Plasma Science and Technology
Room 315 - Session PS+AP-MoM

Plasma Processes for Advanced Interconnects
Moderators: Dr. John Arnold, IBM, **Takeshi Ohmori**, Hitachi

10:00am **PS+AP-MoM-1 Interconnect for 7A and Beyond***, **Scott Allen,*** IBM Research Division, Albany, NY **INVITED**

BEOL scaling continues to challenge the limits of plasma etch process capability. Conventional approaches have shown to have limited extendibility for next generation devices. Challenges with the traditional damascene integration and superior resistance scaling with alternate conductors make transition to subtractive patterning more attractive. Capacitance control using new dielectric materials or schemes requires innovation and examination. Additionally, High-NA EUV and other new patterning techniques provide pathways forward but require significant development. Advances in etch tooling and stack materials are providing options to meet these challenges. Novel use of known techniques can be integrated with these new tools and materials to enable semiconductor technology at 7A and beyond.

10:30am **PS+AP-MoM-3 Epitaxial conductors to replace Cu in advanced interconnect metallization***, **Jean-Philippe Soulie**, François Chancerel, Steven Brems, Chen Wu, Johan Swerts, Seongho Park, Christoph Adelmann,* IMEC, Belgium **INVITED**

Cu interconnects face a steep resistance and reliability penalty when line widths approach dimension of 10nm: electron scattering at surfaces and grain boundaries amplifies the resistivity, while diffusion barriers and liners consume an increasing fraction of the available cross–section and are increasingly difficult to scale[1]. In this context, epitaxial conductors offer a fundamentally different route to sustain conductivity at nanoscale dimensions by eliminating large–angle grain boundaries, reducing microstructural variability, and improving pattern–transfer fidelity during direct metal etch. Here, we summarize our recent progress on epitaxial conductors aimed at replacing Cu in advanced BEOL metallization, with a focus on CMOS–compatible epitaxial Ru and metallic delafossite $PtCoO_2$.

For Ru, we demonstrate honeycomb epitaxy on AlN(0001)/Si(111) using standard PVD at a BEOL–relevant thermal budget, scalable to 300–mm wafers[2]. Structural characterization confirms coherent epitaxial alignment and low mosaicity. Electrical transport measurements reveal bulk–like resistivity (7.8μΩcm at 30nm), resulting in a markedly weaker thickness–dependent resistivity increase than polycrystalline Ru and Cu in the ultrathin regime. These findings highlight the advantage of suppressing grain–boundary scattering through epitaxy.

Beyond elemental metals, we show that metallic delafossite $PtCoO_2$ can deliver even lower resistivity at nanoscale thicknesses when epitaxy is stabilized. Using a multilayer PVD approach combined with repeated oxidation anneals, epitaxial $PtCoO_2$ is stabilized down to 4 nm and exhibits an unusual thickness–independent resistivity of 4.8μΩcm over the 8 to17nm range[3]. This behaviour is enabled by solid–phase epitaxial regrowth, film densification, and defect annihilation, underscoring the critical role of interface chemistry and oxygen control in complex oxide conductors.

Looking forward, the integration of epitaxial conductors into realistic interconnect architectures will require scalable strategies compatible with amorphous BEOL dielectrics. Layer–transfer approaches, such as wafer-to-wafer bonding followed by substrate removal, emerge as a universally applicable pathway for epitaxial conductor integration, enabling the decoupling of epitaxial growth from backend processing. Continued progress in epitaxial growth, interface engineering, and transfer integration positions epitaxial Ru and delafossite oxides as strong contenders for future liner–light or linerless interconnect technologies beyond Cu.

[1]J-Ph. Soulié,J. Appl. Phys.136(17)171101(2024).[2]C. Adelmann,2026 ECTC(2026),Orlando(USA).[3]J-Ph. Soulié,2026 IEEE IITC(2026),San Jose (USA)

11:00am **PS+AP-MoM-5 Reactive High Power Impulse Magnetron Sputtering with Positive Cathode Reversal Using a Rotary Magnetron***, **Nicholas Connolly**, Collin Jeckell,* University of Illinois Urbana-Champaign*; Rajib Paul, Brian Jurczyk,* Starfire Industries, LLC*; David Ruzic,* University of Illinois Urbana-Champaign

This work investigates the novel sputtering technology of HiPIMS with positive cathode reversal (Positive Kick™), herein referred to as HiPIMS+CR, on rotary magnetrons for reactive sputtering. As compared to DC, HiPIMS provides the advantage of higher ion fractions at the target[1] and at the substrate[2]. As compared to standard HiPIMS, positive cathode reversal allows for control of the ion energy at the substrate, allowing for tuning of film properties such as stress as well as increased deposition rate overall[3]. In this work, the deposited film is aluminum nitride (AlN), which has applications in resonator devices, piezoelectric devices, and as a thermal spreader for heat management[4]. Many large-area industrial coating processes utilize rotary magnetrons instead of planar magnetrons, as they offer increased target utilization and higher power throughput due to better heat removal. It has been shown with DC that rotary magnetrons offer some benefits and differing deposition physics when compared to planar targets because of the target shape and rotation[5]. This work characterizes HiPIMS+CR applied to a rotary magnetron with target length of 430mm and target outer diameter of 145mm, identifying where the rotary configuration may offer benefit through a research-scale system.

HiPIMS+CR AlN reactive sputtering in the rotary magnetron configuration is characterized by both plasma diagnostics and film characteristics. To characterize the plasma, a Hiden Analytical PSM probe was used to gather time and energy resolved spectra of each ion species at the substrate location versus various plasma parameters. Whether the target was rotating or not rotating affected both the Al^+ and N^+ ion counts without changing the Ar^+ and N_2^+ counts (see Figures 1 and 2), where the N^+/Al^+ ratio increased by over 50% by simply rotating the target and keeping all other process parameters constant. This indicates target rotation does affect the system and adds another variable to adjust film properties such as stoichiometry. Hysteresis curves were generated at various target rotation speeds to understand how the poisoning point was affected by rotation speed in HiPIMS+CR.

AlN film characterization will be presented across varying HiPIMS+CR process recipe parameters, as well as target rotation speed, for the critical characteristics of the applications of AlN. Characteristics measured include film stoichiometry (including oxygen contamination), crystal structure and orientation measured with X-ray diffraction (XRD), and film density measured with X-ray reflectivity (XRR). Thermal conductivity measurements are also made using time-domain thermoreflectance (TDTR).

11:15am **PS+AP-MoM-6 Two-Step Etching for Suppressing Etch-Depth Variation in Tin Etch-Back***, **Yudai Mashiko**, Makoto Satake, Taku Iwase, Naoyuki Kofuji, Yasushi Sonoda,* Hitachi, Ltd., Japan

In the fabrication of advanced semiconductor devices, uniform TiN etch-back—in which TiN is filled into deep trenches—is essential for contact-plug formation. However, seams are unintentionally formed during the filling process. Consequently, the local etching rate increases due to seam widening, resulting in etch-depth variation between the area around the seam and the surrounding region [1].

In our previous study [2, 3], we reported that radical etching was superior to plasma etching because, in the latter, energetic ions accelerated by self-bias voltage exacerbated seam widening. However, even with conventional radical etching, it remains difficult to suppress the direct exposure of radicals to the seam region. Therefore, we propose a two-step etching process that employs a deposition-film formation step prior to etching. In this method, a deposition film is first formed to serve as a mediating layer, after which TiN is etched by radicals while maintaining this film. This approach is designed to prevent the direct exposure of radicals to the seam.

The mechanism underlying seam-widening suppression was investigated using etch-profile simulations. The deposition film on the TiN surface significantly shortens the effective mean free path of the radicals, thereby preventing their direct exposure to the TiN surface. Consequently, the radical flux reaching the seam interior is markedly reduced, shifting the etching process from a reaction-limited to a supply-limited regime. This transition ensures that etching is governed by the arrival rate of radicals rather than their reactivity, which the simulations confirmed effectively suppresses seam widening compared with conventional radical etching.

Based on these findings, the two-step process was experimentally demonstrated. A $SiCl_x$ deposition film was formed using $Cl_2/SiCl_4$-based plasma, followed by TiN etching with Cl_2-based plasma. Cross-sectional observations confirmed that the standard deviation of the etch-depth variation was significantly reduced from 3.8 nm (conventional) to 1.5 nm. These results demonstrate that the proposed two-step etching is an effective approach for achieving uniform TiN etch-back.

[1] G. Vereecke et al., Microelectron Eng. 200 (2018).

[2] Y. Mashiko, et al., DPS 45th international symposium (2024)

[3] T. Iwase, et al., Proc. SPIE PC13429 (2025)

11:30am **PS+AP-MoM-7 Roughness Generation Mechanisms in Ru Etching Using O_2/Cl_2-Based Plasma for Advanced Interconnects**, ***Miyako Matsui***, *Tomoyasu Shohjoh, Taiga Kasai,* Hitachi Ltd., Japan*; Kiyohiko Sato, Makoto Miura,* Hitachi High-Tech Corporation, Japan*; Kenichi Kuwahara,* Hitachi High-Tech Corporation, Jamaica **INVITED**

Continued device miniaturization necessitates further reduction of metal pitch through advanced patterning technologies such as extreme ultraviolet lithography. As metal pitches shrink, alternative metal interconnects are required to replace Cu in order to achieve tighter pitches in the back end of line. Ru is a candidate for alternative interconnects at metal pitches of 20 nm and below, because Ru interconnects are expected to exhibit lower effective resistance than Cu interconnects at such small dimensions. In addition, Ru can be etched directly, enabling new scaling boosters such as semi–damascene patterning. To realize such patterning technologies, Ru patterns must be etched vertically with high selectivity to hard masks, while roughness and other forms of damage must be suppressed to reduce interconnect resistance.

In this work, we investigated the mechanisms of roughness generation during Ru etching and achieved low–roughness etching of fine Ru patterns using an O_2/Cl_2–based plasma generated by a microwave electron cyclotron resonance etching system. The roughness of Ru line patterns is primarily governed by the transfer of mask pattern roughness, as well as by micromasking effects caused by non–volatile byproducts formed on the sidewalls and by the Ru grain structure.

To analyze the mechanisms of roughness generation in Ru etching, the line edge roughness (LER) of Ru lines and Si_3N_4 masks was evaluated before and after Ru etching using a high–voltage CD–SEM, which simultaneously evaluates Si_3N_4 mask roughness from secondary-electron images and Ru line roughness from backscattered-electron images. Ru etching was performed on 32 nm-pitch Ru patterns with Si_3N_4 mask line widths varied from 23 nm to 10 nm. We found that Ru line roughness is influenced not only by Si_3N_4 mask roughness but also by non–volatile RuO_x and $RuCl_x$ species non–uniformly formed on the Ru sidewalls. In addition, Ru sidewall etching tends to proceed preferentially along grain boundaries. The roughness of Ru sidewalls depends on the balance between ion flux, which generates non–volatile RuO_x and $RuCl_x$ on the sidewalls, and radical flux, which isotropically etches Ru.

To reduce the LER of Ru lines, we proposed adding a passivation gas to the O_2/Cl_2 plasma to form a uniform protective layer on the pattern sidewalls. This uniform protection layer enables stable etching of fine patterns even when the balance between ion flux and radical flux penetrating into the trenches varies to some extent with changes in aspect ratio during Ru etching.

Plasma Science and Technology
Room 315 - Session PS1-MoA

Plasma Diagnostics

Moderators: Prof. Dr. Sumit Agarwal, Colorado School of Mines, USA, **Dr. John Arnold**, IBM

1:30pm **PS1-MoA-1 Plasma Diagnostics for Industry: Restrictions, Reluctance, and Reward**, ***James Ellis***, *Ben Harris, Montu Bhuva, Jordyn Polito, Geoffrey Hassall,* Oxford Instruments Plasma Technology, UK **INVITED**

The compound semiconductor industry continues to push the boundaries of device performance across markets such as power electronics and data communications; however, this success has increased the emphasis on precision in plasma processing. For a capital equipment manufacturer, it is imperative that a pragmatic approach is taken when using plasma diagnostics to bridge the gap between plasma physics and high-volume manufacturing. This presentation will explore the restrictions, reluctance, and rewards of deploying plasma diagnostics within this sector.

There are significant restrictions when using plasma diagnostics within an industrial setting. For example, commercial systems are often limited by their optical access for complex diagnostics. Furthermore, any integrated diagnostic (or sensor) must meet rigorous standards for robustness, cost, and usability to ensure they remain relevant for industrial applications. This presentation will give an overview of these restrictions in contrast to academic constraints.

The semiconductor sector takes a conservative stance against risk due to the high costs involved with change; this understandably gives a 'process-first' mentality that must be considered when using diagnostics. Any diagnostic that risks contaminating the chamber or may cause drift in an already qualified process is a liability. This presentation will discuss how diagnostics need to be tested to ensure that they do not impact the process, with a specific case study on the curling probe.

Whilst the complexities of using diagnostics in industrial settings are apparent, the reward certainly justifies the effort. Integrating diagnostics enables the acceleration of hardware development and provides the ground truth necessary to validate complex plasma models. This can narrow the process optimisation envelope, enabling a faster transition from process development to the satisfaction of a performance specification. Finally, we highlight the role of external academic partnerships in this journey. For example, by utilising more complex laser-based diagnostics we can build greater confidence in the simplified diagnostic approaches used internally and the complex chemistry models that they validate.

2:00pm **PS1-MoA-3 Use of the OES Signal as an Indicator of Si Etch-Rate Uniformity During Fluorocarbon Plasma Etching**, ***Nobuyuki Kuboi***, *Takashi Yagisawa, Yasufumi Miyoshi, Akiko Kawamoto, Shoji Kobayashi, Yoshiya Hagimoto,* Sony Semiconductor Solutions Corporation, Japan*; Hiroshi Akatsuka,* Institute of Science Tokyo, Japan

During the plasma etching of complex structures with high aspect ratios such as advanced CMOS devices and image sensors, the quantitative prediction and accurate control of the etch rate and uniformity is essential to realize process stability and high yield in mass production. However, variations in these properties are almost impossible to detect during plasma etching in mass production, and their real-time monitoring has been limited to optical emission spectroscopy (OES) analysis. Therefore, the OES signal must be used to address this issue.

The authors previously investigated SiN etch-rate variations during $CF_4/Ar/H_2$ plasma etching using the OES signal of the H Balmer line and found that this variation could be tracked[1]. In this work, to better understand the relationship between Si etch-rate uniformity and the OES signal, the authors experimentally measured variations in Si etch-rate uniformities for 75 process conditions using an ICP reactor with $C_4F_8/SF_6/Ar$ plasma. Analysis of the results using PCA and PLS regression suggests that variations in Si etch-rates at the wafer center and in edge regions depend on variations in the OES signals originating from de-excitation on F with a wavelength of 780 nm and de-excitation on CF (240 nm) and CF_2 (246 nm), respectively. This result indicates that these OES signals can be used as indicators of Si etch-rate uniformity.

To confirm the validity of the analysis, we used a collisional-radiative model to model the emissions of F (780 nm), CF (240 nm), and CF_2 (246 nm) considering gas diffusion and wall sticking as loss processes with electron density (N_e), electron temperature (T_e), and ground-state gas density as input parameters. The simulation results showed that the F (780 nm) intensity is large when N_e and T_e are large, which corresponds to the wafer center region in the ICP reactor, whereas the CF (240 nm) and CF_2 (246 nm) intensities have inverse trends in the F intensity. Therefore, these OES signals can be indicators of Si etch-rate uniformity during fluorocarbon plasma etching.

Combining an inverse analysis of the experimental OES signals [2] with our emission models, distributions of N_e, T_e, and ion/radical densities can be quantitatively derived. Using these values as inputs for our voxel-slab model [3], the uniformities of feature profiles and plasma-induced damage can be predicted, reflecting real-time chamber conditions. This future work will be introduced in our presentation.

[1] N. Kuboi *et al*., Jpn. J. Appl. Phys. **49**, 08JD01 (2010).

[2] Y. Yamashita *et al*., J. Vac. Sci. Technol. A**42**, 023003 (2024).

[3] N. Kuboi *et al*., J. Vac. Sci. Technol. A**33**, 061308 (2015).

2:15pm **PS1-MoA-4 Non-Invasive Viewport Plasma Resonance Sensor for in-Situ Monitoring of Plasma Etching via Electron Density Measurement**, ***InYong Park***, *GeonWoong Eom, SangHo Lee, Min Hur, WooSeok Kang, Dae-Woong Kim,* Korea Institute of Machinery and Materials, Korea (Democratic People's Republic of)

In semiconductor plasma etching, process reproducibility is a critical requirement. However, the nonlinear nature of plasma can produce different outcomes under nominally identical recipes. Small variations at the etch endpoint can damage the wafer and the underlying interconnect layers, requiring precise in-situ monitoring. Optical emission spectroscopy (OES) is widely used for end-point detection (EPD), owing to its non-invasive nature and its sensitivity to changes in the plasma emission spectrum at the etch endpoint. However, the OES emission intensity depends on multiple coupled parameters: electron density, electron temperature, and emitting-species concentration. As a result, a single emission line cannot uniquely identify the plasma state. As the critical dimensions of semiconductor devices shrink, the open area exposed to the etchant decreases, reducing the flux of reaction byproducts and degrading the signal-to-noise ratio of EPD. Moreover, OES alone, without supplementary calibration, does not directly yield quantitative plasma parameters, which limits its ability to resolve subtle variations in plasma state.

A microwave probe directly measures the electron density by detecting microwave resonances of the plasma. The electron density, in turn, tracks the etch rate through the ion flux at the wafer surface under controlled plasma chemistry, pressure, and bias. However, conventional microwave probes must be inserted into the chamber, which is an invasive configuration that perturbs the plasma and restricts their use in production-grade equipment.

To overcome this limitation, we developed a viewport plasma resonance (VPR) sensor that measures the electron density non-invasively through a dielectric viewport, with the sensor positioned outside the chamber. To our best knowledge, this is the first viewport-coupled microwave resonance diagnostic for in-situ electron-density measurement during plasma etching. Electron densities measured by the VPR sensor were benchmarked against a conventional invasive microwave probe, and the correlations among etch rate, electron density, and OES intensity were quantitatively analyzed through simultaneous measurement. The resulting multi-sensor framework separates density-driven plasma variations from chemistry-driven emission changes, providing a route to non-invasive, quantitative monitoring of plasma etching for improved process reproducibility.

