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

ALD+ALE - Emerging ALE

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

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

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

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

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

References:

1. US Patent 10,930,515, Feb. 23, 2021.

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

3. Farrell et al., SPIE, 2018, doi: 10.1117/12.2303004

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

ALE-MoP-2 Improving Process Stability in Atomic Layer Etching for Next-Generation Microfabrication*, **Suyoung Jang**, Junyeob Lee, Dohyeon Kim, Jeongwoon Bae, Taehyung Kim, Kyongnam Kim,* Daejeon University, Republic of Korea*; Jihyun Kim,* WONIK IPS, Republic of Korea

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

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

ALE-MoP-3 Synergy in Thermal Atomic Layer Etching: Interplay between Individual Reactions*, Marcel Junige, **Andrew S. Cavanagh**, Steven M. George,* University of Colorado Boulder

The plasma-assisted atomic layer etching (ALE) community has long recognized that an ideal ALE sequence requires the favorable interaction of its individual, separated reaction steps [Kanarik *et al.*, *JVST-A* **33**, 020802 (2015)]. Ideal ALE synergy is characterized by self-limiting A and B half-reactions, whereas spontaneous etch pathways may continuously remove the targeted material. This work utilized *in situ* spectroscopic ellipsometry (iSE) to study and extend this synergy concept to thermal ALE processes:

ALE Synergy = (EPC-α-β)/EPC

The digital etch per cycle (EPC) is the thickness loss derived from the A/B reaction sequence. The spontaneous etch rate αor βmay contribute a thickness loss during the individual A or B reaction. Synergy was evaluated for alumina (Al_2O_3), silica (SiO_2), silicon nitride (SiN_x), and silicon (Si) thermal ALE.

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

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

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

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

ALE-MoP-4 Atomic Layer Etching of ZrO_2, HfO_2 and $HfZrO_4$ Thin Films via Metal-Free Ligand Exchange using Hydrogen Fluoride and Acetylacetone*, **Kyoung-Mun Kim**, Joo-Yong Kim,* Merck KGaA, Darmstadt, Republic of Korea

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

ALE-MoP-5 Isotropic Atomic Layer Etching of Crystalline HfO_2 Thin Films Using F Radical and $Al(CH3)_2Cl$*, **Jehwan Hong**, Gyejun Cho, Changgyu Kim, Hye-Lee Kim,* Sejong University, Republic of Korea*; Byungchul Cho, Min Su Kim, Ju Hwan Park, Min Kim,* Wonik IPS, Republic of Korea*; Won-Jun Lee,* Sejong University, Republic of Korea

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

References [1] J. A. Murdzek and S. M. George, J. Vac. Sci. Technol. A 38, 022608 (2020).

ALE-MoP-6 Atomic Layer Etching of Al2O3 Film by Using Different Metal Precursor for Ligand Exchange*, **Chan Lee**, Chang Kyu Lee, Byung Chul Cho, Ju Hwan Park, Min Kim,* WONIK IPS, Republic of Korea*; Misoo Kim, Khabib Khumaini, Hye-Lee Kim, Won-Jun Lee,* Sejong University, Republic of Korea

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

Reference

1. A. Agarwal and M. Kushner, J. Vac. Sci. Technol. A 27, 37 (2009).
2. S. D. Athavale and D. J. Economou, J. Vac. Sci. Technol. A 13, 966 (1995).

ALE-MoP-7 Fabrication of Ultrathin Ruthenium Films via a Top-Down Approach Using Thermal Atomic Layer Etching*, Jeong Hwan Han, **Eun Ji Ju**, Jae Hyeon Lee,* Seoul National University of Science and Technology, Republic of Korea

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

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

Acknowledgments This work was supported by the Technology Innovation Program(RS-2024-00509266, Development of Next-generation dielectric and electrode process equipment for logic 1nm or less and memory xnm level) funded By the Ministry of Trade Industry & Energy(MOTIE, Korea) and byKorea Institute for Advancement of Technology (KIAT) grant funded by the Korea Government (MOTIE) (RS-2024-00409639, HRD Program for Industrial Innovation

ALE-MoP-8 Thermal Atomic Layer Etching of ZrO_2 Using Chlorine-Based Precursor*, Sang-ik Lee, **Yong-won Kim**,* DNF Co., Ltd, Republic of Korea*; jun-hee Cho, Joong-jin Park,* DNF Co., Ltd., Republic of Korea

