-MoP-4, 1; ALE-MoP-5, 1
Yeom, Geun Young: ALE-MoP-7, 2
Yoo, Danbi: ALE-MoP-18, **4**
Yu, Yu-Hsuan: ALE-MoP-8, 2
— Z —
Zhou, Selina: ALE-MoP-6, 2