2:30pm **PS1-MoA-5 Non-Invasive Detection of RF Plasma Arcing by View-Port-Type Radio Emission Spectrometry**, ***Geon Woong Eom***, *SangHo Lee, In Yong Park, Woo Seok Kang, Min Hur, Dae-Woong Kim,* Korea Institute of Machinery and Materials, Republic of Korea

Arcing in radio-frequency (RF) plasma is a transient, localized discharge that can be triggered by field enhancement near cracks, protrusions, particles, or locally heated surfaces. Because such events can damage the process chamber, generate particles, and degrade wafer yield, real-time detection of arcing is essential for plasma process monitoring. In this work, we propose a non-invasive arcing detection method based on view-port-type radio emission spectrometry (VP-RES), which senses RF electromagnetic emission from the plasma through an optical/electrical access port without direct insertion into the discharge region.

Artificial arcing was generated in a capacitively coupled plasma reactor using an arcing-inducing metal structure. The VP-RES response was compared with voltage and current waveforms measured by a conventional

voltage–current probe. To resolve transient RF signatures, the measured signals were analyzed in the time–frequency domain using wavelet transform analysis, allowing normal plasma operation and arcing events to be distinguished by their spectral and temporal features. In parallel, three-dimensional electromagnetic simulations of the field distribution inside the reactor were used to guide the sensor geometry and viewport location, with the design goal of maximizing signal coupling to arc-induced emission and spatial sensitivity within the discharge volume.

The results suggest that VP-RES can provide a practical, non-invasive diagnostic route for real-time arcing detection in RF plasma systems. By combining view-port-based RF emission sensing with time–frequency analysis, the proposed method offers a potential alternative or complementary approach to conventional electrical monitoring, particularly where direct probe installation is constrained or where localized transient detection is required.

2:45pm **PS1-MoA-6 High Sensitivity Detection of Subtle Electron Density Variations Using a Cutoff Probe***, **Jang Jinhyeok,*** Applied Physics lab for Plasma Engineering (APPLE), Department of Physics, Chungnam National University, Korea (Democratic People's Republic of)*; Cho Chulhee,* Institute of Quantum Systems (IQS), Chungnam National University, Korea (Democratic People's Republic of)*; Seong Inho, Jeong Wonnyoung, Choi Byeongyeop, Seo Seonghyun, Lee Isak,* Applied Physics lab for Plasma Engineering (APPLE), Department of Physics, Chungnam National University, Korea (Democratic People's Republic of)*; You Shinjae,* Applied Physics lab for Plasma Engineering (APPLE), Department of Physics & Institute of Quantum Systems (IQS), Chungnam National University, Republic of Korea

The electron density is one of the key plasma parameters that affect process reproducibility in plasma processing, and even small variations in the electron density can influence the process outcome. Accurately detecting such subtle variations critically depends on the sensitivity of the diagnostic instrument employed, and therefore a comparative evaluation of different diagnostic methods is required.

In this study, we demonstrate the high sensitivity of a cutoff probe for detecting subtle electron density variations. Small variations in the electron density were introduced by slightly varying the RF power, and the resulting changes were simultaneously measured by a cutoff probe and a Langmuir probe to compare their detection performance.

The results showed that the cutoff probe clearly resolved the subtle electron density variations in a stepwise manner, whereas the Langmuir probe could not distinguish the same variations because they were comparable to its measurement scatter.

In conclusion, the cutoff probe was confirmed to detect subtle electron density variations more effectively than the Langmuir probe. These findings can contribute to the selection of appropriate diagnostic methods in environments where the detection of small electron density variations is required

3:00pm **PS1-MoA-7 Young Investigator Awardee Talk: Spatially Resolved Probes for the Measurement of Hydrogen, Oxygen, Nitrogen, Chlorine, and Fluorine Radicals***, **Dren Qerimi,*** University of Illinois **INVITED**

Accurate measurement of reactive radical species in low-temperature plasmas is critical for understanding plasma chemistry, plasma-surface interactions, and semiconductor processing. Conventional optical diagnostics generally provide line-of-sight or volume-averaged measurements and often lack the spatial resolution necessary to resolve localized plasma behavior. In this work, we present spatially resolved catalytic radical probes capable of measuring H, O, N, and F radicals in plasma sources, with ongoing efforts extending the technique to chlorine-containing plasmas. The diagnostic platform utilizes catalytic probe surfaces that convert radical recombination or reactive loss into a measurable thermal response. Arrays of probes with different catalytic materials enable discrimination between multiple reactive species while maintaining sub-centimeter spatial resolution. Measurements of H, O, and N radicals were performed in a helicon plasma source over powers from 300–1100 W and pressures from 10–100 mTorr. Radical densities on the order of 10^{12}–10^{14}cm^{-3} were measured, while electron densities ranged from 10^{10}–10^{12}cm^{-3} and electron temperatures from ~2–8 eV. Radical densities increased with both pressure and power and followed trends consistent with independently measured plasma parameters. The probe framework was further extended to fluorine radical measurements relevant to plasma etching applications. Because fluorine plasmas present chemically aggressive environments, a non-equilibrium radical probe technique was developed in which radical-induced tungsten etching serves as the sensing mechanism. Experiments in NF_3 and SF_6 plasmas demonstrated a linear correlation between probe response and fluorine density up to 10^{21}m^{-3}. Calibration in a research-scale etcher enabled quantitative spatial fluorine density measurements and comparison with actinometry. Spatially resolved measurements revealed substantial radial nonuniformities in fluorine density above the wafer surface that are not captured by conventional optical diagnostics, improving interpretation of silicon etch kinetics and etch probability measurements. Current work focuses on extending these diagnostics to chlorine radical measurements for halogen-based plasma processing chemistries. These results demonstrate that catalytic radical probes provide a versatile diagnostic platform for spatially resolved measurements of reactive species in plasma environments relevant to both fundamental plasma studies and advanced semiconductor manufacturing.

3:30pm **PS1-MoA-9 Operando Plasma-XPS: Platform Development, Capabilities, and Metrology Challenges***, **Andrei Kolmakov,*** NIST

Plasma-driven processes are central to technologies spanning semiconductor manufacturing, advanced materials synthesis, energy systems, aerospace engineering, catalysis, environmental remediation, and biomedicine. Although conventional ultra-high vacuum (UHV) X-ray photoelectron spectroscopy (XPS) is a powerful tool for surface chemical analysis, its inability to operate at plasma-processing pressures has created a major metrological gap for operando measurements. Recent advances in ambient-pressure XPS (AP-XPS) instrumentation open new opportunities for direct studies of plasma-solid, plasma-liquid, and plasma-gas interactions. Here, we report on the hardware development and pilot testing of a plasma-compatible AP-XPS (plasma-XPS) platform for operando characterization of plasma-assisted processes and reactive environments [1]. We demonstrate conditions under which XPS spectra can be collected directly during plasma operation, enabling simultaneous monitoring of transient surface chemistry, gas-phase species, and mass- and optical spectra. We observed plasma-induced oxidation/reduction reactions, metastable surface species, and the importance of plasma-chamber wall reactions on local plasma chemistry [2]. Wealso observed RF/AC plasma-induced shifts in binding energy, XPS peak broadening, and splitting associated with surface charging and neutralization, particularly in poorly conducting materials. Gas-phase XPS spectra acquired during these plasma conditions also exhibit plasma-dependent binding-energy shifts and satellite structures, offering additional opportunities for real-time plasma diagnostics [3]. Overall, plasma-XPS emerges as a potentially versatile operando metrology platform for real-time diagnostics, process monitoring, and mechanistic studies across a broad spectrum of plasma-enabled technologies.

References

[1] J.T. Diulus, A.E. Naclerio, J.A. Boscoboinik, A.R. Head, E. Strelcov, P.R. Kidambi, A. Kolmakov, The Journal of Physical Chemistry C, 128 (2024) 7591-7600.

[2] J. T. Diulus, A. R. Head, J. A. Boscoboinik, and A. Kolmakov, J. Vac. Sci. Technol. A 43, 040401, (2025)

[3] J. T. Diulus, A. R. Head, J. A. Boscoboinik, C. Corbella, A. Tselev, and A. Kolmakov, J. Vac. Sci. Technol. A 44, 020405 (2026)

Plasma Science and Technology
Room 315 - Session PS2-MoA

Plasma Catalysis and Synthesis

Moderators: Prof. François Reniers, Université Libre de Bruxelles, **Prof. Dr. Mohan Sankaran**, University of Illinois at Urbana-Champaign

4:00pm **PS2-MoA-11 Electrifying C1 Chemistry via Nonthermal Plasma Catalysis***, **Tomohiro Nozaki,*** Institute of Science Tokyo, Japan **INVITED**

The growing demand for both reducing anthropogenic CO_2 emissions and utilizing CO_2 as a renewable carbon resource has accelerated global interest in circular carbon technologies. In this context, extensive efforts are being devoted to the development of next-generation chemical conversion processes capable of transforming CO_2 into value-added chemicals. Because such chemical transformations inevitably require external energy input, the integration of low-carbon energy sources, particularly renewable electricity, has become indispensable for realizing sustainable CO_2 conversion systems. Among these technologies, Plasma Catalysis - a combination of nonthermal plasma and heterogeneous catalysts - has attracted tremendous interest as a promising low-carbon technology where renewable electricity is readily

coupled into chemical conversion processes [1]. In the meantime, significant challenges remain in establishing a fundamental understanding of plasma–surface interactions, reaction pathways under non-equilibrium conditions, and catalyst functions specific to plasma environments. Further advances, therefore, require not only reactor engineering and process optimization, but also the development of plasma-adapted catalytic materials and scientifically grounded reaction design methodologies. This invited lecture presents recent progress in plasma-catalytic CO_2 conversion, with particular emphasis on CO_2 methanation, as one of the most extensively studied in modern C1 chemistry for carbon recycling and mechanistically understood plasma-catalytic reactions. First, in situ FTIR and XAFS spectroscopy of CO_2 hydrogenation over Pd_2Ga/SiO_2 are discussed, which emphasizes the key role of vibrationally excited CO_2 [2]. Moreover, an Eley-Rideal-type reaction, induced by atomic hydrogen, is explained as necessary to overcome the rate-determining step (decomposition of formates) [3]. Second, a large-scale methanation is introduced, where exothermic reaction heat also promotes the methanation reaction: the bifunctional contribution of plasma catalysis, cooperative interaction between reaction heat and activated species, is clarified [4,5]. These findings are not limited to the methanation reaction but are applicable to various types of CO_2 conversion in the scope of C1 chemistry. Finally, a future perspective is presented.[1] D-Y Kim, et al., *ACS Catalysis*, **15**, 19424, 2025.[2] D-Y Kim, et al., *J Am Chem Soc*, **144**, 14140, 2022.[3] D-Y Kim, et al., *JACS Au*, **5**, 169, 2025.[4] W Zhang, et al., *Chem Eng J*, **512**, 162520, 2025.[5] W Zhang, et al., *J Ener Chem*, **115**, 858, 2026.

4:30pm **PS2-MoA-13 Methane Reforming in Nanosecond-to-Millisecond Pulsed Plasmas***, Norleakvisoth Lim,* ***Michael Gordon****,* University of California Santa Barbara

Plasma-assisted methane reforming provides an electrified pathway for producing hydrogen and value-added hydrocarbons without direct CO_2 emissions while potentially enabling co-production of solid carbon. Here, we systematically investigate how the timescale of energy deposition governs methane plasma chemistry by examining atmospheric-pressure pulsed CH_4 discharges spanning six orders of magnitude in pulse duration, from nanoseconds to milliseconds, while maintaining comparable pulse energies of 10–50 mJ/pulse. Experiments were conducted in a coaxial flow reactor operated at low repetition frequencies (50–300 Hz) to specifically minimize pulse-to-pulse interactions. Plasma characteristics (gas temperature, electron density, presence of radicals, etc.) were quantified using electrical diagnostics and high-resolution OES, and reaction products were analyzed via online mass spectrometry.

Substantial changes in discharge physics and reaction products were observed across the ns-to-ms pulse-width range. Electron density varied from ~10^{14}–10^{18} cm^{-3} and gas temperature ranged from ~2500–5200 K, depending on pulse duration and discharge current. Short-pulse discharges (<1 µs) generated high electron densities (10^{17}–10^{18} cm^{-3}) and highly non-equilibrium conditions, where methane conversion proceeded through both electron-impact and thermal dissociation pathways. In contrast, longer pulses (>10 µs) operated at lower electron densities (10^{14}–10^{17} cm^{-3}) and were dominated primarily by thermal chemistry. Nanosecond discharges exhibited the highest total C_2 selectivity (>70%), producing approximately 17% C_2H_6, 18–20% C_2H_4, and 35% C_2H_2. Increasing pulse duration shifted product distributions toward sequential dehydrogenation pathways consistent with Kassel-type chemistry, promoting acetylene formation at the expense of ethylene and ethane.

Energy deposition timescale produced a distinct tradeoff between selectivity and conversion. Rapid energy deposition and quenching in short-pulse plasmas favored partially dehydrogenated intermediates, whereas longer pulses improved methane conversion and process efficiency through increased reaction volume and residence time. The best overall performance was achieved near 100 µs pulse duration, yielding methane conversion energy cost as low as ~370 kJ/mol CH_4 and specific energy requirements of ~15 kWh/kg for C_2H_2 and ~40 kWh/kg for H_2, comparable to thermal plasma processes. These results demonstrate that pulse duration serves as a powerful control parameter for tuning plasma reaction pathways and optimizing selective methane conversion to hydrogen and value-added hydrocarbons.

4:45pm **PS2-MoA-14 Asymmetric Plasma-Electrocatalyst Process for Tunable Nitrogen Fixation***, Mohammad Ali Eslamisaray,* Department of Nuclear, Plasma, and Radiological Engineering, University of Illinois Urbana-Champaign, Champaign, IL, USA*; Hee-Eun Kim, Xiao Su,* Department of Chemical and Biomolecular Engineering, University of Illinois Urbana-Champaign, Urbana, IL, USA*; R. Mohan Sankaran,* Department of Nuclear, Plasma, and Radiological Engineering, University of Illinois Urbana-Champaign, Champaign, IL, USA

Nitrogen-containing compounds, such as ammonia and nitrate, are critical to applications in agriculture, polymer synthesis, and biomanufacturing. Industrially, ammonia is primarily produced by the Haber-Bosch process, in which nitrogen reacts with fossil-fuel-derived hydrogen over a catalyst bed, and nitrate or nitric acid is produced by subsequent oxidation of ammonia via the Ostwald process. Both the Haber-Bosch and Ostwald processes are carried out in large, centralized manufacturing facilities with substantial capital expenditure and supporting infrastructure. Such production schemes create significant logistic and economic challenges, including transportation, safety and handling, and supply chain vulnerabilities. In addition, both processes require elevated temperatures and pressures making them incompatible with intermittent renewable energy. Recently, there has been a growing interest in sustainable and decentralized alternatives for nitrogen fixation. Electrochemical approaches have been challenged by the activation of molecular nitrogen but can efficiently reduce nitrate to ammonia. In comparison, nonthermal plasmas can react air to efficiently produce nitrate. These complementary features have been exploited in combined strategies, but only as separate reactors.

In this work, we investigated an asymmetric plasma-electrocatalyst process that directly converts air and water into tunable nitrogen products within a single reactor. Specifically, the plasma and electrocatalytic electrodes share the same electrical circuit and electrolyte, with a plasma serving as the anode and a cobalt oxide-based electrocatalyst acting as the cathode. We first evaluated the performance of the system in a single-supply configuration, in which the plasma and electrocatalyst operating conditions are coupled. We then introduced an independent cathodic bias to decouple the plasma and electrocatalyst operating conditions. With the latter configuration, we were able to demonstrate significant control over product selectivity, with final compositions ranging from nitrate-dominant to ammonia-dominant and solution pH ranging from acidic to alkaline.

5:00pm **PS2-MoA-15 Operando Spectroscopic Insights into Plasma-Driven Ammonia Synthesis via Isocyanate Intermediates***, Casey O'Brien,* Texas Tech University

Coupling nonthermal N_2 plasmas with heterogeneous catalysts offers a promising route to sustainable ammonia synthesis under mild conditions. Here, we demonstrate a plasma-catalytic pathway that utilizes H_2O as a carbon-free hydrogen source and leverages trace CO_2/CO_x impurities as catalytic promoters rather than undesirable contaminants. Using a multi-modal operando spectroscopy platform capable of simultaneously probing plasma-phase species and surface-bound intermediates, we identify a distinct vibrational feature at ~2200 cm^{-1}. Isotopic labeling confirms this band arises from surface-bound isocyanate (NCO) species formed via reactions between plasma-activated nitrogen and trace CO_x present at ppm levels in commercial N_2 feeds.

We show that these NCO intermediates react readily with water vapor to produce ammonia at ambient temperature and pressure. Notably, NCO formation is observed across a broad range of metal catalysts, including Pd, Ni, Ag, Au, and Cu, with metal-dependent vibrational signatures, binding energetics, and reaction kinetics for NCO + H_2O conversion. These results indicate that ammonia synthesis via NCO intermediates is a generalizable pathway and that both catalyst identity and gas composition can be tuned to control activity and selectivity. This work highlights the potential of plasma-catalyst coupling to access new reaction mechanisms enabled by trace species and metastable intermediates under non-equilibrium conditions.

5:15pm **PS2-MoA-16 Structural Changes of Plasma Modified Polymers for Applications in Catalytic Deconstruction***, Aunic Goodin,* North Carolina State University*; Sujoy Bepari,* North Carolina A&T State University*; Tridip Das,* California Institute of Technology*; Duncan Trosan,* North Carolina State University*; Zahidul Islam,* North Carolina A&T State University*; William Goddard III,* California Institute of Technology*; Debasish Kuila,* North Carolina A&T State University*; Steven Shannon,* North Carolina State University

1. **Introduction**

The disposal of plastic waste has become an increasing global challenge as single use consumer plastics continues to grow. Catalytic deconstruction is a potential method for upcycling this plastic waste, with plasma being added at different steps to improve the yields or vary/modify the products.