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

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

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

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

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

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

ALE-MoP-9 Highly Precise Atomic Layer Etching of SiO_2 with SF_6 Radicals and TMA Surface Modification*, **Min Kyun Sohn**, Seong Hyun Lee, Jieun Kim, Sun Kyu Jung, Min-A Park, Jin Ha Kim, Jaeseoung Park, Jeong Woo Park, Dongwoo Suh,* ETRI, Republic of Korea

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Atomic Layer Etching
Room Samda Hall AB - Session ALE1-TuM
Thermal Gas Phase ALE

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

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

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

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

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

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

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

We present a new thermal ALE process for etching of Mo, where the surface of Mo is oxidized with O_2 and the resulting oxide etched with $NbCl_5$. The ALE process was studied using XRR thickness measurements and *in vacuo* XPS studies. The films were characterized before and after etching using XRD, EDS, SEM, AFM, and four-point probe.

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

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

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

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

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

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

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

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

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

Acknowledgement

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

9:30am **ALE1-TuM-7 Isotropic Atomic Layer Etching of HfO-$_2$ using Plasma Fluorination with NF$_3$ and Ligand Exchange with BCl$_3$*,* *Hyeongwu Lee,*** *Heeju Ha, Daeun Hong, Heeyeop Chae,* Sungkyunkwan University (SKKU), Republic of Korea

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

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

ALE Applications I

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

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

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

11:15am **ALE2-TuM-14 Controlled Electron-Enhanced Silicon Etching with H$_2$ Background Gas and Positive Sample Voltage***,* *Sumaira Yasmeen,* University of Colorado at Boulder*;* *Harsono Simka,* Samsung Semiconductor*;* ***Steven George,*** University of Colorado at Boulder

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

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

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

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

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

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

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

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

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

ALE Tools & ALE Modeling

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

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

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

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

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

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

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

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

Acknowledgments. This work was supported by Samsung Electronics.

References [1] Appl. Phys. Lett. 120, 122901 (2022), [2] J. Vac. Sci. Technol. A 38, 022608 (2020), [3] J. Vac. Sci. Technol. A 40, 022604 (2022), [4] Chem. Mater. 32(8), 3414-3426 (2020)

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

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

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

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

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

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

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

References

[1] Mannequin, Vallée, Akimoto, Chevolleau, et al., JVST A, (2020)
[2] Kounis-Melas, Vella, Panagiotopoulos, Graves, JVST A, (2025)
[3] Rasoanarivo, Mannequin, Roqueta, Boufnichel, Rhallabi, JVST A, (2024)

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

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

References

[1] T. Lill, “Atomic Layer Processing: Semiconductor Dry Etching Technology” (Wiley-VCH, Weinheim, 2021).

[2] B. Kim, S. Chung, and S. M. Cho, “Layer-by-later Etching of Cl-adsorbed Silicon Surfaces by Low Energy Ar^+ Ion Irradiation”, Appl. Surf. Sci. 2002, 187, 124-129.

[3] S. Park, K. Min, B. Yoon, D. Lee, and G. Yeom, “Precise Depth Control of Silicon Etching using Chlorine Atomic Layer Etching” Jpn. J. Appl. Phys. 2005, 44, 389-393.

[4] K. J. Kanarik, T. Lill, E. A. Hudson, S. Sriraman, S. Tan, J. Marks, V. Vahedi, and R. A. Gottscho, “Overview of Atomic Layer Etching in the Semiconductor Industry”, J. Vac. Sci. Technol. A, 2015, 33, 020802.

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

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

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

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

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

ALE Applications II

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

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

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

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

Reference

[1] M.N. Yoder, Atomic Layer Etching, US4756794A, 1988.

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

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

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

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

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

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

ZnO ALD produced polycrystalline Wurtzite material with a (100) preferred orientation. The growth rate was measured to be 1.86 Å per cycle, with a uniformity (after 500 cycles) of ~ 2% over a full 200 mm wafer. The measured resistivity (~8.5 X 10^{-3} Ω cm), mobility (~30 $cm^2 \cdot V^{-1} \cdot s^{-1}$) and carrier concentration (~2 x 10^{19} cm^3) are typical of ALD grown nominally undoped ZnO. The ALE of nominally undoped ZnO proceeds at a linear etch rate (~0.29 Å) for 400 cycles albeit at a lower etch rate as compared to Mameli et al. [1]. Etch uniformity is shown to be ~ 5 % across the full 200 mm wafer. The electrical properties were unchanged by the etching process beyond a small degradation of resistivity (8.5 x10^{-3} to 1.5 x 10^{-2} Ω cm) after 400 cycles.