This work investigates the effects of a plasma pre-treatment using atmospheric pressure air plasma to pre-treat polymers prior to catalytic deconstruction. The structural changes of the polymers and the effect on the product distribution under different plasma conditions is investigated.

2. **Methods**

Plasma treatment is performed in a sealed vial with a rubber septum cap. A steel hypodermic needle is used to both deliver synthetic air and apply a high voltage in a pin-to-cup configuration. The grounding cup is made up of a copper pipe soldered to a copper plate. The vial is placed the copper "cup" with the whole assembly surrounded with a 3D printed holder to prevent arcing from the high voltage to ground. The treatment voltage, frequency, flow rate, and power are varied and the modification of polypropylene and polyethylene are investigated using XPS, FTIR, NMR, and MALDI-TOF measurements.

3. **Results and Discussion**

Plasma pre-treatment has been shown to improve yields and modify product distribution depending on the plasma parameters. Previous work has shown this trend with polypropylene and ZSM-5/SBA-15 composite catalyst [1]. The method has been shown to apply with polyethylene and a FeRu-HM catalyst to improve the yield of jet fuel (C_8-C_{16}) products. Further investigation of the structural changes of the plasma treated polymers is therefore necessary to better understand this process.

4. **Conclusion**

Through variations in plasma pre-treatment, catalytic deconstruction can be tuned to produce different product distributions. This method can be applied to other polymer based catalytic deconstruction applications but requires more understanding of the changes in the pr-treatment step.

Acknowledgement

This material is based upon work supported by U.S. Department of Energy (DOE) no. DE-EE0009945.

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5:30pm **PS2-MoA-17 Dynamics of Intermediates Formed from Ionizing Radiation of Aqueous Salt Solutions: A Transient Absorption Study**, ***William Maza***, US Naval Research Laboratory*; Sara Gebre,* us naval Research Laboratory*; Adam Dunkelberger,* US NAval Research Laboratory

The ionization products of laser-induced plasmas generated in water are of great interest; in particular, as they relate to plasmas generated in marine waters. However, despite the complexities involving the ionization of neat water we have endeavored to study ionization of aqueous solutions that mimic the conditions found in seawater. To simplify the strong ionization power of intense pulsed-laser interactions with seawater leading to the formation of undersea plasmas, and to provide a baseline for the study of undersea plasmas, we have begun investigating the softer ionization of aqueous salt solutions by two-photon absorption. We find that the spectra and dynamics observed from two-photon absorption of simulated seawater solutions are complex and indicate the formation of multiple meta-stable intermediates that can be temporally resolved. These include the very short lived (< 50 ns) hydroxyl radical, longer-lived hydrated electron (up to ~ 1 µs), and even longer-lived products of anion ionization like Cl_2^- and CO_2^- (> 10 µs). The presence of humic acids, meant to model dissolved organic matter typically found in seawater, further complicates our analysis. We will discuss these results and their potential significance to underwater plasma formation under similar conditions.

Atomic Scale Processing Mini-Symposium
Room 316 - Session AP+EL+EM+PS+TF-TuM

Area Selective Processing and Patterning

Moderators: Prof. Dr. Greg Parsons, North Carolina State University, **Dr. Silvia Armini**, IMEC, Belgium

8:00am **AP+EL+EM+PS+TF-TuM-1 ASCEND: A Novel Solution-Based Method To Control Deposit Composition and Placement**, *Jevalyne Vienes,* ***Amy Walker,*** University of Texas at Dallas

We introduce a novel selective deposition process called ASCEND, or "Additive and Surface Control of Electroless Nanostructure Deposition." ASCEND integrates mechanistically-informed and well-controlled extensions of electroless deposition (ELD) and chemical bath deposition (CBD). It uses hybrid ELD-CBD conditions and patterned surfaces to deposit strongly adherent metallic and metal chalcogenide films and nanowires. It is inexpensive, easily scaled, and compatible with technologically relevant substrates. We illustrate ASCEND using Cu and CuS deposition. First, we employ ethanolamine additives in Cu ELD using dimethylamine borane (DMAB) on –OH and $–CH_3$ terminated alkanethiolate self-assembled monolayers (SAMs) either to deposit nanowires or perform area-selective deposition. Using monoethanolamine or triethanolamine copper nanowires are formed at the junction of patterned –OH/$–CH_3$ terminated SAMs. In contrast using diethanolamine, area selective deposition is observed in the $–CH_3$ terminated SAM area. Using TOF SIMS data we show that monoethanolamine and triethanolamine adsorb vertically (or at an angle) with the amine group interacting with the $–CH_3$ terminated SAM and leaving the hydroxyl groups free to interact with the bath components. This causes repulsion of the DMAB reducing agent, hindering deposition on the $–CH_3$ terminated SAM areas leading to nanowire formation. In contrast, diethanolamine adsorbs flat on $–CH_3$ terminated SAMs and no nanowire formation is observed; rather area-selective deposition occurs.

In the second experiment we control the deposit composition in Cu ELD using thiourea, which is a common bath additive, on -OH, -COOH and $–CH_3$terminated SAMs. At < 10^{-2} M thiourea, Cu films are deposited on all substrates. At ≥ 10^{-2} M the deposited layers are copper sulfides. At pH 5 and pH 9, the film is composed of CuS for all functionalized SAMs studied, while at pH 12 the deposit is Cu_2S. We attribute this to the role of thiourea in the bath. At low concentrations, thiourea acts as a complexing and reducing agent, while at high concentrations (> 10^{-2} M) the dominant reaction is thiourea hydrolysis leading to the formation of copper sulfides. Finally, exploiting this understanding we demonstrate a simple method to deposit layered Cu/Cu_xS and CuS nanowires on patterned SAM substrates by changing the TU concentration in the bath.

8:15am **AP+EL+EM+PS+TF-TuM-2 Using Acetylacetates to Control Chemical Reactivity and Physical Properties of Surfaces**, ***Andrew Teplyakov,*** University of Delaware

Over the last few years, the applications of various acetyl acetates in tuning both chemical reactivity of surfaces in deposition and etching processes and physical properties of the interfaces and thin films have received a substantial attention both from fundamental perspective and from applications point of view. This presentation will analyze the chemistry of several acetylacetates, including the ligands formed on surfaces by acetylacetone (acacH), hexafluoroacetylacetone (hfacH) and 1,1,1-trifluoroacetylacetone (tfacH) and the implications of this chemistry in area-selective atomic layer deposition (AS-ALD), atomic layer etching (ALE), and tuning optoelectronic properties of oxide surfaces and thin films. The effects of the gas-phase keto-enol equilibrium and the acid/base properties of oxide surfaces on the adsorption mechanisms will be discussed. The applications of this knowledge to design non-growth and growth surfaces for ALD and to propose new chemistries for ALE of 2D materials will be demonstrated.

8:30am **AP+EL+EM+PS+TF-TuM-3 Atomic Layer Etching for Advanced Logic Devices**, ***Masanaga Fukasawa,*** National Institute of Advanced Industrial Science and Technology (AIST), Japan **INVITED**

The dimensions of advanced logic devices require atomic-level control of variability, and atomic-layer etching (ALE) is a promising technique to meet this requirement. By separating adsorption and desorption, ALE improves controllability compared with conventional RIE. Currently, however, the long process time—leading to increased manufacturing cost—remains a major challenge, and thus industrial adoption has been limited. Nevertheless, in next-generation highly scaled 3D transistors such as CFETs, further improvements in etch selectivity, mitigation of pattern loading, and reduction of etch-induced damage are required. As a result, the importance of ALE is expected to increase [1].

To further improve etch selectivity, we have developed a technique that integrates area-selective deposition (ASD) and ALE within a single etching chamber to achieve ultra-high etch selectivity [2]. In atomic-scale processes such as ALD and ALE, understanding surface reactions and process performance at the atomic level enables more precise process design through the combination of individual reaction steps. Moreover, this approach is beginning to be adopted not only for ASD + ALE but also for ASD + RIE [3] in various process modules. In particular, with High-NA EUV lithography reducing resist thicknesses to below 30 nm, extremely high etch selectivity becomes even more critical. Thus, integration schemes that combine ASD with RIE/ALE will play an increasingly important role.

Regarding low-damage processing, although several studies have reported blanket-level evaluations, examples that demonstrate practical-level performance have been limited. In this work, we applied ALE or RIE to the bottom-break step of contact hole etching and compared the resulting electrical characteristics of contact chains. The results clearly show that ALE provides superior performance [4].

ALE delivers the controllability, reproducibility, and integrability required for next-generation semiconductor technologies, and elevates semiconductor fabrication to a new level of precision. I believe ALE will become increasingly essential in advanced logic device manufacturing.

Acknowledgement: This paper is based on results obtained from the project, "Research and Development Project of the Enhanced Infrastructures for Post-5G Information and Communication Systems" (JPNP20017), subsidized by New Energy and Industrial Technology Development Organization (NEDO).

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9:00am **AP+EL+EM+PS+TF-TuM-5 Band Practice: Tuning Gold's Workfunction Through NHC d-Band Interactions**, ***Sean Barry,*** Carleton University, Canada*; Wai Tung Shiu, Paul Ragogna,* Western University, Canada

N-heterocyclic carbenes (NHCs) have emerged as robust small-molecule inhibitors (SMIs) for modifying metal surfaces, yet a quantitative understanding of their influence on surface electronic structure remains limited. Here, we investigate the modulation of the d-band center of a gold surface by NHC adsorption using a combination of solution- and vapour-phase deposition. Four structurally distinct NHCs were deposited on Au substrates, and the resulting interfaces were characterized using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS).

All NHCs formed stable monolayers on Au, with surface coverages that depended on both molecular structure and deposition method, ranging from 1.88 to 3.56 NHC/nm^2. UPS measurements revealed significant reductions in the Au work function (up to ~1.2 eV), with vapour-deposited films exhibiting larger shifts, consistent with differences in interfacial structure and electron redistribution. Analysis of the valence band spectra shows a systematic lowering of the Au d-band center upon NHC adsorption, indicating increased filling of antibonding states and weakened adsorbate–metal interactions.

Three primary factors governing d-band modulation were molecular orientation and the formation of Au(NHC)$_2$ adatom complexes, which lead to enhanced electron donation. Surface coverage plays a critical role, with higher coverages producing stronger modulation due to increased adsorbate–metal interactions. Finally, ligand electronics, particularly backbone substitution, influence the NHC's σ-donating ability and thus the extent of electronic perturbation at the interface.

This presentation will discuss the structure-function relationships of NHC substitution and coverage as well as absorption interactions.

9:15am **AP+EL+EM+PS+TF-TuM-6 Inhibition of SiO_2 by plasma treatments for bottom-up gap-fill applications**, ***Aurelia Trevisan,*** *Adrie Mackus, Erwin Kessels,* Eindhoven University of Technology, The Netherlands

As the features in electronic devices become smaller, top-down processes based on lithography need eventually to be complemented by bottom-up processes such area selective atomic layer deposition (AS-ALD). Although

ALD allows for conformal deposition on 3D features, it is challenging to fill high aspect ratio (AR) trenches without the formation of defects such as voids and seams in the middle. To obtain a defectless bottom-up gap-fill of a trench by ALD, the growth per cycle (GPC) of the employed ALD process should be lower at the top of the trenches than at the bottom. Different approaches that result in a decreased GPC on the top of AR trenches for seamless gap-fill have been studied employing molecular inhibition species[1] and NH_3 plasma pre-treatments.[2]

In this work, we investigated the mechanisms of inhibition of SiO_2 by NH_3, N_2/H_2 and SF_6/H_2 plasma exposures aiming at the application of such plasma pre-treatment for achieving gap-fill with SiO_2. We exposed the SiO_2 surface to NH_3, N_2/H_2 and SF_6/H_2 plasma at different conditions and we studied the surface chemistry by reflection-absorption infrared spectroscopy (RAIRS). For a NH_3 plasma exposure, we found that the substitution of the OH groups with NH_2 groups is almost complete[3] at low NH_3 pressure from the comparison of the areas of the OH peak (~3740 cm^{-1}) in the RAIRS spectra acquired after the plasma exposures at different NH_3 pressures. Next, to investigate the inhibition of the SiO_2 surface by plasma, RAIRS spectra were also obtained after dosing the Si precursor, bis(diethylamino)silane (BDEAS), with and without the plasma treatment step. From the IR spectra, we found that the amount of adsorbed BDEAS molecules on SiO_2 pre-treated with NH_3 plasma (60s, 0.01 mbar) is reduced by ~82%.

A NH_3 plasma pre-treatment was added before the dose of the precursor to every cycle of the SiO_2 PE-ALD process. The effect of the NH_3 plasma pre-treatment on the growth was investigated by conducting spectroscopic ellipsometry (SE) after every cycle. When the NH_3 plasma pre-treatment was added, a 53% reduction of the GPC was obtained. We expect this reduction to be enough to achieve gap-fill of high AR trenches, which will be studied by cross-sectional transmission electron microscopy.

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9:30am **AP+EL+EM+PS+TF-TuM-7 Precursor Isomerization-Enabled Etching Amplification: A Novel Route to Area Selective Deposition of SiOC Films**, ***Xiaocheng Huang**, Junjie Zhao,* Zhejiang University, China

Self-aligned patterning via area selective deposition (ASD) is a promising approach to mitigate overlay variations challenges in photolithography for advanced nanomanufacturing. However, it remains difficult to achieve area selective deposition when the adsorption and/or film growth on the target non-growth surface (NGS) exceeds that on the target growth surface (GS). We developed an etching amplification strategy based on precursor isomerization for selective deposition of SiOC when adsorption and/or film growth was higher on the target NGS than on the target GS. *In-situ* DRIFTS demonstrated that V_3D_3 cyclosiloxane undergoes ring-opening on CoO_x surfaces. This ring-opening reaction significantly enhances the etching rate under O_2/Ar plasma by 243% compared to the pristine pV_3D_3, as confirmed by *in-situ* QCM measurements. *In-situ* QCM during ASD cycles showed higher mass gain on CoO_x than on SiO_2 during V_3D_3 deposition steps; however, the subsequent etching step completely removed the adsorbed species from the NGS due to etching amplification. By integrating deposition and etching processes, we achieved selective deposition of a ca. 18.36 nm thick SiOC film on pre-patterned Co/SiO_2 substrates with nearly 100% selectivity. This work sheds light upon etching amplification by precursor isomerization for developing highly selective ASD processes.

9:45am **AP+EL+EM+PS+TF-TuM-8 A Novel Hybrid Approach to Area-Selective Deposition: Combining Two Strategies for Blocking Growth**, *Jay Swarup, James Jensen, Gokul Rajagopal, **James Engstrom**,* Cornell University

Area-selective atomic layer deposition (AS-ALD) has emerged as a promising bottom-up nanofabrication strategy for next-generation semiconductor manufacturing, where continued device scaling makes conventional lithographic patterning increasingly difficult and costly. Selectivity can be achieved by passivating non-growth surfaces (NGS) with blocking molecules while permitting growth on designated growth surfaces (GS), and it depends critically on precursor chemistry, blocking molecule identity and application method, and reactor temperature. Here we systematically investigate two blocking strategies for AS-ALD of Al_2O_3 targeting selective growth on Cu (GS) with suppression on SiO_2 (NGS) using BDMADA-Al, a bulky, non-pyrophoric precursor [1]. We employ *in situ* real time quartz crystal microbalance (QCM) techniques, coupled with selected *ex situ* techniques including X-ray photoelectron spectroscopy (XPS).The first strategy employs sequential dosing of a small molecule, while the second strategy introduces a co-adsorbate dosed simultaneously with the precursor to enable competitive adsorption at NGS reactive sites. In the first strategy, dimethylamido trimethylsilane (DMATMS) was applied repetitively in an ABC-type cycle (T = 285 °C), which produced modest blocking efficacy, where detectable growth from QCM could be delayed for the first ~ 20 cycles, while Al is clearly observed with XPS after 40 cycles.In the second strategy we also employ an ABC-type cycle, but also introduce a co-adsorbate dosed simultaneously with BDMADA-Al at T = 120 °C.We examined six different co-adsorbates, all possessing reactive functional groups, which revealed stark differences in blocking efficacy depending on the co-adsorbate used.Three co-adsorbates did not enhance blocking but, rather, produced linear (with exposure time) CVD-like growth during the combined precursor/co-adsorbate pulse.In contrast, three co-adsorbates yielded *complete blocking* of growth on SiO_2 for at least 40 cycles of ALD, confirmed by both QCM and XPS.In order to verify the operative mechanism of competitive adsorption we varied both the partial pressure of the co-adsorbate and the reactor temperature.We found that by either decreasing the partial pressure of the co-adsorbate, or increasing the temperature led to less effective blocking of growth, confirming the mechanism based on competitive adsorption.These results demonstrate that an approach that combines two strategies can produce synergy and a more effective method to enable area selective deposition.

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11:00am **AP+EL+EM+PS+TF-TuM-13 Probing Reactivity at Heterointerfacial Sites Using Area Selective Atomic Layer Deposition**, *Shani Monadeev, **Oz M. Gazit**, Alexander Stook,* Technion Israel Institute of Technology, Israel

Background

Heterointerfaces are a sub-class of defects arising from atomic mismatches across material boundaries. These coordinatively unsaturated sites modulate the electronic and geometric structure of catalysts to facilitate specific reactive adsorption, activation, and transformation of reactant molecules.[1] In electronic devices the critical heterointerfaces are “buried” between the layers,[2] whereas for catalysts, the reaction performance can depend on both the buried interfaces (i.e. metal support interactions) and on the exposed heterointerfacial (defect) sites, interacting with substrate and product molecules, see **Scheme 1**.

Results and discussion

In the current work, we use a bottom-up area selective atomic layer deposition (AS-ALD) to form supported thin layer raft-like oxides. To facilitate the AS geometry, we developed a new approach, which uses NaCl nanocrystals as masking domains during the ALD process. This unique approach allows us to apply this methodology onto silicon wafers and on different surface area particulate silica support materials. The HRSEM-EDS (Energy Dispersive Spectroscopy) mapping in **Figure 1** shows an example of a well-defined multilayer structure, formed following the sequential deposition of TiO_2 (≈20 nm) and subsequently Al_2O_3 (≈20 nm) layers onto an NaCl-mask before and after mask removal. Leveraging on the strength of AS-ALD we study the structure, binding energy, strain and more of the exposed heterointerface, aiming to decuple those from the exposed basal plan and bulk effects. We compare our AS-ALD materials to materials obtained using a top-down deposition of thin nanosheets of layer double hydroxides. All materials are extensively characterized using XPS, DRIFT-IR, HRSEM and HRTEM, grazing angle-WAXS and probe molecules TPD-MS. The functionality of the heterointerfacial sites is tested using Aldol type condensation reactions for the conversion of biomass derived platform molecules as a target and probe reaction.

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11:15am **AP+EL+EM+PS+TF-TuM-14 Area-selective Atomic Layer Deposition of Al2O3 on SiNx with Aminosilane-Functionalized SiO2 as the Nongrowth Surface**, ***Andrew Kaye**,* Colorado School of Mines*; Bhushan Zopé,* Intermolecular, Inc.*; Xinjian Lei, Ronald Pearlstein, Haripin Chandra, Agnes Derecskei,* EMD Electronics*; Sumit Agarwal,* Colorado School of Mines

SiO_2 and SiN_x are two of the most extensively used dielectric materials in semiconductor manufacturing. Previously, we showed that area-selective ALD of Al_2O_3 can be achieved on SiN_x by passivating the SiO_2 surface with

aminosilanes. Using *in situ* attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy (see Figure 1), we will show that the aminosilanes react with both the SiO_2 and SiN_x surfaces, but the coverage of aminosilanes on the SiN_x surface is incomplete, which does not prevent ALD of Al_2O_3 from dimethylaluminum isopropoxide (DMAI) and H_2O, but simply introduces a nucleation delay of 5-10 cycles. However, selective growth of Al_2O_3 on SiN_x was limited to ~1 nm at which point DMAI started to react with the SiO_2 surface to nucleate film growth.

Based on these initial studies, our hypothesis was that there are residual Si–OH groups that remain on the SiO_2 surface react with DMAI to initiate growth of Al_2O_3. We have also shown that DMAI likely coordinates with Si–O–Si groups on aminosilane-functionalized SiO_2 films, which also leads to nucleation; therefore, simply reducing the surface Si–OH group density is inadequate. To extend the nucleation delay on SiO_2, we created a set of plasma-deposited SiO_2 surfaces with a controlled density of surface Si–OH groups by first preheating from the deposition temperature of 150 °C up to 500 °C, and then by cooling the substrate to a lower temperature prior to ALD of Al_2O_3. We used aminosilanes with different size head groups to study the uptake of aminosilanes and the steric blocking effects of both Si–OH and Si–O–Si sites to block Al_2O_3 ALD. The headgroup size did not significantly impact the initial uptake of aminosilanes with the same size leaving groups (see Figure 2). Using *in situ* ellipsometry, we show that aminosilanes with larger head groups resulted in more selective growth on SiN_x over SiO_2. Next, we showed that increasing the aminosilane dose increased the nucleation delay of Al_2O_3 ALD on both SiO_2 and SiN_x surfaces due to increased coverage, but selectivity did not improve significantly. Finally, we show that using a two-step aminosilane passivation scheme with sub-saturation doses of a large aminosilane and then a small aminosilane resulted in >3 nm of selective Al_2O_3 ALD on SiN_x over SiO_2 surfaces (see Figure 3).

11:30am **AP+EL+EM+PS+TF-TuM-15 Beyond Two-Color Selectivity: Area Selective Deposition on Multi-Oxide Surfaces Using Small Molecules Inhibitors***, **Benjamin Sanhueza,** Marc J. M. Merkx, Wilhelmus M. M. Kessels,* Eindhoven University of Technology, Netherlands*; Tania E. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile*; Adriaan J.M. Mackus,* Eindhoven University of Technology, Netherlands

Area-selective deposition (ASD) using small molecule inhibitors (SMIs) emerges as a promising bottom-up alternative, enabling selective deposition on growth areas (GAs) while inhibiting the non-growth areas (NGAs). Although ASD has shown strong potential, most studies are limited to two-surface-selectivity, which does not capture the multi-material complexity of modern semiconductor devices.[1]. In this context, we investigate the selectivity of SiO_2 ASD in a multi-oxide system by evaluating the role of different SMIs and their impact on inhibition selectivity, with relevance on 3D memory [2] and 3D logic devices.[3]

Here, we employ a previously developed SiO_2 ASD process on Al_2O_3 and SiO_2 surfaces,[4] using the bis(diethylamino)silane (BDEAS) precursor, H_2 and O_2 plasma as co-reactants, and different SMIs. Building on this process, we investigate multi-surface selectivity by introducing ZrO_2 as an additional third oxide surface.

Among the SMIs investigated, acetylacetone (Hacac) is presented as a representative case. *In situ* reflection–absorption infrared spectroscopy (RAIRS) shows that Hacac reacts with ZrO_2, achieving surface saturation and up to 96% blocking of a single BDEAS dose, which is comparable to that observed on Al_2O_3 as an NGA. Preliminary results further indicate that the H_2 plasma pre-treatment increases the density of isolated and vicinal –OH groups, enhancing Hacac coverage and improving blocking up to 99.5%, demonstrating the strong influence of this plasma pre-treatment on the ZrO_2 surface.

In situ ellipsometry measurements show that ZrO_2 acts as an effective NGA, exhibiting a nucleation delay of up to 28 cycles (~2.6 nm of selective SiO_2 deposition). Remarkably, similar selectivity is achieved on both Al_2O_3 and ZrO_2 surfaces, indicating consistent inhibition behavior across different oxides.[1], [5]

In addition to the results of this case study, it will be discussed that the choice of SMIs can tune inhibition behavior enabling different growth across surfaces. In this way, the loss of selectivity can be preferentially initiated on one NGA prior to another through SMI selection, enabling controlled thickness variations across different materials.

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11:45am **AP+EL+EM+PS+TF-TuM-16 Surface Hydroxyl Topology and Relative Orientation Effects on Surface-Inhibitor Reactivity: Revisiting Chemical Passivation in Alumina and Zirconia.***, Lucas Lodeiro, Nicolás Rozas-Castro,* Universidad Tecnica Federico Santa Maria, Chile*; Dennis Hausmann, Rachel Nye de Castro,* Lam Research Corporation*; Adriaan Mackus,* Eindhoven University of Technology, Netherlands*; **Tania Sandoval,*** Universidad Tecnica Federico Santa Maria, Chile

Hydroxylated metal oxide surfaces are paramount for catalysis and thin–film processing. In this context the reduction of surface reactivity via molecular inhibitors or chemical passivation is a common and necessary practice. Small–molecule inhibitors (SMIs) such as acetylacetone (Hacac) and acetic acid (HAc) are widely employed to inhibit growth by reactive site consumption on hydroxylated oxides.[1] Despite their ubiquitousness, the influence of **surface site configuration** on inhibitor reactivity remains unexplored.

Experimental evidence that chemically distinct hydroxyl motifs exhibit different reactivities toward SMIs is available.[2] In this work, we revisit the chemical passivation of hydroxylated alumina and zirconia by SMIs, with emphasis on the role of surface site configuration, defined as a combination of Local Topology and Relative Orientation of hydroxyl groups on metal oxide surfaces. Rather than treating hydroxylated sites as a whole entity, we examine how geometrically and electronically distinct surface motifs modulate inhibitor binding modes and reactivity.

Considering that systematic exploration of all possible site configurations rapidly becomes challenging due to the large chemical space, we further investigate whether simple surface descriptors, derived from local electronic structure and geometry, can provide predictive insight into surface reactivity toward SMIs. Our goal is to identify descriptor trends (e.g., charge distribution, coordination, or accessibility metrics) that correlate with inhibitor adsorption behavior, enabling informed prioritization of surface motifs prior to exhaustive site screening.

By linking surface site configuration, inhibitor-surface reactivity and descriptor–based analysis, this work aims to understand the nuances in the chemical passivation of metal oxide surfaces, and provides guidance to design descriptor–informed screening strategies.

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12:00pm **AP+EL+EM+PS+TF-TuM-17 Can pFA Invert Selectivity? The Chemistry of TiO_2 Nucleation on Chlorinated and Aminated Si(111) Surfaces During Thermal Atomic Layer Deposition***, **Tyler Parke,** Andrew Teplyakov,* University of Delaware

Recently, the near-atomic level precision offered by atomic layer deposition (ALD) has been exploited by developing area-selective schemes which can be used to fabricate complex three-dimensional nanostructures, such as modification of a substrate's surface functionality to induce a "selectivity inversion" between growth surfaces (GS) and non-growth surfaces (NGS). This is a newly developing technique, which has only been demonstrated thus far with few vapor-phase treatments, and which requires a molecular level understanding of the chemistry between surface and modifying reactant, as well as between modified surface and precursor. Here, single-crystal Si(111) surfaces terminated with hydrogen [H-Si(111)] or chlorine [Cl-Si(111)] monolayers, which are typically NGS's in thermal TiO_2 processes, are proposed as potential substrates to modify with a basic amine, para-fluoroaniline (pFA), and invert their selectivity. Amination with pFA is demonstrated to selectively modify the H-Si(111). Thermal TiO_2 ALD is subsequently attempted to test the aminated surface's capability as a GS or NGS. The fundamental chemistry of the interaction between the pFA and either surface, as well as between the aminated surface and ALD precursors $TiCl_4$ and tetrakis(dimethylamido)titanium (TDMAT), are probed with a combination of X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), density functional theory (DFT), and time of flight secondary ion mass spectrometry (ToF-SIMS) in order to determine the structure of the aminated surface and understand its effect on reactivity under ALD conditions.

Plasma Science and Technology
Room 315 - Session PS1-TuM

High Aspect Ratio and Cryogenic Etching I

Moderators: Prof. Kenji Ishikawa, Nagoya University, Japan, **Dr. Eric Miller**, IBM

8:00am **PS1-TuM-1 Challenges in Etching High Aspect Ratio Patterns for Memory Devices**, *Seokhyun Lim, Wonbong Jung, In-Joong Kim, JungHwan Um,* ***Sung-Il Cho,*** Samsung Electronics Co., Republic of Korea **INVITED**

Since the first V-NAND was introduced in 2013, high aspect ratio contact(HARC) etching has become the most critical technology for developing 3D devices. As aspect ratio of vertical patterns increases, both profile fidelity and throughput become more demanding. Consequently, the etch-rate reduction known as aspect ratio dependent etching(ARDE) must be overcome first, and traditional development has focused on raising ion energy to meet this requirement. Recently, however, the requirement to minimize local variations, such as distorted patterns and abnormal critical dimensions, has grown substantially. For example, non-circular patterns in vertical-channel structures induce abnormal operation because of undesirable electric field distributions. This deformation is mainly caused by non-uniform polymer deposition and bent ion trajectories, which has led the semiconductor industry to adopt precise waveform control and polymer management technologies. Increasing ion energy, meanwhile, narrows the arcing margin of the equipment and raises charge-up damage concerns. The recently intorduced cryogenic etching can mitigate these problems associated with high bias power, but it brings its own set of requirements. At present, industrial cryogenic etching is limited to etch SiO2 and SiN selective to organic hardmasks. Therefore, a broader range of chemistries and plasma conditions should be exploited for various applications. In this presentation we will outline the various technical obstacles that arise in HARC etching and propose development directions to address them.

8:30am **PS1-TuM-3 High-Aspect-Ratio Carbon Hard-Mask Etch Using High-Density Plasma and a Novel Additive Gas Chemistry**, ***Koki Mukaiyama,*** *Shuji Funada, Ryusuke Seino, Maju Tomura, Yoshihide Kihara,* Tokyo Electron Miyagi Limited, Japan

In 3D NAND flash memory manufacturing, carbon is commonly used as a hard mask for channel-hole etching. As the number of stacked memory cells increases, the carbon mask must be made thicker, necessitating high-aspect-ratio (HAR) etching. Current carbon-mask etch processes employ oxygen with a sulfur-containing additive using high-density inductively coupled plasma (ICP) with high applied bias. Because sulfur-based sidewall protection becomes insufficient at high aspect ratios, process conditions that narrow the mask openings are often adopted to prevent enlargement of the critical dimensions (CDs). However, this narrowing restricts radical transport to the feature bottom, substantially reducing the etch rate in HAR regions. To address this issue, we focused on additive gas chemistry. Since the discovery of sulfur-containing additive gases [1,2], no additive gas that outperforms them has been reported. In this study, we introduced a novel additive gas (hereinafter referred to as “Gas A”) into oxygen plasma and evaluated its effects on etching characteristics. We found that Gas A reacts with carbon to form a passivation layer on the sidewalls even at high aspect ratios, yielding smaller hole CDs than those obtained with sulfur-based protection. In addition, Gas A removes deposits from the mask openings and suppresses CD narrowing at the openings during etch progression, while leaving the mask itself intact. Because fewer reactive species are consumed at the sidewalls and the mask openings remain larger, more radicals and ions can reach the HAR regions. As a result, the etch rate is enhanced while hole CDs are reduced. Furthermore, combining Gas A with sulfur-containing gases results in additional etch-rate enhancement and CD reduction. Using Gas A enables HAR etching of carbon masks thicker than 4 μm with feature diameters of approximately 100 nm.

[1] M. Pons *et al*., Jpn. J. Appl. Phys. 33 (1994).

[2] J. K. Kim *et al*., J. Vac. Sci. Technol. A 31 (2013).

8:45am **PS1-TuM-4 Passivation-less Etching in Cryogenic Regime**, ***Hiroto Ohtake,*** *Radhe Agarwal, Alvaro Garcia, Tina Dhekial-Phukan,* Applied Materials Inc.*; Han Luo,* Applied Materials Inc., Canada*; Jeong Hwan Kim, Teris Liu,* Applied Materials Inc.

As semiconductor devices continue scaling, feature dimensions have become increasingly narrow. These trends impose requirements on highly anisotropic etching in confined spaces. Conventionally, vertical etch profiles are achieved with passivation gases, such as oxidizing species, fluorocarbons, or oxygen halogenides, to suppress lateral etching of silicon. However, excessive passivation gas addition is causing etch stop or top clogging. Therefore, reducing or eliminating passivation gases is highly desirable.

Cryogenic etching technology might offer a promising path for passivation-less anisotropic etching. At cryogenic substrate temperatures, physisorption of reactive species is enhanced, while spontaneous chemical reactions are suppressed. As a result, a higher concentration of radicals can be delivered effectively to the etch front without excessive lateral attack. But high pressure and high source power impact the sidewall etch even at cryogenic temperature.

In this study, plasma operation at low pressure (0.5 mTorr) and low RF power (50 W) with cryogenic substrate temperature was stabilized in a 300 mm diameter etching chamber through optimization of the coil and top structure. To validate the concept, carbon etching was employed as a model. Under low-pressure and low-power conditions, the ion-to-radical flux ratio increases, enabling directional etching even in a pure oxygen plasma without passivation additives. By lowering the substrate temperature from −40 °C to −90 °C, the ratio of vertical to lateral carbon etch rates improved substantially from 2.8 to 7.2. This indicates that spontaneous reactions are significantly reduced at cryogenic temperatures, allowing the formation of anisotropic profiles with reducing the use of passivation gases. The anisotropy was also found to be sensitive to process pressure. At −90 °C, the vertical-to-lateral etch rate ratio decreased to 3.7 when the pressure was increased to 10 mTorr. Plasma simulations indicate that lower pressures yield a higher ion-to-radical ratio, which directly contributes to enhanced anisotropy.

In conclusion, cryogenic etching under low-pressure and low-power conditions might be a promising approach for next-generation semiconductor etching, enabling highly anisotropic profiles with less passivation chemistries.

9:00am **PS1-TuM-5 The Evolution of CVD-C Mask Profile During High-Aspect-Ratio Hole Etching**, ***Mitsuhiro Omura,*** *Li Wu, Junichi Hashimoto, Chihiro Sakamoto, Chihiro Abe, Yuta Manabe, Hirotaka Tsuda, Toshiyuki Sasaki,* KIOXIA, Japan

The advent of AI has increased the importance of semiconductor devices in modern technology. New generations of 3D flash memory have joined logic devices and DRAM as key components enabling this new era. To meet the increasing bit density demand, flash devices incorporate an ever-increasing number of word lines. These, in turn, complicate the dry etching of memory holes, which form the space for channels and functional thin films. This high-aspect-ratio memory hole etching process requires precise profile control, with challenges such as low mask selectivity, necking, clogging, bowing, striation, hole bottom distortion, etc[1].

Here, we focus on the issue of mask sidewall encroachment known as ‘necking’. The mechanism behind this effect has been simulated by considering polymer deposition from neutrals and ion sputtering using a vertical cross section perspective [2]. In this analysis, we turn our attention to the neck shape revealed in the less understood horizontal cross section. We began by etching a typical SiO/SiN film stack in a fluorocarbon-mixed gas plasma. The test structure also contained a CVD-deposited carbon (CVD-C) hard-mask with a dense hole pattern. We then observed the neck shape on the CVD-C mask in a horizontal cross section for two types of hole patterns in equilateral and isosceles triangle arrangements. Distortion in the isosceles triangles far exceeded that shown in the equilateral triangles despite identical processing conditions. By observing the evolution of mask surface morphology, we find that early local mask erosion at the narrower hole-to-hole spaces in the isosceles triangle arrangement eventually leads to significant variation in the mask height remaining. This variation might lead to neck profile variation such as height, width, and taper angle in a vertical cross section. We speculate that variation in the remaining height of the CVD-C mask could lead to inconsistent neck profiles which manifest in the horizontal cross sections as hole distortion.

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[1] G. S. Oehrlein et al., J. Vac. Sci. Technol. B 42(4), 041501 (2024).

[2] D. Kim et al., Thin Solid Films 515, 4874 (2007).