The laminate doping of ZnO at a 19:1 ratio introduce complexity in doping process, Under the same etching conditions Al doped ZnO did not appear to etch even after 400 cycles, whereas the Hf doped ZnO appeared to undergo etching that terminated after an initial number of cycles due to the formation of an etch barrier or poisoned layer. Here we present physical (XRD, XPS, AFM, SKPFM) and electrical data to elucidate the mechanism of etch retardation

[1] A. Mameli, M. A. Verheijen, A. J. M. Mackus, W. M. M. Kessels, and F. Roozeboom. ACS Applied Materials & Interfaces 2018 10 (44), 38588-38595

5:00pm **ALE2-TuA-15 Ale of Tin Using Sf_6:H_2 Plasma: The Role of H, F, and Hf in Defining the Ale Window***, **Guillaume Krieger**, Silke Peeters, Erwin Kessels,* Eindhoven University of Technology, The Netherlands*; Harm Knoops,* Oxford Instruments Plasma Technology, UK, Eindhoven University of Technology, Netherlands

Recently, etching processes relying on in-situ HF formation in plasmas have proven to tackle several challenges in the semiconductor industry such as etching high aspect ratio (HAR), enabling atomic scale control, and achieving high selectivity.[1] The selectivity between a nitride and its oxide counterparts is an important research field in the development of HF-based atomic layer etching (ALE) processes, with a strong focus on the selective etching between SiN and SiO_2.[2] Beyond Si-based materials, good selectivity between metal oxides and metal nitrides is also of interest. SF_6:H_2 mixtures have been used to selectively etch the oxidized top-layer of TiN over the bulk of the film, enabling an ALE process of TiN by alternating the oxidation and plasma etch step.[3] This selectivity is suggested to be driven by the formation of HF in the plasma. However, the roles of the various plasma species in defining the SF_6:H_2 upper and lower boundaries of the ALE window remains unclear.

In our work, we experimentally confirm that the formation of HF is driving the aforementioned ALE processes. Additionally, we demonstrate that the presence of HF cannot, by itself, explain the ALE window as a function of the SF_6/(SF_6 + H_2) gas ratio of the etch step. We have correlated this window with various species measured in the plasma including H and F atoms by optical emission spectroscopy (OES) and HF, H_2S, and SF_6 by quadrupole mass spectroscopy (QMS). These measurements demonstrate that the upper bound, in terms of the SF_6/(SF_6 + H_2) ratio, is determined by the presence of F atoms in the plasma leading to spontaneous TiN etching. For establishing the lower bound, an ABC-type recipe with an H_2 plasma between the oxidation step and the SF_6:H_2 plasma has been used to highlight the role of the H radicals in the ALE process. The H_2 plasma quenches the etching of the SF_6:H_2 plasma, suggesting prominent role of H in reducing TiO_2 top-surface, which prevents the etching by HF. These results suggest a strong interplay between H, F, and HF in the selective etching mechanism. This understanding can act as a stepping stone to expand this ALE process to other conductive nitrides.

References:

1. Kihara, Y., et al., *IEEE Symposium on VLSI Technology and Circuits,* 1–2 (IEEE, Kyoto, Japan, 2023).
1. Hsiao, S. N. *et al., Vacuum* **210**, 111863 (2023).
1. Hossain, A. A. *et al.*, *Journal of Vacuum Science & Technology A* **41**, 062601 (2023).