9:15am **PS1-TuM-6 ASSD Student Award Finalist Talk: Plasma Chemistry and Cryogenic Control of Etching, Passivation, and Surface Modification in Hydrogenated Amorphous Carbon Thin Films**, ***Jhonatan Gil Romero,*** *Kenneth Lathrum, Seonhee Jang,* University of Louisiana

Hydrogenated amorphous carbon (a-C:H) is used as a hard-mask material for semiconductor patterning, which requires a precise balance between

etch rate, passivation, surface roughness, wettability, optical response and oxide/a-C:H selectivity. This work maps how plasma chemistry, cryogenic temperatures, inductively coupled plasma (ICP) and radio frequency (RF) power in the etching process tune these coupled responses.

a-C:H films were deposited on Si (100) by plasma-enhanced chemical vapor deposition (PECVD) using a cyclohexane precursor at room temperature. They were processed in an inductively coupled plasma deep reactive ion etching (ICP-DRIE) system under RF-only or ICP+RF power modes. Four primary fluorine gases (SF_6, CF_4, CHF_3, and C_4F_8) and three secondary gases (O_2, Ar, and N_2) were evaluated across temperatures between -120 and 20 °C and pressures between 3.333 and 9.999 Pa. Film thickness and optical constants were measured by ellipsometry, surface morphology and roughness by atomic force microscopy (AFM), and wettability by a contact-angle goniometer. Tetraethyl orthosilicate (TEOS) oxide was used to determine TEOS/a-C etch selectivity, calculated when both films had positive net etch rates.

Under fixed ICP+RF power, gas chemistry controlled the transition between film removal and passivation. Oxygen (O_2) containing mixtures yielded the highest etch rates, led by CF_4+O_2 at median 2.43 nm/s versus 1.03 nm/s for CF_4. Fluorocarbon-rich chemistries suppressed etching or promoted net film growth: CF_4+CHF_3 yielded the lowest median etch rate at 0.10 nm/s, while C_4F_8 and CF_4+C_4F_8 showed median growth rates of 1.12 and 0.562 nm/s. Cryogenic conditions (-30 to -120 °C) increased median passivation growth relative to 20 °C by 84% for CF_4+C_4F_8. Under ICP+RF, C_4F_8 passivation also increased root mean square (RMS) roughness by 140%, relative to CF_4 at 0.1834 nm. Passivation further increased hydrophobicity, with median change in contact angle (ΔCA) up to +6.94°. In contrast, O_2-assisted etching produced hydrophilic surfaces, with median ΔCA reaching -33.1° for RF-only CF_4+O_2. The highest selectivity value was 2.740 for CF_4+CHF_3 under ICP+RF. ICP+RF power enhanced a-C:H removal in 13/16 paired (RF-only) comparisons; lowering pressure increased ICP+RF etch rate but reduced selectivity by 28%. Optically, passivation increased the final extinction coefficient by 33.5%, and CF_4+O_2 etching by 67.6% relative to CF_4.

These results define the process windows for O_2-assisted a-C:H removal, fluorocarbon passivation, and pressure/power tradeoffs, providing a framework for balancing TEOS/a-C selectivity, surface properties, and optical response in advanced patterning.

9:30am **PS1-TuM-7 Characterizing Spontaneous Etching of Si_3N_4 Sidewalls in Ar/Fluorinated Precursor Plasmas Using a Small-Gap Structure: Role of Precursor and Substrate Temperature**, ***Md Intaqer Arafat,*** University of Maryland College Park*; Pierre Ricou, Behnaz Ghaffari, Jessica DeMott,* Arkema Inc*; Gottlieb S. Oehrlein,* University of Maryland College Park

High-aspect-ratio (HAR) etching of ONO stacks for 3D–NAND is challenging due to profile defects and non-uniform selectivity; fluorinated precursors control etch and passivation, but the underlying plasma–surface mechanisms remain unclear. This study investigates a series of $C_2H_{5-x}F_{1+x}$ precursor candidates in low-pressure plasma, focusing on their deposition behavior and impact on isotropic etching (sidewall) of HAR structures. Key parameters include hydrofluorocarbon (HFC) film deposition rate, film properties, etch rate, and the degree of sidewall etching of silicon nitride (Si_3N_4), all evaluated as functions of precursor composition. To mimic HAR conditions, horizontal trench structures with aspect ratios (AR) up to 30 were used to examine the role of neutral radicals generated from $C_2H_{5-x}F_{1+x}$ plasmas. Nitride trenches were processed by inductively coupled plasma, with spatial analysis via ex situ ellipsometry and real-time ellipsometry on blanket films. Findings reveal systematic variations in the film deposition rate, refractive index, and sidewall etching behavior, with notable changes in spontaneous etching of Si_3N_4 observed for different $C_2H_{5-x}F_{1+x}$ precursors. Increasing fluorine content within the C_2 precursor family enhances deposition rates and reduces refractive index. At the same time, spontaneous etching of Si_3N_4 becomes more pronounced, particularly near trench entrances. For fluorine-rich precursors with H/F < 1, this etching extends further into HAR features, suggesting deeper penetration of reactive species. Experiments were conducted at substrate temperatures of 10 °C and –45 °C to examine sidewall etching. Lowering the substrate temperature from 10 °C to −45 °C significantly reduces Si_3N_4 sidewall etching. This reduction is accompanied by decreases in both HFC deposition rate and refractive index compared to 10 °C, indicating modified film growth characteristics. Additionally, operation at −45 °C limits the penetration of fluorine and carbon species into HAR structures and reduces the formation of fluorinated nitride. These results suggest viable strategies in which the chemical characteristics of the precursor are leveraged to control the balance between protective passivation and chemical removal on vertical surfaces during HAR etching, enabling improved precision in etching processes.

This material is based upon work supported by Arkema, USA.

9:45am **PS1-TuM-8 Effect of Substrate Temperature on Neutral Species Transport in High-Aspect-Ratio Holes During Plasma Etching** , ***Yusuke Imai,*** *Takayoshi Tsutsumi, Sekine Makoto, Kenichi Inoue, Kenji Ishikawa,* Nagoya University, Japan

The continued scaling and three-dimensional integration of semiconductor devices have significantly increased the complexity of plasma etching processes. In advanced device fabrication, such as high-aspect-ratio (HAR) patterning for 3D NAND structures, highly anisotropic and precisely controlled etching is required. Substrate temperature is one of the key parameters governing etching characteristics and is carefully controlled during the etching process. Recently, it has been reported that lowering the substrate temperature enables faster and deeper etching in HAR processing for 3D NAND fabrication compared with conventional processes. [1] Substrate temperature is considered to play an important role not only in surface reactions during etching but also in neutral species transport [2]; however, its influence has not yet been fully understood.

In this study, we investigated the effect of substrate temperature on neutral species transport in HAR holes using a quadrupole mass spectrometer (QMS). A cylindrical orifice mimicking a HAR hole was installed at the inlet of the QMS, enabling aspect-ratio-resolved mass spectrometry (ARMS). In addition, a temperature-controlled assembly was mounted around the orifice to control the orifice temperature during measurements. Neutral species transport through the HAR hole was investigated while varying the orifice temperature. The experiments were performed using a capacitively coupled plasma (CCP) reactor. RF power at 13.56 MHz was applied to the upper electrode, while argon and fluorocarbon gases were introduced into the reactor, where the pressure was maintained at 2 Pa.

As the orifice temperature decreased, the measured Ar intensity increased. This behavior is considered to originate from a reduction in the local gas temperature near the cooled structure, resulting in an increase in neutral gas density and flux into the orifice. These results suggest that low-temperature conditions during plasma etching may enhance the neutral species flux entering HAR features.

[1] R. Suda et al., J. Vac. Sci. Technol. B 43, 062210 (2025).[2] T. Lill et al., J. Vac. Sci. Technol. A 41, 023005 (2023).

Plasma Science and Technology
Room 315 - Session PS2-TuM

High Aspect Ratio and Cryogenic Etching II

Moderators: Dr. Hisataka Hayashi, Daikin Industries, Ltd., **Dr. Pingshan Luan**, TEL Technology Center America

11:00am **PS2-TuM-13 Plasma-Material Interactions in Cryogenic Hydrogen-Fluoride Plasma Etching**, ***Shih-Nan Hsiao,*** *Yusuke Imai, Makoto Sekine,* Nagoya University, Japan*; Ryutaro Suda, Yoshihide Kihara,* Tokyo Electron Miyagi Limited, Japan*; Masaru Hori,* Nagoya University, Japan **INVITED**

For more than half a century, reactive ion etching (RIE) has served as a cornerstone of semiconductor manufacturing, facilitating the high-throughput production of silicon wafers. Its success is fundamentally rooted in the ion-neutral synergy—the collaborative interaction between reactive chemical species and high-energy ions—which has been pivotal to the evolution of microelectronics [1]. However, as device architectures transition toward sub-nanometer scales and complex high-aspect-ratio (HAR) 3D structures, conventional RIE processes encounter significant physical and chemical bottlenecks. Specifically, the degradation of traditional ion-chemical synergy in these advanced regimes often leads to diminished etching efficiency and reduced production yields. To address these limitations, cryogenic plasma etching utilizing hydrogen fluoride (HF)-based chemistries has emerged as a sophisticated alternative [2]. This approach exploits a distinct interplay between incident ions, physisorbed surface layers, and the substrate. Despite its potential, the underlying etching mechanisms of cryogenic HF plasma remain partially obscured [3-5]. In this work, we elucidate the plasma-material interactions during the cryogenic etching of dielectric materials. By employing in-situ diagnostics, including spectroscopic ellipsometry and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), we systematically characterize the influence of bias voltage, substrate temperature, and HF

partial pressure on the etching behavior of SiO_2 and SiN. Based on our findings, we propose a comprehensive mechanistic framework for dielectric etching in cryogenic HF plasmas. Furthermore, we extend this discussion to the synergistic interactions governing plasma-assisted atomic layer processes using HF chemistries for nanofabrication.

References

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[2] Y. Kihara et al., VLSI symposium T3-2 (2023).

[3] S. N. Hsiao et al., Small Methods, 8, 2400090 (2024).

[4] S. N. Hsiao et al., Chem. Eng. J., 522, 167517 (2025)

[5] S. N. Hsiao et al., Small Methods, 10, e01744 (2026).

11:30am **PS2-TuM-15 Investigation of Surface Reactions of SiO_2 and SiN Films Under Cryogenic Etching Process via in-Line/Situ Analysis***, Hiroyuki Fukumizu,* Kioxia Corporation, Japan **INVITED**

This study explores cryogenic etching processes for SiO_2 and SiN films, which are essential for high aspect ratio hole etching in 3D Flash Memory. The blanket SiO_2 films were etched by $H_2/F_2/Ar$ gas mixture plasma over a temperature range from 25 to −200 °C, examining the mechanisms involved in cryogenic conditions via in-situ FT-IR analysis. The etch rate at −100 °C is about 3.2 times higher than at 25 °C due to co-adsorption of H_2O and HF. However, below −100 °C, the solidification of H_2O decreases etching efficiency. In addition to SiO_2, the study addresses the etching behavior of SiN films, where cryogenic etching using HF/PF_3 gas mixtures was investigated. To clarify the factors influencing SiN etch rates, we employed a plasma beam irradiation apparatus equipped with low-temperature in-line XPS analysis to examine surface reactions in detail. Additionally, findings show that the ammonium salt NH_4F forms on the SiN surface under cryogenic conditions, enhancing etch rates. The introduction of PF_3 promotes the formation of NH_4PF_6, which can be decomposed by energetic ion irradiation to further boost etching efficiency. These insights contribute significantly to optimizing cryogenic etching processes.

12:00pm **PS2-TuM-17 Dynamics of Charge Conduction in Water Layers Formed During Cryogenic Etching of HAR SiO_2 Features***, Chenyao Huang, Yeon Geun Yook, Yifan Gui,* University of Michigan*; Steven Shannon,* North Carolina State University*; Mark J. Kushner,* University of Michigan

During the fluorocarbon plasma etching of dielectric materials, differential charging within features arises from the disparity between the arrival onto the wafer of energetic ions with narrow angular spread and low-energy electrons with broad angular distributions. The resulting intra-feature electric fields can deflect particle trajectories, leading to defect formation and reduced etch rates. Cryogenic plasma etching (CPE) is being investigated as an alternative due to its high etch rate and attractive sidewall profile control for high aspect ratio (HAR) features. During cryogenic etching of dielectrics using HF containing gas mixtures, water layers containing solvated HF form along the feature sidewalls in addition to charge deposition from incident charged particle fluxes. These liquid layers may have significant conductivity due to the ionic solute concentrations (e.g., H_3O^+ and F- when solvating HF in water). This conductivity can alter the potential distributions within the feature by conducting externally deposited charges and facilitating self-polarization.

In this work, we computationally investigated charging dynamics including conductive layers for pre-formed SiO_2 features, and during plasma etching of HAR SiO_2 features using Ar/HF gas mixtures in multi-frequency capacitively coupled plasmas. Feature evolution is modeled and using the 3D voxel-based Monte Carlo Feature Profile Model (MCFPM). Fluxes and energy angular distributions (EADs) of incident species are produced by the reactor-scale Hybrid Plasma Equipment Model (HPEM). The MCFPM samples incident fluxes to statistically launch pseudoparticles representing charged and neutral species, which are tracked until they interact with solid materials. We have developed and integrated modules into the MCFPM to account for charge conduction and redistribution within conductive water layers during etching. Our results indicate that these highly conductive, thin layers transform local maxima of electric potential into a broadened profile with lower peak potentials within the features. During SiO_2 etching, the water layer counteracts externally deposited charges through the redistribution of external and intrinsic charges, resulting in a reduced electric potential that correlates inversely with the intrinsic charge densities represented by the dissolved ions.

This work was supported by the Department of Energy Office of Fusion Energy Sciences (DE-SC0024545) and Samsung Electronics.

Atomic Scale Processing Mini-Symposium
Room 316 - Session AP1+EL+MS+PS+TF-TuA

Advanced Atomic Scale Processing through Modeling and Simulation

Moderators: Prof. Dr. David Graves, Princeton University, **Prof. Dr. Satoshi Hamaguchi**, Osaka University, Japan

2:15pm **AP1+EL+MS+PS+TF-TuA-1 Design and performance of AI agents interfacing with atomic layer deposition tools**, ***Angel Yanguas-Gil,*** Argonne National Laboratory **INVITED**

In recent years there has been an increased interest in exploring the integration of generative AI in combination with experimental tools to create multipurpose autonomous systems that can solve complex research problems. This vision relies on AI agents based on LLMs that can autonomously interact with experiments to solve multiple tasks (e.g. "Grow 20 nm of tin oxide" or "selectively grow 10 nm of Cu on Co but not on silicon oxide"). However, in order to be useful, these systems have to be compatible with state of the art manufacturing tools and they have to perform reliably well in a broad enough set of materials synthesis tasks.

In this presentation, I will focus on these two aspects in the context of atomic scale processing. First, I will describe how we have augmented an existing ALD tool so that it can be integrated with generative AI models. Our approach relies on defining a Python interface and API that abstract all the specific details of the hardware from the AI agent, while making it compatible with standard approaches for tool use with LLMs. I will also describe how we have implemented AI agents that can communicate with this ALD tool as well as with existing data, such as data logs and background data on ALD and area selective deposition.

In the second part of the presentation, I will introduce a general methodology to evaluate the performance of AI agents on atomic scale processing tasks. We have applied it to evaluate the performance of state of the art models in instruction, process discovery, and materials discovery challenges in the context of atomic scale processing, primarily ALD and selective growth. In all these cases the output of the challenge is a specific instruction to run one or more processes in an ALD tool. Our results show that state of the art models excel at instruction tasks, but they struggle on process and materials discovery tasks where they involve processes and materials that are underrepresented in the literature, pointing to potential limitations and areas of improvement for for future AI models specialized in materials synthesis and atomic scale processing.

This research is based upon work supported by Laboratory Directed Research and Development (LDRD) funding from Argonne National Laboratory, provided by the Director, Office of Science, of the U.S. Department of Energy under Contract No. DE-AC02-06CH11357.

2:45pm **AP1+EL+MS+PS+TF-TuA-3 A Multiscale Framework for ALD/ALE Process and Precursor Development Using Neural-Network-Potential Atomistic Simulations and COSMO-SAC Thermodynamic Modeling**, ***Yukihiro Shimogaki,*** The University of Tokyo, Japan

Atomic layer deposition (ALD) is indispensable for gate-all-around transistors, high-aspect-ratio DRAM capacitors, and 3D NAND, where conformality and precise thickness control are both required. Atomic layer etching (ALE), the reverse of ALD, matters for low-damage, selective integration, while area-selective deposition (ASD) is attractive but suffers "selectivity loss": unwanted nuclei form on non-growth areas and degrade selectivity over time. We present a multiscale framework coupling COSMO-SAC thermodynamic modeling for precursor down-selection with neural-network-potential (NNP) atomistic simulations for reaction-mechanism analysis; an integrated ALD+ALE scheme designed within it enables highly selective, robust ASD.

An ideal precursor reaches saturation adsorption and is delivered stably; a vapor pressure >=100 Pa below 100 C, preferably ~1000 Pa, broadens the process window. Conventional COSMO-SAC is often inaccurate for metal-containing organometallics. By tuning dispersion-related parameters we obtained good agreement between predicted and measured vapor pressures, enabling efficient down-selection. For Co precursors the framework predicted a high vapor pressure for CpCoCOTFE; the synthesized compound showed ~1060 Pa at 85 C. The same volatility prediction directly guides ALE, where formation and removal of volatile products are central.

Surface-reaction analysis has long been limited by the cost of reaction-path and vibrational searches. NNP-based simulations (e.g., Matlantis) now provide near-DFT accuracy at large scale, making ALD/ALE surface mechanisms tractable. For the Co precursor, NNP indicated that controlling surface hydrogen coverage prior to dosing suppresses carbon incorporation from side reactions; this was confirmed experimentally, showing precursor design (vapor pressure) and reaction design (surface state) must be co-optimized.

For ASD with CCTBA, NNP molecular dynamics showed facile reaction on Cu but low reactivity on SiO_2, and selective growth on Cu was experimentally confirmed. Residual Co nuclei on SiO_2 degrade selectivity; we designed an ALE path in which Co is chlorinated by SO_2Cl_2 and reacts with Hfac to form volatile products whose volatility is supported by COSMO-SAC. The resulting ALD (growth) + ALE (nuclei removal) scheme restores robust selectivity. Finally, sub-monolayer growth per cycle (~0.1 ML) is rationalized by steric hindrance, and NNP-MD with kinetic Monte Carlo captures these collective adsorption dynamics. This COSMO-SAC + NNP framework offers a unified route to co-develop ALD/ALE processes (Atomic Layer Process, ALP) and precursors and to overcome ASD selectivity loss.

3:00pm **AP1+EL+MS+PS+TF-TuA-4 Re-designing ALD Experiments for AI-ready Data: The IGZO Case Study**, ***Eleni Poupaki,*** *Cas Visser, Freek Klabbers, Adrie Mackus, Erwin Kessels,* Eindhoven University of Technology, The Netherlands

The AtomicLimits ALD database [1] is a community-driven repository of ALD processes from the literature. The next step is to populate it with more data suitable for artificial intelligence (AI) and machine learning (ML) models. [2] Recent efforts have used large language models for structured data extraction from publications. [3] However, literature data remains fundamentally limited for data-driven modeling: it is incomplete, often missing key process parameters, biased toward successful experiments, and inconsistently reported. ML can accelerate ALD development by predicting film properties, guiding experiment design, and identifying optimal recipes. Unlocking this potential requires not only more data, but experiments designed to produce data suitable for ML. We address this challenge using ALD of InGaZnO (IGZO) as a case study. IGZO is a quaternary oxide semiconductor that has emerged as an alternative to crystalline silicon channels, used in displays and increasingly explored for DRAM. Amorphous IGZO exhibits high electron mobility, ultralow leakage, and a low thermal budget. [4,5] ALD is well-suited for IGZO, due to its sequential, self-limiting surface reactions, enabling precise control of thickness and composition. [6] For multicomponent materials like IGZO, composition is controlled via the supercycle approach, with subcycles of In_2O_3, Ga_2O_3, and ZnO. Their relative ratios and sequence strongly influence the resulting film properties [7], creating a vast, interdependent parameter space. In this work, we develop a protocol for generating AI-ready ALD experimental data, demonstrated on IGZO. The protocol proceeds stepwise from binary to ternary to quaternary processes, with explicit criteria at each stage: binary processes are characterized for saturation and nucleation, and the ternaries (GaZnO, InZnO, InGaO) are screened to identify supercycle criteria. Using these findings, we explore the supercycle parameter space, focusing on cycle ratio and mixing, with consistent characterization. We discuss preliminary trends in crystallinity and electrical properties across the explored space, contrasting with conventional optimization-driven experimentation. Finally, we outline how the resulting datasets enable ML-guided exploration of the IGZO supercycle space, paving the way toward AI-assisted ALD process optimization and a richer experimental foundation for community resources such as AtomicLimits.

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[7] Oh et al., Ceram. Int. 2025.

3:15pm **AP1+EL+MS+PS+TF-TuA-5 Atomistic Modeling of Atomic Layer Etching and Deposition: HF/SiO2 ALE and TMA/Al2O3 ALD**, ***Fedor Goumans,*** Software for Chemistry & Materials, Netherlands

Atomic layer processes rely on surface reactions that are sequential, self-limiting, and highly sensitive to local chemical structure. Understanding these reactions at the atomistic level is essential for improving atomic layer deposition, atomic layer etching, and area-selective processing, but many key reaction steps occur at buried, transient, or chemically heterogeneous interfaces that are difficult to characterize directly. In this presentation, we

discuss how reactive atomistic simulations can support the interpretation and design of atomic layer processes, with examples from HF-based SiO_2 etching and TMA/Al_2O_3 deposition.

Reactive force fields and machine-learned interatomic potentials provide complementary routes for exploring surface chemistry over length and time scales beyond conventional first-principles molecular dynamics. Using these approaches, one can follow bond breaking and formation, surface hydroxylation, ligand exchange, fluorination, densification, and volatile product formation under process-relevant conditions. For SiO_2 etching, simulations can help identify how HF exposure modifies hydroxylated and strained oxide surfaces, how local bonding environments influence fluorination and material removal, and which surface motifs may control etch initiation. For Al_2O_3 deposition, simulations of TMA reactions with hydroxylated alumina surfaces can reveal the molecular origin of saturation behavior, steric effects, methane elimination, and the evolution of reactive surface sites across ALD cycles.

The broader goal is to connect the relevant calculated parameters such as sticking rate, thermal accommodation coefficients, and atomistic reaction mechanisms with experimentally observable trends in growth, etch rate, selectivity, and film quality. We highlight practical considerations for building reliable reactive models, including training data selection, validation against quantum chemical calculations, and the use of accelerated workflows. These examples illustrate how atomistic modeling can complement experiments by exposing reaction pathways, identifying limiting surface structures, and guiding the development of more predictive models for ALD and ALE process optimization.

4:00pm **AP1+EL+MS+PS+TF-TuA-8 Characterizing Directionality, Energy and Spatial Uniformity of Plasma Generated Neutral Beams for Low-Damage Material Processing**, ***Gonçalo A. Cardoso***, *Mark J. Kushner,* University of Michigan, Ann Arbor

Ion bombardment onto biased wafers during plasma etching can result in charge buildup within features that can deflect incoming ion trajectories, resulting in feature defects such as bowing or notching, or lead to device damage. UV photons emitted from the plasma might also cause surface defects such as dangling bonds [1]. These issues are exacerbated as device dimensions are scaled down, due to larger electric fields for a given charging potential and increased surface-to-volume ratio. This is particularly the case for the fabrication of 2-dimensional materials consisting of nearly monolayer thickness. Energetic neutral beams have been proposed as an alternative, low-damage and charge-free technique for etching and deposition, and particularly so for 2D materials. Such beams can be produced through ion acceleration and subsequent neutralization, either through charge-exchange collisions (volume neutralization) or by reflection from surfaces (surface neutralization) [2, 3]. The primary technical challenges for neutral beam sources involve optimization of directionality, energy and spatial uniformity of the energetic neutral fluxes striking the substrate.

In this paper, we discuss the results of a computational investigation of a neutral beam source consisting of an inductively coupled plasma separated from the wafer by a radio frequency (RF) biased grid powered at 10 MHz. Typical conditions for this source are pressures of tens of mTorr, gas mixtures containing Ar, O_2 and Cl_2 and biases on the grid of hundreds of volts. This source has been simulated using the Hybrid Plasma Equipment Model (HPEM).The Plasma Chemistry Monte Carlo Module (PCMCM) in the HPEM tracks the motion of ions (and neutrals) as they are accelerated by electric fields, collide with background gas particles and neutralize by reflecting from the grid. The PCMCM records the resulting neutral energy and angular distributions (NEADs) at the wafer. This work investigates the characteristics of these NEADs and how they are influenced by grid surface roughness (non-specular scattering), inelastic scattering from the grid, gas-phase charge-exchange reactions and pressure gradients across the grid.

This work was supported by the US Department of Energy, Office of Science, Fusion Energy Sciences (FES) and Basic Energy Sciences (BES) as part of the Extreme Lithography & Materials Innovation Center (ELMIC), a Microelectronics Science Research Center (MSRC), through the Plasma-enabled 2D Materials project (DEAC02-09CH11466); and by FES (SC-00274510).

4:15pm **AP1+EL+MS+PS+TF-TuA-9 Plasma Etching of Diamond: Molecular Dynamics Studies and Comparison to Experiments**, ***Louis Hoffenberg***, Princeton University; *Justin Boles,* University of Houston; *Jack Draney,* Princeton University; *Igor Kaganovich,* Princeton Plasma Physics Laboratory; *Vincent Donnelly,* University of Houston; *David Graves,* Princeton University

Nitrogen-vacancy (NV) centers in diamond are promising for multiple applications in quantum information processing and sensing, including in the fields of high-power/high-frequency electronics, quantum computing, and quantum sensing.[1] Diamond NV centers near surfaces can locally detect and measure physical quantities such as magnetic and electric fields with unprecedented sensitivity. However, these devices are currently limited by near-surface (<10 nm) defects that compromise charge stability and spin coherence.[2] Plasma etching of diamond has been widely employed to process and pattern diamond, but there is limited understanding of the mechanisms of plasma etching. In this work, classical molecular dynamics (MD) simulations are used to simulate O_2/Ar plasma etching of diamond, with comparisons to experiment. We explore both conventional reactive ion etching (RIE) and atomic layer etching (ALE) conditions. The experimentally validated MD simulations are used to identify fundamental etch mechanisms. Based on the MD simulations, we propose a parameterized reduced order model of diamond plasma etching that relates etch yield to ion flux, ion energy, and ion composition, as well as neutral O• radical to ion flux ratio.

References:

[1] Janitz et al. "Diamond surface engineering for molecular sensing with nitrogen-vacancy centers." J. Mat. Chem. C 10.37 (2022): 13533-13569.

[2] Sangtawesin et al. "Origins of diamond surface noise probed by correlating single-spin measurements with surface spectroscopy." Phys. Rev. X 9.3 (2019): 031052.

4:30pm **AP1+EL+MS+PS+TF-TuA-10 Predictive Screening of Sustainable Etchants via DFT Thermodynamics, Machine-Learned Vapour Pressures, and Infrared Spectra**, ***Christopher Pashartis***, *Philippe Bezard, Konstantina Philippidou, Geoffrey Pourtois,* IMEC Belgium; *Hideharu Shimizu, Yoshiki Nakoyama,* NSC, Belgium

Fluorinated etchants are heavily used in semiconductor processes for their high etch rates and material selectivity. Typical etchants such as CF_4 and c-C_4F_8 have global-warming potentials in the range of 7,400-13,900 over 100 years and atmospheric lifetimes exceeding hundreds of years, raising concern about the by-products of such processes. While abatement downstream is standard practice, it runs continuously and is never fully effective. Therefore, a more impactful path to reducing the climate footprint of fabrication is to identify replacement etchants that are intrinsically more sustainable while remaining competitive in performance.

Experimentally screening new etchants includes sourcing gases, fine-tuning reactor conditions, characterising effluent; it can be very slow and time consuming. We present a predictive screening workflow built on Density Functional Theory (DFT) rather than specialised plasma simulations: DFT-derived Gibbs free energies are used to solve the closed-system equilibrium for each etchant-substrate pair, giving both the predicted etch capability and the by-product distribution as a function of temperature, pressure, and stoichiometry. To translate predicted species into global warming potential, we couple this with two further ingredients: a graph neural network trained on open-source vapourpressure data to determine which by-products are most likely to be gaseous, and DFT-computed infrared spectra to estimate their radiative efficiency. We will present results aggregated across more than ten candidate etchants and three substrates (Si, SiO_2, Si_3N_4), demonstrating how the combined thermodynamics-volatility-impact screen can rank chemistries by their projected greenhousegas burden.

Atomic Scale Processing Mini-Symposium
Room 316 - Session AP2+EL+PS+TF-TuA

Advancing X-Ray Photoelectron Spectroscopy to enable Atomic Scale Processing

Moderators: Dr. Robert Bruce, IBM Research, T. J. Watson Research Center, **Dr. Eric Joseph**, IBM T.J. Watson Research Center

4:45pm **AP2+EL+PS+TF-TuA-11 Understanding the Chemical Reaction Mechanisms of Oxide, Nitride and Metal ALD: Insights from Operando X-Ray Photoelectron Spectroscopy***, **Joachim Schnadt,*** Lund University, Sweden **INVITED**

Over the past decades, atomic layer deposition (ALD) has emerged as a leading thin-film deposition technique, particularly within semiconductor technology. The reason is that ALD provides excellent thickness control down to the atomic scale, as a result of the use of sequences of self-limiting surface reactions. However, continued device miniaturization imposes more and more stringent demands on process control. Interfaces need to be engineered with extremely high precision, and lateral dimension control grows in importance. This implies that the exact surface chemistry underlying ALD – and this chemistry is both process and surface specific – needs to be understood in true detail. Experimental *operando* techniques provide an avenue towards the monitoring and characterization of the ALD surface chemistry in a time-resolved manner; these techniques can be applied during the deposition and at measurement rates that allow to resolve the time evolution of surface species and surface structure. Ambient pressure X-ray photoelectron spectroscopy (APXPS) is such an *operando* tool. In contrast to conventional X-ray photoelectron spectroscopy, it is carried out at pressures up to the millibar range, i.e. exactly the operational pressure regime of ALD. Time-resolved APXPS provides precise insight into the occurrence and time evolution of surface and subsurface species and their chemical state and provides information that can be used to formulate chemical reaction mechanisms in the different stages of deposition. In my presentation, I will discuss the capabilities of *operando* APXPS for research into ALD, using examples of research into the ALD of metal oxides and nitrides from transition metal amido or metal tetraisopropoxide complexes and water or ammonia. I will also highlight the first APXPS study into Pt metal ALD. Due attention will be given to instrumental aspects, foreseen future developments and a discussion of what can and what cannot be learned from APXPS.

5:15pm **AP2+EL+PS+TF-TuA-13 In vacuo XPS for Studying ALD Processes***, Matthias Minjauw, Tippi Verhelle, Jin Li, Jolien Dendooven,* ***Christophe Detavernier,*** Ghent University, Belgium **INVITED**

X-ray photoelectron spectroscopy (XPS) is a well-established technique for probing near-surface composition and chemistry. When employed as an in vacuo technique—i.e., without intermittent air exposure—it becomes a powerful tool for investigating surface chemistry during atomic layer deposition (ALD) processes. Three case studies will be presented: (1) the well-known TMA-based chemistry for ALD of alumina, (2) metal ALD with a focus on Pt growth (as reported by Li et al., J. Phys. Chem. C 2024, doi:10.1021/acs.jpcc.3c07568), and (3) ALD on lithium foil substrates (as reported by Verhelle et al., J. Mater. Chem. A 2026, doi:10.1039/D6TA00751A).

Plasma Science and Technology
Room 315 - Session PS1-TuA

Atmospheric and Liquid Plasmas

Moderators: Prof. Michael Gordon, University of California at Santa Barbara, **Prof. Dr. Mohan Sankaran**, University of Illinois at Urbana-Champaign

2:15pm **PS1-TuA-1 Synthesis of Organic and Inorganic Spatially Differentiated Coatings by Cold Atmospheric Plasma***, Marie Brabant, Celine Dergham,* ***Francois Reniers,*** Université libre de Bruxelles, Belgium

In earlier studies, we have shown that one could immobilize filaments in an atmospheric pressure dielectric barrier discharge (DBD). This setup allows to deposit coatings presenting spatially differentiated chemistries that lead to tunable surface properties, such as, for instance, coatings presenting simultaneously hydrophobic and hydrophilic areas [1].

In this talk will methyl metacrylate (MMA) and hexamethyl disiloxane (HMDSO) are used as precursor to deposit localized PMMA and SiOx coatings, respectively. The chemistry, roughness and thickness of the coatings obtained under the filaments and between the filaments is studied by XPS, FTIR, Raman, profilometry and SIMS. The effect of the nature and flow rate of the plasma gas and the power injection mode on the resulting coating is presented and discussed.

For PMMA deposit, a drastic influence of the plasma gas nature is evidenced: transparent, sticky coatings are obtained with Ar, with excellent preservation of the ester function, whereas well polymerized yellow – orange coatings are obtained with N_2. In these last coatings, nitrogen is incorporated.

SiOx coatings deposited under the filaments are much thicker than those deposited between the filaments, with a chemistry depending on the ratio HMDSO/O_2. Adhesion of such coatings on glass substrates is superior.

This study highlights the versatility of plasma polymerization for microscale patterning and surface functionalization. Localized AP-PACVD enables micron–scale deposition and controlled chemical tuning without vacuum infrastructure [2], making it a promising technique for advanced surface engineering. The ability to modulate plasma chemistry through gas composition opens new perspectives for designing functional polymer and inorganic coatings with spatially selective properties.

Acknowledgements :

This work was funded by the FNRS (Belgium) (StreamCoat project).

References :

[1] A. Demaude et al, *Advanced Science* Adv. Sci. **9**, 2200237 (2022)

[2] A. Demaude et al, *Plasma Chemistry and Plasma Processing*. **43**(6), 1731–48 (2023)

2:30pm **PS1-TuA-2 Atmospheric Plasma-Induced Surface Modification of Carbonaceous Thin Films***,* ***Thea Ferley,*** School of Physics, Clinical and Optometric Sciences, TU Dublin, Ireland*; Vladimir Milosavljevic,* School of Physics, Clinical and Optometric Sciences, TU Dublin, Ireland & Faculty of Physics, University of Belgrade, Serbia, Ireland

This study investigated the influence of operating conditions in a pulse resonance atmospheric pin plasma system on the surface modification of carbonaceous thin films representative of contaminant layers found in fusion environments. The work focused on the effects of applied voltage, pulse frequency, duty cycle, and working gas environment on the wettability, thickness, roughness, and void fraction of the films. Samples were exposed to controlled plasma conditions using ambient air, He and Ar as working gases and were characterised using contact angle measurements and ellipsometric analysis.The results demonstrated that plasma-induced surface modification strongly depends on both the electrical operating parameters and the gas environment. Among the investigated parameters, applied voltage produced the clearest effect on wettability, where increasing voltage resulted in larger reductions in contact angle, indicating an increase in surface energy. In contrast, duty cycle showed limited and inconsistent influence on the measured surface properties, while pulse frequency mainly affected structural properties such as roughness and void fraction through repeated plasma–surface interactions.Statistical analysis confirmed a highly significant effect of plasma exposure on contact angle ($F=115.036$, $P<0.001$), with gas type and the interaction between exposure and gas also being statistically significant ($F=3.476$, $P=0.045$). Ambient air produced a smaller reduction in contact angle (-10.32°), while Ar and He produced larger reductions of -19.30° and -17.27°, respectively, demonstrating stronger surface modification under inert gas conditions. Thickness measurements showed a slight increase in ambient air (+1.4 nm) and reductions for He (-4.3 nm) and Ar (-9.5 nm). Surface roughness decreased for all gases, with the largest separation of 17.5 nm observed between Ar and He conditions. Void fraction measurements further highlighted the differences between gas environments, with He producing the largest decrease (-6.8%) compared to Ar (-1.5%).The observed differences indicate that ambient air promotes chemically driven surface interactions through reactive O_2 and N_2 based species, whereas Ar and He primarily contribute through physical plasma mechanisms such as ion bombardment and momentum transfer. Overall, the results demonstrate that the pulse resonance atmospheric plasma pin system can produce controlled and measurable changes in surface properties. These findings support the potential of this system as a flexible atmospheric-pressure plasma technology for surface cleaning and conditioning applications in fusion-relevant environments.