5:15pm **ALE2-TuA-16 Atomic Layer Etching of Ruthenium Using Surface Oxidation with O_2 Plasma and Chelation with Formic Acid***, **Hojin Kang**, Eunsu Lee, Minsung Jeon, Heeyeop Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Atomic layer etching (ALE) was developed via oxidizing the Ru surface with O_2 plasma, followed by removing the oxidized surface with a chelation reaction using formic acid (HCOOH). Surface oxidation reactions were performed up to 300 °C, and the RuO_2 layer after oxidation was identified using X-ray photoelectron spectroscopy (XPS). The Ru^{2+} oxidation state and Ru to O atomic ratio of 1:2 suggest that the oxidation layer formed is RuO_2. In the removal step, the RuO_2 layer is removed via a chelation reaction with HCOOH at process temperatures above 150 °C. The etch per cycle (EPC) of Ru is about 3 Å/cycle at a process temperature of 150 ~ 200 °C, and the EPC gradually decreases at temperatures above 200 °C, possibly due to the decomposition reaction of HCOOH. The EPC of Ru increases with increasing O_2 plasma exposure time without any saturation. The EPC of Ru was saturated at 3 Å/cycle with an HCOOH injection time of 100 sec. The surface roughness increases from 0.57 to 1.68 nm after ALE cycles, which can be attributed to etch rate differences according to facets. Ru has a hexagonal polycrystalline structure of (1,0,0), (0,0,-2), (1,0,1), (1,0,2), (1,1,0), (1,0,3), (1,1,2), and (2,0,1), which was confirmed by X-ray diffraction (XRD). No crystal structure changes after 100 cycles of ALE, and the maximum strength decreases by 97, 66, 74, 68, 89, 63, 52, and 75%, respectively. The surface oxide residue is less than 4% after ALE, which is similar to the pristine Ru. The Ru to SiO_2, HfO_2, and Si_3N_4 selectivity is infinity, and 56 for TiN and 77 for TaN.

Atomic Layer Etching
Room Samda Hall AB - Session ALE1-WeM
Plasma and/Energy-Enhanced ALE + Sustainability

Moderators: Jane P. Chang, University of California, Los Angeles, **Sung-Il Cho**, Samsung Electronics

8:00am **ALE1-WeM-1 Centering Sustainability in Future Plasma-Enhanced ALE Processes***, Nathan Marchack, Robert Bruce, **Eric Joseph**,* IBM Research Division, T.J. Watson Research Center **INVITED**

Recent progress in the field of artificial intelligence has also highlighted the critical role of semiconductor manufacturing in delivering the necessary compute requirements. Simultaneously, the prospect of future proliferation of such technologies presents serious ramifications for the environment. Examinations of the increases in resource consumption as both software [1] and hardware [2] advance have raised awareness of the need to consider the sustainability of future development. In this talk we will examine this idea as it pertains to plasma-enhanced atomic layer etching (PE-ALE), building off our recent work on reducing gas usage in deep Si etching. [3] We review new results studying mechanisms of halogen substitution on Si surfaces and the need for synergy between all facets of the development process, from substrate materials to gas precursor development. Adopting this focus as soon as possible will strengthen the fundamental role of atomic layer processes in enabling future technologies.

[1] E. Strubel et al., Energy and Policy Considerations for Deep Learning in NLP, Proc. of the 57th Annual Meeting of the Association for Computational Linguistics, 2019, pp. 3645–3650, Florence, Italy.

[2] M.G. Bardon et al., DTCO including sustainability: Power-performance-area-cost-environmental score (PPACE) analysis for logic technologies, IEEE International Electron Devices Meeting (IEDM), 2020, pp. 41.4.1-41.4.4, San Francisco, CA, USA.

[3] O. Isowamwen et al., Characterization of TSV Etch from a Sustainability Standpoint, Proc. SPIE 12499, Advanced Etch Technology and Process Integration for Nanopatterning XII, 2023, 124990H, San Jose, CA, USA.

8:30am **ALE1-WeM-3 Cryogenic Atomic Layer Etching of SiO_2 by Physisorption of HF/C_2H_5OH and Ar Plasmas***, **Shih-Nan Hsiao**, Makoto Sekine,* Nagoya University, Japan*; Yoshihide Kihara,* Tokyo Electron Miyagi Limited, Japan*; Masaru Hori,* Nagoya University, Japan