2:45pm **PS1-TuA-3 Influence of Pulsed Power Parameters on the Properties of Submerged Argon Plasmas**, ***Michael Johnson***, US Naval Research Laboratory; *Mackenzie Meyer,* National Research Council; *David Boris, Scott Walton,* US Naval Research Laboratory

Atmospheric pressure plasmas create a unique chemical and electrical environment that is well-suited for liquid treatment applications, such as decontamination and remediation. These plasmas can operate in a nonthermal regime when driven by pulsed power of sufficiently short duration. However, the influence of pulse power parameters on plasma behavior in gas-liquid systems is challenging to understand given the strong spatial and temporal variations that can arise. In this work, we discuss the use of short duration (< 1 ms), high voltage (> 10 kV) pulses driven at frequencies between 100 Hz and 10 kHz to produce an argon plasma submerged in flowing water. Varying the pulse width, impacts the induced plasma chemistry since excitation of the argon feed is dominant early, while hydrogen emission increases over time as water vapor dissociates. Spatial profiles show uniform hydrogen emission, while argon emission is stronger near the negative electrode. Stark broadening analysis reveals that the lifetime of electrons after the pulse is strongly influenced by the pulse width, as electron density can persist for several microseconds post-pulse. Varying the repetition frequency reveals that higher frequencies decrease the breakdown voltage because residual reactive species facilitate easier plasma reignition. Discharge current rises with frequency until limited by power supply resistances, with energy delivered per pulse peaking near 500 Hz for the present system. Higher water flow rates increase the frequency required for consistent ignition, suggesting liquid dynamics influence the quenching of residual species. Electron density peaks between 800 Hz and 3 kHz, beyond which it decreases as molecular gases like H_2 and O_2 alter formation conditions. Optical emission spectroscopy also indicates greater electrode erosion at higher frequencies. The implications of these results are discussed in terms of water treatment applications. This work supported by the Naval Research Laboratory base program.

This work was partially supported by the U.S. Naval Research Laboratory Base Program.

3:00pm **PS1-TuA-4 Non-Invasive Short-Wave Infrared Imaging for High-Resolution Thermal Mapping of Graphene-Growth Atmospheric Plasmas**, ***Logan Holler***, *Mia Sawkik, Brenna Miller, Parker Hayes, Drhuval Patel, David Ruzic,* University of Illinois at Urbana-Champaign; *Michael Stowell,* Lyten; *Dren Qerimi,* University of Illinois at Urbana-Champaign

Atmospheric-pressure plasma synthesis of graphene has emerged as a promising route for scalable carbon nanomaterial production. While it is well established that graphene formation is highly temperature-dependent, the distinction between the formation of graphene flakes versus nodules remains insufficiently characterized within plasmas. A key step forward centers on better mapping the temperatures across our different plasma mixtures. However, conventional diagnostic tools often fall short: most diagnostic systems only provide one-dimensional snapshots, and physical probes degrade rapidly when exposed to atmospheric plasmas.

The development of Short-Wave Infrared (SWIR) imaging has allowed time-averaged spatially-resolved temperature profiles to be developed for these systems. SWIR imaging leverages thermal radiation emissions to determine temperature by integrating spectral radiance over the detectable range of our camera. Provided that the camera's solid angle to the plasma remains fixed, changes in the integrated spectral intensity can be used to derive temperature ratios emitted by heated graphite. By calibrating the system using a known temperature, SWIR snapshots can correlate image intensity with absolute temperature. Within the capacity of pure plasma imaging, this allows for dynamic temperature mapping throughout the plasma, which is limited only to the refresh rate of the SWIR Camera.

Graphite was chosen for these experiments due to its capacity to survive exposure in these plasmas, while also having a near-blackbody emissivity. Having developed a calibration curve for each rod, it is then possible to map the full temperature profile of the plasma by incrementally raising the rod through the plasma. A snapshot is taken at each point once the rod is in thermal equilibrium with the plasma. Stitching these images together forms a complete spatial map to better show thermal gradients across the plasma. A future development of this system aims for a plug-and-play plasma temperature profiling of unobstructed, in-situ plasma temperatures. This would allow for graphene growth modules to be better correlated to the different temperature profiles within the atmospheric plasma. This diagnostic provides a pathway toward in-situ, non-invasive plasma thermal profiling to better understand graphene growth morphology.

3:15pm **PS1-TuA-5 Spatially Resolved Spectroscopic Imaging of Plasma in Contact with a Liquid Interface**, ***Robert Pierrard***, University of Illinois at Urbana-Champaign; *Shurik Yatom,* Princeton Plasma Physics Laboratory; *Davide Curreli, Sean M. Peyres, Mohan Sankaran,* University of Illinois at Urbana-Champaign

Atmospheric-pressure plasmas (APPs) are highly effective at driving complex chemical reaction pathways. When coupled with a liquid interface, these plasmas deliver reactive species directly to a solution, enhancing chemical kinetics and enabling new reactions. Plasma-liquid systems have found applications across diverse fields, including nanomaterial synthesis, wound healing, environmental remediation, and sustainable agriculture via nitrogen fixation. Here we discuss the application of optical spectroscopy to provide deeper insight into plasma-based nitrogen fixation.

Our investigation focuses on a low-temperature APP formed in contact with liquid water, where gas-phase electrons are injected into solution to generate solvated electrons, the strongest known chemical reducing species, capable of reducing molecular nitrogen (N_2) to ammonia (NH_3). However, competing radicals are simultaneously created, yielding concurrent reduction and oxidation pathways and a wide range of chemical products.

To unravel this complex system, our work was divided into two phases. In the first, we constructed a simplified experiment without a liquid interface, introducing controlled concentrations of water vapor into a nitrogen plasma to isolate its effect on reaction pathways. Using optical emission spectroscopy (OES) with an argon actinometer and laser-induced fluorescence (LIF), we measured steady-state densities of intermediate species to validate a global chemical kinetic reaction network. We found that increasing water vapor dramatically suppresses atomic nitrogen density by quenching two key excited states of N_2. Moreover, the oxidative pathway toward NO and NO_2 was strongly favored over the reductive pathway toward NH_3 due to kinetic bottlenecks, explaining the enhanced oxidative species production commonly observed in the literature.

These findings informed our second phase, where we transitioned to the targeted plasma-liquid system. We extended our OES measurements to spatially resolve the plasma, enabling mapping of gas temperatures, electron temperatures, and key radical species. Measurements revealed striking variation in temperature and species profiles along the discharge, localized either near the metal electrode where the plasma emanates or near the liquid water surface. These results indicate that plasma properties are not uniform, and resolving the inhomogeneities is critical to understanding plasma-liquid processes.

Plasma Science and Technology
Room 315 - Session PS2+EUV-TuA
Plasma Processes for Feature Scaling

Moderators: Prof. Dr. Erwin Kessels, Eindhoven University of Technology, the Netherlands, **Dr. Pingshan Luan**, TEL Technology Center America

4:00pm **PS2+EUV-TuA-8 Advanced Logic Pitch Scaling in the High NA EUV Era**, *Arame Thiam,* ***Yannick Feurprier***, TEL Europe, Belgium **INVITED**

High NA (0.55 NA) EUV lithography enables the single exposure of critical layers for future generations of logic (14A and below) and DRAM (1d and below) devices. Its implementation, however, introduces challenges in meeting both technology and high-volume manufacturing requirements. We will review and discuss the challenges of certain processes for logic use cases (Place and Route and Tip-to-Tip CD control, random logic via) and for the memory cases (contact holes and pillar). Co-optimization of the lithography process (resist, source, mask and development method) together with the etch pattern transfer process and the defectivity assessment enables the demonstration of a failure free process window for Place and Route (PnR) logic clips at tight pitches (down to 18 nm pitch) and for 28 nm pitch pillars for the memory use case.

The stringent tip-to-tip (T2T) CD control required by the technology in the PnR also creates opportunities for directional etch techniques. Gas Cluster Beam (GCB) technology can complement high NA EUV lithography by providing precise T2T CD control, reducing LER and helping to mitigate defectivity. Finally, further validation of the high NA EUV and etch patterning transfer is presented through electrical test.

Keywords: High NA EUV, Etch patterning, PnR, DRAM, Defectivity, Directional etch, Electrical test

4:30pm **PS2+EUV-TuA-10 Dry Resist Patterning Solutions for High-NA EUV Lithography**, ***Ali Haider,*** Lam Research Corp.*; Zhengtao Chen, Shruti Jambaldinni,* Lam Research Belgium BV, Belgium*; Anuja De Silva,* Lam Research*; Rich Wise,* Lam Research Corp. **INVITED**

High-NA EUV lithography patterning at increasingly tight pitches introduces significant challenges, including elevated defectivity, reduced depth of focus (DOF), shrinking process windows, and the need for dose reduction without degrading pattern quality. These challenges become increasingly severe near ultimate resolution at P18 L/S and limit the extendibility of conventional wet solution processed resists.

In this work, we demonstrate the performance of Lam's Aether® dry resist technology for dense P18 line/space patterning using high-NA EUV lithography. We address key challenges such as defectivity, DOF, and line wiggling through co-optimization of dry resist deposition, underlayer, post exposure bake (PEB), and dry development. We introduce next-generation dry resists based on novel precursor chemistries with enhanced EUV sensitivity, enabling reduced dose to size without compromising roughness, while expanding the defect-free process window through co-optimization with dry development. We further introduce new dry development schemes that increase the effective resist budget after development, resulting in improved defect performance and lower roughness.

To address the high NA EUV challenge of limited DOF and profile control, we have introduced 3D engineered dry resist films using multi layer deposition with controlled composition and tunable EUV sensitivity in the vertical direction.1,2 We show that 3D engineered resist provides lower dose to size, improved profile control, reduced line wiggling, and enhanced DOF.

Overall, we show that Aether dry resist and development solutions address key challenges in high-NA EUV P18 L/S through innovations in dry resist and development strategies with co optimization of process parameters.

[1]Gulati, Saumya, et al. "Evaluating three dimensionally engineered dry resist film performance for 0.33 NA and High-NA EUV patterning." Advances in Patterning Materials and Processes XLIII. Vol. 13983. SPIE, 2026.

[2]A. Haider et al., "Advances of dry resist towards next-generation lines-spaces patterning in high-NA EUV lithography," Proc. SPIE 13686, 1368608 (2025)

5:00pm **PS2+EUV-TuA-12 Study of Electron-Induced Etching Mechanisms for Chromium and Ruthenium** , ***Michael Hinshelwood****, Gottlieb S. Oehrlein,* University of Maryland, College Park*; Hubertus Marbach, Michael Remmel, Gerson Mette, Michael Budach, Daniel Rhinow, Klaus Edinger, Maik Szafarska,* Carl Zeiss SMT GmbH, Germany

Chromium (Cr) and ruthenium (Ru) are materials critical for semiconductor manufacturing, particularly as part of DUV and EUV photomasks, respectively. Both can be effectively etched with plasmas containing both oxygen and a halogen. Cr can be etched through the formation of CrO_2Cl_2 or CrO_2F_2, while Ru is etched through the formation of RuO_4 or volatile RuO_xCl_y. To limit surface damage caused by ion bombardment during plasma etching, there is significant interest in isolating ions from the reaction system.

Y. Li et al. demonstrated rapid etching of Ru by combining a low-energy electron beam (EB) with a remote plasma (RP)-created flux of O_2/Cl_2-derived neutrals [1]. The combination of EB and RP resulted in a synergistic etch effect, while RP or EB alone caused either low-rate etching or growth. Here, we aim to describe the mechanism that leads to this synergistic effect and expand it to the etching of Cr, and also investigate how etching selectivity between the two materials may be achieved.

Using in-situ ellipsometry, we model the real-time etching and modification of the metal surfaces. This modelling is complemented by direct chemical characterization of the surface with X-ray photoelectron spectroscopy (XPS). In the case of Ru, we have found that the EB increases the uptake of Cl on the Ru surface, which in turn activates the Ru toward oxidation to volatile compounds. The growth rate and composition of this chlorinated layer formed by the EB are investigated via XPS measurements with increasing EB/Cl_2 exposure time. In the case of Cr, we find a stronger synergistic effect with F/O etch chemistry as opposed to Cl/O. The etch rate with RP alone is highly dependent on the oxygen percentage in the feed gas as well as the oxidation state of the Cr. With a fluorine-rich feed gas, the surface quickly forms a CrF_x passivation layer, preventing further etching. The EB can break through this passivation and continue the Cr etch process by forming vacancies that allow O radicals to diffuse into the surface and form volatile Cr–O–F compounds. By combining ellipsometric observations with chemical quantification from XPS, we obtained mechanistic insight for the development of low-damage etch processes for Cr and Ru, and insights on paths to high Cr hard mask and Ru capping layer selectivity.

[1] Y. Li *et al.*, "Investigation of ruthenium etching induced by electron beam irradiation and O_2/Cl_2 remote plasma-based neutral fluxes: Mechanistic insights and etching model," *J. Vac. Sci. Technol. A*, vol. 43, no. 2, p. 023005, Feb. 2025, doi: 10.1116/6.0004219.

5:15pm **PS2+EUV-TuA-13 3 Layers Dielectric Patterning in Grid Module for OSC 3DDRAM Application**, ***Yuchao Jiang****, Jeongsoo Kim, Alejandro Fernandez Rodriguez, Hemant Kumar Raut, Nouredine Rassoul, Eren Canga, Robert Carpenter, Attilio Belmonte, Katia Devriendt,* IMEC, Belgium

3 layers dielectric patterning in Grid module for OSC 3DDRAM application

Yuchao. Jiang[1], Jeongsoo Kim[1], Alejandro Fernandez Rodriguez[1], Hemant Kumar Raut[1], Nouredine Rassoul[1], Eren Canga[1], Robert Carpenter[1], Attilio Belmonte[1] and Katia Devriendt[1]

[1]Imec, Kapeldreef 75, B-3001 Heverlee, Belgium

DRAM applications have reached a limiting point with 2D design (planar device) because of the process challenges for ~12nm nodes and scaling difficulty of density. Since 2011, monolithic 3DDRAM has been explored with different integration approaches (HBL, VBL, capacitorless etc), and recently it has experienced renewed interest by major players in memory market.

In this presentation, a dry–etch process for grid patterning in MOLD–based monolithic 3D DRAM was reported, the process enables robust isolation of active regions in vertical–bit–line architectures. The method addresses morphology degradation and sidewall profile asymmetry arising from pattern–loading effects and hard–mask facet evolution in multi–layer SiN/SiO_2 ONO stacks. By optimizing passivation balance, ion directionality, and process conditions, the approach achieves stable dielectric grid formation with controlled critical dimensions and near–vertical sidewalls. The demonstrated process provides reproducible grid patterning suitable for high–aspect–ratio 3D DRAM integrationIn monolithic 3DDRAM with MOLD–based vertical–bit–line (VBL) architecture, the Grid module (SINGRID) is the key dielectric–etch step that isolates active areas by etching through a multi–layer SiN/SiO_2 ONO structure (~355 nm). The grid lines have tight CD requirements and require near–vertical profiles (>87°) to ensure VBL alignment and prevent capacitor/gate shorts.

The grid exhibits major–axis vs. minor–axis HM (hard–mask) facet differences, caused by imbalanced ion/radical flux between dense vs. semi–dense regions. Consequences include:

1. Unequal CD narrowing
1. Facet tilt differences (leading to asymmetric top rounding)
2. Risk of local bowing when ARDE.

For morphology improvements, a leaner DARC open step is applied (with reduced CHF3 and increased CF4/O2 flow) to reduce the morphological deformation.

For sidewall profile improvements, the process mitigates these effects through controlled anisotropic dry etching, combining directional ion bombardment with carefully tuned sidewall passivation.

5:30pm **PS2+EUV-TuA-14 Role of Interfacial Force Balance in Gap Filling of TEOS-based Flowable CVD: Insights from Molecular Dynamics**, ***Hu Li,*** Tokyo Electron America Inc.*,; Takeo Nakano, Nobuo Matsuki, Masaaki Matsukuma,* Tokyo Electron Ltd., Japan*; Raymond Joe, Anthony Dip,* Tokyo Electron America Inc.,

Achieving void-free gap filling in high-aspect-ratio structures is one of the key challenges in advanced semiconductor processing. Flowable chemical vapor deposition (CVD) has been widely studied as a promising approach, and its behavior is often interpreted in terms of wettability or viscosity. However, these conventional descriptors do not always explain the differences observed in gap-fill performance across various precursor chemistries and geometries.

In this work, we focus on the pre-cure stage of flowable CVD and investigate the transport-driven filling behavior using classical molecular dynamics simulations. By intentionally excluding chemical reactions, we isolate the role of intermolecular interactions and interfacial forces in confined geometries. The simulation system consists of siloxane-based liquids on SiO_2 substrates, with trench structures of varying aspect ratios.

To better understand the filling mechanism, we introduce a force-based analysis by decomposing the total force acting on liquid molecules into liquid-substrate and liquid-liquid contributions. This approach reveals a clear spatial variation in the driving forces within the trench. Near the sidewall, strong downward forces promote infiltration, while in the center

region, the driving force is significantly reduced, which leads to incomplete filling and void formation.

We further show that increasing the aspect ratio enhances this imbalance in force distribution, making uniform filling more difficult. In addition, surface modification, such as Si-rich surface, can reduce the interfacial interaction strength and improve liquid mobility.

These results suggest that gap-fill behavior cannot be fully described by wettability alone, and that a force-based perspective provides more direct insight into the underlying mechanism. This study offers a more detailed understanding of pre-cure transport processes and may help guide the design of future flowable CVD processes.