The continues reduction of the chip size and development of innovative 3D integrated device architectures have required the adoption of advanced processing methods. Plasma-assisted atomic layer etching (PE-ALE) has emerged as a promising technique for sub-nanoscale material removal in semiconductor processes due to its unique self-limiting surface reactions. Cryogenic plasma etching enabling the unique feature of physisorption of neutrals/condensed layer has been reported for ALE of dielectric materials [1]. Our recent reports indicates that the cryogenic plasma etching can significantly enhance the etching throughput of SiO_2 through the co-adsorption of H_2O/HF species using the CF_4/H_2 gases [2]. Building on this, we developed the cryogenic ALE (Cryo-ALE) process involving an HF dose for surface modification and Ar ion bombardment for SiN etching. This work extends the Cryo-ALE process to SiO_2, utilizing an HF/C_2H_5OH dose for etchant physisorption followed by an Ar ion bombardment. *In situ* monitoring techniques, including spectroscopic ellipsometry and attenuated total reflectance Fourier transformation infrared spectroscopy (ATR-FTIR), were used to analyze the surface structure and etching characteristics. The substrate temperature (T_s) was controlled from 20 to –60 °C using a coolant circulating system connect to the bottom electrode. The etched depth per cycle (EPC) of the SiO_2 after the process increased from approximately 0.28 nm/cycle to 0.79 nm/cycle as the T_s was decreased from 20 to –60 °C. (see supplemental document for details). ATR-FTIR analysis revealed that this increase in EPC correlates with an enhanced amount of surface-adsorbed HF/C_2H_5OH during the surface modification step. Conversely, the EPC vs T_s for the SiN exhibited an opposite trend, indicating that the etching selectivity between SiO_2/SiN can be effectively tuned by adjusting T_s.

[1] D. N. Shank et al., J. Vac. Sci. Technol. A 41, 052601 (2023).

[2] S. N. Hsiao et al., Small Methods, 2400090 (2024).

[3] S. N. Hsiao et al., Chem. Mater. 36, 11042 (2024).

8:45am **ALE1-WeM-4 Cryogenic ALE of SiO_2 using CF_4 Plasma***, Madjid Adjabi, Jack Nos, Sylvain Iseni,* GREMI - CNRS/Orleans University, France*; Gilles Cunge, Martin Kogelschatz,* LTM - CNRS/Grenoble Alpes University/Grenoble-INP, France*; Philippe Lefaucheux, Loïc Becerra,* GREMI - CNRS/Orleans University, France*; Emilie Despiau-Pujo,* LTM - CNRS/Grenoble Alpes University/Grenoble-INP, France*; **Thomas Tillocher**, Rémi Dussart,* GREMI - CNRS/Orleans University, France

Cryogenic Atomic Layer Etching of SiO_2 (“Cryo-ALE”) has been developed several years ago to address some limitations when it is performed at room temperature.The ALE process achieved under these last temperature conditions involves a C_4F_8 plasma in the modification step. This results in fluorocarbon deposition on the reactor walls, and eventually to process drifts, which affects reproducibility. Consequently, chamber cleaning is necessary. This can be addressed by flowing C_4F_8 in gas phase and cooling the SiO_2 substrate at cryogenic temperature. C_4F_8 molecules are physisorbed only on the cooled surface and therefore, wall pollution is greatly reduced. The thin physisorbed C_4F_8 layer is then used as a reservoir to etch around one SiO_2 monolayer in the subsequent Ar plasma of one ALE cycle.

Alternatively, a relevant approach consists in selecting a gas with a higher F/C ratio, which polymerizes much less than low F/C ratio gases such as C_4F_8. For instance, a CF_4 plasma is in etching regime at room temperature and does not promote polymer deposition on the chamber walls at room temperature too. Nevertheless, it is shown by absorption spectroscopy that the sticking coefficient of CF radicals increases dramatically when the surface is cooled at cryogenic temperature. This means that a CF_4 plasma can be used to deposit a fluorocarbon layer only on cooled surfaces, in particular SiO_2. But the chamber walls, at room temperature, are polymer-free.

Consequently, a CF_4 plasma can be used as a modification step in a SiO_2 Cryo-ALE process. It is demonstrated that repeating cycles of a CF_4 plasma step followed by an Ar plasma with low energy ion bombardment, with each cycle separated by a purge step, enables sequential etching of SiO_2 cooled at cryogenic temperature. The EPC increases as the substrate temperature decreases and reaches 0.46 nm/cycle at -130°C. This process, provided deposition during CF_4 plasma is well balanced with etching in the Ar removal step, exhibits a high synergy that can approach 100%.

Acknowledgments: The authors thank Tokyo Electron Limited for financial support and helpful discussions and acknowledge ANR, which
supports the project PSICRYO for “Understanding Plasma-Surface Interactions in CRYOgenic etching for advanced patterning applications” (No. ANR-20-CE24-0014). This work was also supported by CERTeM platform, which provides most of the equipment.

9:00am **ALE1-WeM-5 Atomic Layer Etching of Indium Oxide Thin Films via Ligand Addition and O_2 Plasma Reactions***, **Minchan Kim**, Jihyun Gwoen, Hae Lin Yang, Jin-Seong Park,* Hanyang University, Korea

The Oxide semiconductors (OSs), which utilize materials like IGZO as channel layers, have been gaining increased attention as the demand for high mobility and low off - current in semiconductor devices continues to grow.Especially, InOx is emerging as a key material for next-generation devices due to its outstanding electron mobility. Achieving these characteristics requires high-quality thin films, which can be precisely and uniformly fabricated using atomic layer deposition (ALD), a technique essential for high-mobility InOx and next-generation device applications. While ALD enables precise deposition, achieving the desired crystallinity in InOx at low thickness remains challenging due to issues like nucleation and non-uniform film growth. To address this, an etch-back process using Atomic Layer Etching (ALE) is often employed, depositing the film to the required properties before selective removal. However, in the case of InOx, the low volatility of modified byproducts like $InCl_3$ or InF_3 makes their removal chemically difficult, posing significant limitations to the applicability of ALE technique

In this study, we explored the operation of Atomic Layer Etching (ALE) for InOx by incorporating an additional hydrogen treatment modification step into the conventional ligand-based ALE process using Hacac (acetylacetone). The process was evaluated through Spectroscopic Ellipsometry (SE), X-ray Photoelectron Spectroscopy (XPS), and X-ray Diffraction (XRD) to determine whether the ALE cycles proceeded in a layer-by-layer manner driven by self-limiting reactions. The findings showed that the thickness of the indium oxide thin film could be controlled with precision, while an improvement of approximately 37% in RMS roughness was observed, indicating better film quality after the ALE process.

Furthermore, XPS and XRD analysis confirmed that the bulk chemical composition remained unchanged following the hydrogen modification step, suggesting that the mechanism effectively induced reactions at the surface level. These results provide useful insights into controlling oxide semiconductor deposition and improving thin-film quality for potential device applications.

9:15am **ALE1-WeM-6 Development of a Novel Magnetically-Confined Plasma Source for Advanced Semiconductor Manufacturing**, *Tae S Cho,* Wonik IPS; *Jihyun Kim,* ***Giwon Shin****, Hakmin Kim, Jeonghun Kim, Sooyoung Hwang, Jaehoon Choi,* Wonik IPS, Republic of Korea

The relentless pursuit of miniaturization in the semiconductor industry, characterized by sub-10 nm feature sizes, 3D stacked architectures, and complex gate-all-around (GAA) structures, demands increasingly sophisticated plasma processing techniques. These advanced applications require plasma sources capable of operating over a broad pressure range while providing a high radical density with minimal ion-induced damage to delicate device structures.

To address these critical requirements, we have developed a novel ignitor-free remote plasma source utilizing a magnetic core configuration. Preliminary test with argon and argon-nitrogen gas mixtures demonstrates a stable operating pressure range of 0.1 to 17 Torr and 0.1 to 4.5 Torr, respectively.

Furthermore, this source exhibits a unique capability for plasma mode transition. By adjusting the magnetic core's winding ratio, the plasma can be dynamically transitioned between voltage mode and current mode operations. This flexibility allows for optimized process control, enabling the generation of high radical density for rapid etch rates in current mode, while minimizing ion bombardment for delicate deposition processes in voltage mode. Optical emission spectroscopy (OES) measurements confirm a significant enhancement in radical density in current mode compared to voltage mode.

Based on these promising results, ongoing efforts are focused on optimizing the plasma reactor, magnetic core geometry, and radio frequency (RF) generator to further enhance the performance and versatility of this innovative plasma source for advanced semiconductor manufacturing applications.

9:30am **ALE1-WeM-7 Low-Damage Plasma Atomic Layer Etching of Silicon Dioxide and Nitride via DC Substrate Bias and Remote Inductively Coupled Plasma Source**, *Hee Chul Lee,* ***HongHee Jeon****, SoWon Kim,* Tech University of Korea

Atomic Layer Etching (ALE) is an advanced etching technique consisting of two sequential steps: surface modification and removal of the modified surface. This process enables precise atomic-scale thickness control through its self-limiting characteristics, making it highly suitable for next-generation semiconductor device fabrication.

In this study, low-damage and high-productivity ALE process for SiO_2 and SiNx was developed using both inductively coupled Remote Plasma (RP) and DC substrate bias. The process focuses on the effective removal of interfacial defects and residual byproducts. The proposed ALE process is designed to support next-generation DRAM technologies, where precise etch control and material stability are essential.

For Direct Plasma (DP)-ALE, the process conditions were set to RF Power of 50W, process pressure of 100 mTorr with Ar, CF_4, C_4F_8, and CHF_3 discharge gases. The reactor configuration featured a 40 mm showerhead-to-substrate distance. The experiments were conducted with process parameter changes in adsorption time, desorption time, and DC substrate bias. To ensure process stability and reduce contamination, O_2 plasma cleaning was performed before and after each ALE cycle to effectively remove residues from the chamber walls. Ellipsometry was employed to measure thickness variations before and after etching, confirming fluorocarbon (FC) film deposition, with additional characterization planned using X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM).

The DP-ALE results indicated FC film deposition per cycle of 1.2 Å for SiO_2 and 2.2 Å for SiNx at an adsorption time for 3 seconds. Under conditions RF power of 50W, DC substrate bias of 90V, and a desorption time for 60 seconds, the achieved etch-per-cycle (EPC) was 0.18 nm/cycle for SiO_2 and 0.15 nm/cycle for SiNx, confirming the presence of self-limiting characteristics.

The goal of this research is to effectively apply CP(Co-plasma)-ALE including RP and DP plasma and substrate DC bias to next-generation semiconductor technologies to minimize device damage while increasing process control and reliability. And the results of a comparative study will be presented at the conference.

Atomic Layer Etching
Room Samda Hall AB - Session ALE2-WeM
ALE Applications III

Moderators: Keun Hee Bai, Samsung Electronics Co., **Younghee Lee**, Lam Research Corporation

10:45am **ALE2-WeM-12 In-Situ Observation of Surface Reaction and Advanced Process for Damage-Less Atomic Layer Etching**, ***Takayoshi Tsutsumi****,* Nagoya University, Japan **INVITED**

11:15am **ALE2-WeM-14 Isotropic ALE of 2D Crystalline MoS_2 using SF_6:H_2 Plasma and O_2 Plasma**, ***Sanne Deijkers****, Christian Palmer, Nick Chittock, Guillaume Krieger, Silke Peeters, Marcel Verheijen,* Eindhoven University of Technology, The Netherlands; *Harm Knoops,* Oxford Instruments Plasma Technology, Netherlands; *Erwin Kessels, Adrie Mackus,* Eindhoven University of Technology, The Netherlands

Two-dimensional crystalline MoS_2 is an emerging material for nanoelectronics, where it can be applied as a channel material in field effect transistors. MoS_2 exhibits a high carrier mobility, even at the monolayer thickness of 6.5 Å, and therefore it is expected to replace Si in the future [1]. Application of MoS_2 in nanoelectronics requires highly controlled deposition and etching processes. Currently available ALE processes either require an external step like a wet treatment [2], or are optimized for amorphous MoS_2 [3]. Here, we present a plasma-enhanced ALE process, which can etch crystalline MoS_2 in an isotropic manner.

In the ALE cycle, the crystalline ALD-grown MoS_2 film was first fluorinated and subsequently oxygenated to create volatile $Mo_xO_yF_z$ species. The fluorination step employs a plasma mixture containing SF_6 and H_2, which is believed to produce *in situ* HF, as suggested by previous studies on H_2-diluted fluorine plasmas [4,5]. F radicals, which are known to etch MoS_2 continuously [6,7], are scavenged by the hydrogen to form HF as observed in the plasma [8]. The SF_6:H_2 ratio was tuned to ensure modification occurs without continuous etching. For the oxygenation half-cycle an O_2 plasma was used, whereas O_2 gas and H_2O did not result in significant etching.

The resulting etch per cycle combining the SF_6:H_2 plasma and O_2 plasma is 0.92 ± 0.02 Å. Before ALE the crystallinity of the films was confirmed by observation of the characteristic MoS_2 peaks in Raman spectroscopy, and after ALE a decrease in these peaks is seen, verifying etching of the crystalline material. Furthermore, no F contamination was observed after ALE by x-ray photoelectron spectroscopy (XPS). However, XPS showed the presence of some oxidation of Mo and S. The isotropic nature of the ALE process was confirmed using transmission electron microscopy in 3D trenches.

[1] Kim *et al., Nat. Nanotechnol.,* 2024

[2] Lee *et al., Applied Physics Express,* 2017

[3] Soares *et al., Chem. of Mater.,* 2023

[4] Jung *et al., JVST A*, 2020

[5] Kihara *et al., 2023 IEEE Symposium on VLSI Technology and Circuits,* 2023

[6] Jeon *et al., Nanotechnology*, 2015

[7] Xiao *et al., Sci Rep*, 2016

[8] Krieger *et al., ALD/ALE 2024*, 2024

11:30am **ALE2-WeM-15 Design of Multi-Coil Single-Switch Induction Heating System with PI-Based Burst Mode Control for ALD/ALE Processes to Achieve High Efficiency and Rapid Transient Response**, ***Sang-Wook Ryu****,* Dongguk University, Republic of Korea; *Jihyun Kim, Hakmin Kim,* Wonik IPS, Republic of Korea; *Tae S. Cho,* Wonik IPS; *KWANGSEON JIN,* Wonik IPS, Republic of Korea

Atomic layer deposition (ALD) and atomic layer etching (ALE) processes commonly rely on conventional resistive heating methods, which suffer from significantly low efficiency and slow transient response. To overcome these limitations, this paper proposes an induction heating system and control technique specifically tailored for ALD/ALE applications to achieve higher efficiency and faster transient response. Because ALD/ALE processes require localized temperature control, multiple coils must be employed to provide precise heating across different regions. Therefore, unlike typical multi-switch designs such as full-bridge or half-bridge topologies, which require multiple semiconductor switches per coil, the proposed system adopts a single-switch topology for each coil, thereby reducing hardware complexity while enabling fine-grained temperature control across the entire region. Because a single semiconductor switch must handle the entire load voltage and current in a single-switch topology, the proposed multi-coil single-switch design is restricted to a narrow switching frequency range to ensure system reliability while controlling the temperature. To enhance stability under this constraint, a burst-mode operation at a fixed switching frequency is introduced to facilitate near-linear temperature control, with its burst interval precisely regulated by a proportional–integral (PI) controller. A prototype of the proposed induction heating system is developed using a TI-TMS320F28335 digital signal processor (DSP). The performance of the proposed multi-coil induction heating system, integrating a PI-based burst mode for ALD/ALE applications, is validated through comparative experiments, demonstrating significantly improved efficiency and faster temperature response than conventional resistive heating.

11:45am **ALE2-WeM-16 Enhanced Plasma Ignition and Sustaining of Transformer-Coupled Plasma Source with a Secondary Coil***, Tae S Cho,* ***Jae Hoon Choi****, Hak Min Kim, Gi Won Shin, Soo Young Hwang, Ji Hyun Kim,* Wonik IPS, Republic of Korea

The need for miniaturization in the semiconductor industry, characterized by sub-10 nm features, 3D stacked architectures, and complex gate-all-around structures, requires increasingly sophisticated plasma processing technologies. These advanced applications require plasma radical sources such as transformer-coupled plasma (TCP) that can operate over a wide pressure range while providing high fluxes of reactive species with minimizing ion-induced damage to delicate device structures. However, ignition with electronegative gases in TCP sources requires high breakdown voltages, often requiring initial plasma generation with an inert gas such as argon, which reduces process throughput. To overcome this limitation, a secondary coil was introduced to generate the high voltage for plasma ignition. The ignition and sustain ranges in argon-nitrogen mixtures were investigated using a TCP source incorporating several ferrite cores. One of the ferrite cores integrated both primary and secondary coils, with the secondary coil terminals connected to reactors on both sides of the core. The current induced in the secondary coil generated an additional electric field between the reactors, enhancing both plasma ignition and sustaining. Experiments were performed at pressures of 0.5–2 Torr and radio frequency (RF) powers up to 3000 W at frequencies of several hundred kHz using various argon-nitrogen gas mixing ratios. The secondary coil enabled stable plasma ignition across a wider range of argon-nitrogen mixtures, eliminating the need for initial plasma generation with inert gas, unlike conventional TCP discharges. This enhanced ignition and sustain ranges provide significant advantages for precise control of process gases and short plasma on/off times in advanced manufacturing processes such as atomic layer deposition (ALD) and atomic layer etching (ALE).

Author Index

Bold page numbers indicate presenter

Author Index