Atomic Scale Processing Mini-Symposium
Room 316 - Session AP+EL+PS+TF-WeM

Thermal and Plasma Enhanced Atomic Layer Etching

Moderators: Dr. Eric A. Joseph, IBM Research Division, T.J. Watson Research Center, **Prof. Dr. Erwin Kessels**, Eindhoven University of Technology, the Netherlands

8:00am **AP+EL+PS+TF-WeM-1 Cyclic dielectric etching challenges for next-generation FDSOI logic and quantum devices**, ***François Boulard,*** CEA-LETI, France*; Ramy Ayoub,* CEA-LETI, France, Lebanon*; Emmanuel Petitprez, Stéphane Pocas, Nicolas Gauthier, Benoit Martin, Pierre Brianceau, Antoine Ronco,* CEA-LETI, France*; Bernard Pelissier,* LTM-CNRS, France*; Nicolas Posseme,* CEA-LETI, France **INVITED**

As logic devices dimensions scale down[(1)] and quantum gates advance in scalability and environment resilience[(2)], the demand for gentle, selective, and highly controlled fabrication processes has become critical. Atomic-scale processing—particularly cyclic approaches like Atomic Layer Etching (ALE) and quasi-ALE—has emerged as a potential solution. By leveraging fluorocarbon-based chemistries in sequential deposition/removal cycles, these methods have already demonstrated superior performances in terms of SiO_2 to Si_3N_4 selectivity, such as in Self-Aligned Contact (SAC) etching[(3)]. While the fundamental mechanisms of these cyclic processes are increasingly well understood[(4)], their industrial applicability—especially for advanced integration schemes—still faces challenges in versatility, robustness, and throughput. In this presentation, we will highlight recent advances in adapting cyclic etching strategies to selectively etch dielectric materials (SiO_2, SiON, Si_3N_4) for two cutting-edge applications: Contact multipatterning in next-generation FDSOI CMOS logic devices and intertwined gate patterning for cryogenic FDSOI quantum chips. This study explore the critical role of process parameters, including fluorocarbon precursor selection, multi-step cyclic strategies, substrate temperature and plasma power modulation, and their collective influence on etch per cycle stability, selectivity, uniformity, throughput, and pattern transfer fidelity.

By bridging fundamental insights with integration-driven optimization, this work clears the path to highly scalable, atomic-precision etching—a key enabler for both classical and quantum semiconductor technologies.

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8:30am **AP+EL+PS+TF-WeM-3 Atomic Layer Etching of TiN using O_2/Ar Plasma and SF_6/H_2/Ar Plasma Half-Cycles**, ***Kazuya Tajima,*** Hitachi High-Tech Corporation, Japan*; Andrew P. Kaye,* Colorado School of Mines*; Kazumasa Okuma, Hiroaki Ishimura,* Hitachi High-Tech Corporation, Japan*; Sumit Agarwal,* Colorado School of Mines

Titanium nitride (TiN) has become a widely adopted material for both logic and memory devices due to its appropriate work function with high-k gate stacks and excellent barrier properties against fluorine and oxygen diffusion. Atomic layer etching (ALE) of TiN was performed by a combination of surface modification by oxidation during the O_2/Ar plasma half-cycle and release of volatile etch products in the SF_6/H_2/Ar plasma half-cycle. [1,2] For the ALE experiments, we used low-resistivity TiN deposited by atomic layer deposition. In the O_2/Ar plasma half-cycle, TiN was oxidized to TiO_x with O radicals. For the SF_6/H_2/Ar plasma cycle, the SF_6-to-H_2 flow ratio was tuned to minimize continuous etching of TiN. Quadrupole mass spectrometry (QMS) was used to identify conditions that maximize the production of HF in the SF_6/H_2/Ar plasma, which acts as the etchant for surface modified TiO_x layer, and does not spontaneously etch TiN. Using QMS, we also identified the primary reaction products produced in each half-cycle. Our data show that NO was the primary nitrogen-containing product in the Ar/O_2 plasma half-cycle. TiF_2^+ and TiF^+ ions were detected by the QMS in the SF_6/H_2/Ar plasma half-cycle, which most likely originate due to cracking of TiF_4 parent molecules in the ionizer. The likely O-containing product during the SF_6/H_2/Ar plasma half-cycle is H_2O, which could not be detected due to the background signal in the QMS. In addition, we also detected SO^+ and SO_2^+ ions during both half-cycles due to the presence of S on the substrate and/or the chamber walls.

The etching process was performed at 200 °C. While the oxidation of TiN was quasi-self-limiting during the O_2/Ar plasma half-cycle, subsequent etching in the SF_6/H_2/Ar plasma half-cycle was not self-limiting. The synergy parameter, *S*, [3] is an indicator of the ideality of the ALE process. We show that the ALE end point could be determined by the time decay of the reaction products measured by the QMS, and the synergy parameter could be optimized by limiting the duration of the SF_6/H_2/Ar plasma half-cycle. We were able to obtain a synergy parameter of ~82% under optimized conditions.

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8:45am **AP+EL+PS+TF-WeM-4 Atomic Layer Etch Process for InGaAs Using (CH4+H2)/Ar+ Plasma**, ***Burak Okur,*** *Ryan Walsh, J. Russell Renzas,* University of Nevada, Reno

Precise, damage-free etching of InGaAs with Angstrom-scale control is a critical requirement for next-generation III-V semiconductor device fabrication, including gate recess etching in InGaAs HEMTs, which require very precise etching of ~20 nm of InGaAs. Conventional plasma etching is insufficiently precise for this application and introduces subsurface damage and surface roughness, motivating the development of atomic layer etching (ALE) processes that achieve controlled material removal through sequential, self-limiting surface reactions.

In this work, we investigate a plasma-based ALE process for InGaAs using $(CH_4+H_2)/Ar^+$ chemistry, consisting of alternating surface modification and removal half-cycles. The expected volatile products are $In(CH_3)_3$, $Ga(CH_3)_3$, and AsH_3. The effects of chamber conditioning, process pressure, and Ar flow rate are systematically investigated to achieve self-limiting ALE behavior. Real-time optical emission spectroscopy (OES) measurements are used to monitor plasma species and investigate the role of residual CH-related species in the transition between self-limiting ALE and RIE-like behavior. For a process at 10 mTorr with 200 W ICP power, 5 sccm Ar, a 1 sec dose of 5 sccm CH_4 and 20 sccm H_2, and 5 sec etch time, an ALE window is present from 10-15 W RF bias, with EPC of 0.25 nm/cycle. The etched surfaces are characterized using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), atomic force microscopy (AFM), and profilometry to evaluate etch per cycle (EPC), surface morphology, roughness evolution, and compositional uniformity of the InGaAs surface. Synergy is also measured.

9:00am **AP+EL+PS+TF-WeM-5 O2/CF4/Ar+ 3-Step Plasma Atomic Layer Etch Process for Aluminum**, ***Ryan Walsh,*** *Burak Okur, J. Russell Renzas,* University of Nevada, Reno

Aluminum is a light, conductive metal used in an incredible assortment of device fabrication processes, including in superconducting devices, where performance is highly sensitive to material impurities, interface damage, and critical dimensions. Most aluminum reactive ion etch processes use Cl_2 or BCl_3, which have the dual disadvantages of toxicity and post-etch corrosion. Fluorine is not typically used as an etchant for Al films because of the high melting point of AlF_3. It is known, however, that fluorinated AlO_x has a lower sputter threshold than untreated AlOx[1]. We present a novel 3-step plasma Atomic Layer Etch (ALE) process for Al using O_2, CF_4, and Ar^+. This room-temperature cyclical process starts by oxidizing Al in O_2 in Step A. Step B consists of a tetrafluoromethane dose to create an aluminum oxyfluoride modified layer. In Step C, this modified layer is removed via argon ion bombardment, using the oxide as an etch stop for the removal of the more easily sputtered oxyfluoride layer.

EPC of 0.08 nm/cycle and synergy of >99% were achieved with 100 W ICP power and 7 W table bias during step C. Etch control is governed by the thickness of the grown oxide and the depth of fluorine diffusion. We also present AFM, SEM, and XPS to show the effect of this process on the Al surface. This process could provide an avenue toward improved performance in aluminum-based superconducting devices.

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9:15am **AP+EL+PS+TF-WeM-6 Directional Atomic Layer Etching of Lithium Niobate for Nonlinear Integrated Nanophotonics**, ***Ivy Chen,*** California Institute of Technology*; Frank Greer,* Jet Propulsion Laboratory (NASA/JPL)*; Austin Minnich,* California Institute of Technology

Atomic layer etching (ALE) is of intense interest in microelectronics, photonics, and other fields owing to increasing demands for nanofabrication with nanometer-scale precision, aspect-ratio independent etching, and sub-nanometer surface roughness. Nonlinear integrated nanophotonic devices typically employ complex oxides like lithium niobate for which dry etching processes perform poorly. Fundamental improvements in nanofabrication processes are vital to realize the full potential of nonlinear integrated nanophotonics for on-chip quantum information processing and beyond. Here, we report a directional ALE process for LN consisting of sequential exposures of HBr/BCl_3/Ar plasma for surface modification and Ar plasma for removal. We observe an etch rate of 1.04 ± 0.01 nm/cycle with a synergy of 84.6% at a temperature of 0°C. At higher process temperatures, the HBr chemistry is found to decrease redeposition compared to F- and Cl-based plasmas, which we attribute to the higher vapor pressures of Br-based products. A grating pattern etched entirely by the process (total etch depth of 220 nm) exhibits no aspect-ratio dependent etching (ARDE) down to the smallest tested gap of 150 nm, in contrast to ion milling in which ARDE manifests even at 300 nm gaps for the same etch depth. Additionally, we present results on applying our ALE processes to TFLN devices to obtain higher aspect ratios, smoother sidewalls, and precise etch depths, yielding enhanced performance metrics for coupler gratings, ring resonators, and spontaneous parametric downconverters for on-chip quantum information processing.

9:30am **AP+EL+PS+TF-WeM-7 Native Oxide Removal and Passivation of Niobium for Superconducting Devices**, ***Jessica Jones,*** Argonne National Laboratory*; Jeffrey Elam,* Argonne National Laboratory, USA

Superconducting materials are foundational to many quantum technologies, yet surface and interfacial disorder remain important barriers to device performance and scalability. In particular, native oxide formation on superconducting metals is believed to contribute to loss and decoherence, creating a need for processing methods that provide precise surface control while maintaining the integrity of the underlying material. Niobium is an attractive superconducting material because of its relatively high critical temperature and broad relevance to quantum circuit platforms. However, complex native oxide formation and near-surface chemical disorder complicate its integration into devices such as Josephson junctions and other superconducting circuit elements. Here, we investigate an atomic-scale surface treatment and passivation approach for niobium thin films aimed at improving control over the metal/oxide interface. Our results show that thermal atomic layer etching can effectively remove native surface oxides from niobium while preserving the underlying metallic surface. Subsequent atomic layer deposition prevents reformation of the native oxide layer on the surface. Together, these findings establish a promising pathway for interface control in superconducting niobium and support the development of improved fabrication strategies for quantum circuit technologies.

9:45am **AP+EL+PS+TF-WeM-8 Thermal Atomic Layer Etching of the Semiconductor Oxide Channel Materials by Sequential Surface Modification and Volatile Release Reactions**, ***Muhammad Hamza Ansar,*** *Steven George,* University of Colorado Boulder

Indium gallium oxide (IGO) and Indium gallium zinc oxide (IGZO) can be used as channel materials in metal oxide semiconductor thin-film transistors (TFTs). These TFTs have high carrier mobility, low leakage current and a wider bandgap compared with silicon. Etching the channel material to a precise and controlled thickness is important for device performance. Thermal atomic layer etching (ALE) of these metal oxide semiconductors is possible using surface modification and volatile release reactions.

In this study, the thermal ALE was performed with sequential exposures of boron trichloride (BCl3) and hydrogen fluoride (HF). In situ spectroscopic ellipsometry (SE) measurements on flat films determined etch rates for IGO of 2.1 Å/cycle at 225°C and 3.0 Å/cycle at 255°C. The etch rate for IGZO was 2.5 Å/cycle at 205°C and 5.6 Å/cycle at 255°C. The etch rates were observed to be nearly self-limiting versus the BCl3 and HF exposures.

Quadrupole mass spectrometry (QMS) investigations identified the volatile products during the BCl3 and HF exposures on In2O3, Ga2O3 and ZnO powders. The initial BCl3 exposure reacted with the In2O3, Ga2O3 and ZnO powders and produced InCl3, GaCl3 and ZnCl2, respectively. These products are consistent with conversion to B2O3. The next HF exposure then produced BF3 and H2O from the spontaneous etching of B2O3. The HF then proceeded to yield additional H2O from the fluorination of the metal oxide. The subsequent BCl3 exposure first yielded BF3 from ligand-exchange with the metal fluoride. The BCl3 exposure then proceeded to produce metal chloride by conversion of the underlying metal oxide. The QMS results for Ga2O3 powder are displayed in **Figure 1**.

Additional studies on flat films explored the effect of IGO composition on the etch rate. **Figure 2** shows that the IGO etch rates were 2.8, 3.6, and 4.2 Å/cycle at In:Ga ratios of 1:1, 2:1 and 4:1, respectively at 230 °C. The etch rate then decreased to 0.8 Å/cycle at an In:Ga ratio of 8:1. The thermal ALE was also observed to smooth the initial roughness of the IGZO surface.

11:00am **AP+EL+PS+TF-WeM-13 Isotropic Atomic Layer Etching via Thermal-Cyclic Processing: Broad Material Capabilities with a Focus on Work–Function Metal Films**, ***Kazunori Shinoda,*** Hitachi High-Tech Corporation, Japan*; Thi-Thuy-Nga Nguyen, Shunya Hirai,* Nagoya University, Japan*; Nobuya Miyoshi,* Hitachi, Ltd., Japan*; Masaru Izawa,* Hitachi High-Tech Corporation, Japan*; Kenji Ishikawa, Masaru Hori,* Nagoya University, Japan **INVITED**

An isotropic atomic layer etching (ALE) process based on thermal–cyclic processing (thermal-cyclic ALE), consisting of repeated plasma exposure and infrared lamp heating, has been developed for advanced semiconductor manufacturing applications. This approach enables highly controllable and selective isotropic material removal through self–limiting surface reactions driven by cyclic thermal activation. A key advantage of this approach is the independent optimization of the adsorption and desorption temperatures, which enables enhanced material selectivity, improved surface smoothness, and sufficient etch per cycle (EPC). To realize this process at a manufacturing scale, a dedicated 300–mm wafer tool, referred to as a Dry Chemical Removal (DCR), has been developed and commercialized. Using this DCR tool, isotropic ALE processes have been developed for a wide range of materials used in semiconductor device fabrication, including oxides, nitrides, carbides, metals, and compound films. Furthermore, surface reaction mechanisms during the ALE steps have been systematically investigated using in–situ X–ray photoelectron spectroscopy (XPS), providing direct insight into adsorption and desorption steps governing the self–limiting etching behavior. These analyses reveal material–dependent reaction pathways and clarify the roles of plasma–induced surface modification and thermally activated removal of the modified surfaces. This invited presentation provides a comprehensive overview of the thermal–cyclic ALE technology, covering its historical development, process fundamentals, tool design, and mechanistic understanding across multiple material systems.In particular, recent progress in the isotropic ALE of work–function metal films, such as TiC and TiN, will be highlighted, with an emphasis on surface reaction mechanisms investigated by in–situ XPS. These materials are of increasing importance for advanced semiconductor devices, where precise thickness and surface control are critical. Process characteristics and surface chemistry insights obtained by in–situ XPS will be discussed.

11:30am **AP+EL+PS+TF-WeM-15 Selective Thermal Chemical Vapor Etching (CVE) and Atomic Layer Etching (ALE) of Ge Versus Si**, ***Micah Duffield,*** *Marcel Junige, Steven George,* University of Colorado at Boulder

The fabrication of gate-all-around nanosheet transistors employs multi-layer stacks of crystalline SiGe and Si. Completely removing sacrificial SiGe and precisely recessing SiGe may be accomplished by chemical vapor etching (CVE) and atomic layer etching (ALE), respectively. Facile Si CVE has been shown previously using anhydrous HF vapor above 150°C. This Si CVE is ceased by co-dosing H_2O+HF. The present work explored selective CVE and ALE pathways for Ge compared with Si using HF only or with oxidants.

Quadrupole mass spectrometry (QMS) measurements identified the volatile etch products during different reactant gas exposures at ramped or isothermal temperatures. Exposing Ge nanopowder to HF during an up-ramp from 25 to 400°C discovered that facile Ge CVE produced volatile GeF_4 at 50-75°C and then turned off due to non-volatile GeF_2 polymer formation. The GeF_2 polymer could then be volatilized at >300°C. Additional experiments at varied ramp rates, a reversed down-ramp, and isothermal HF exposures corroborated this non-volatile GeF_2 polymer formation.

Exposing a mixture of Ge & Si nanopowders to HF during a temperature ramp showed that the GeF_4 etch product in turn etched Si, producing volatile SiF_4 at 75-110°C (**Figure 1a**). Co-dosing H_2O+HF still etched Ge (or GeO_2) and produced volatile GeF_4. However, co-dosing H_2O+HF eliminated

the parasitic Si etch pathway via GeF_4 (**Figure 1b**). Introduced H_2O oxidized Si and formed an ultra-thin chemical oxide. This SiO_2 was not etched by GeF_4.

Repeatedly exposing GeO_2 nanopowder to HF at 100°C revealed that GeO_2 etched spontaneously without the self-termination observed for Ge. This finding inspired a unique Ge ALE mechanism: A first oxidant exposure may oxidize Ge to form an ultra-thin GeO_2 surface layer. A subsequent HF exposure may volatilize this GeO_2 surface layer but self-terminate on the underlying Ge due to GeF_2 polymer buildup. The following oxidant exposure may remove the GeF_2 polymer and again oxidize Ge.

Exposing Ge nanopowder to a sequence of oxidant and HF exposures at 100 and 150°C, respectively, revealed that volatile GeF_4 was released after each oxidant exposure in a self-terminating fashion. To refresh the Ge surface after HF exposures, H_2O was ineffective, whereas O_2 was effective, and O_3 was even more effective than O_2 (**Figure 2**). To verify these QMS findings, *in situ* spectroscopic ellipsometry (iSE) studies were employed on Ge thin film samples. Ge ALE using an alternating O_2/HF sequence at 150°C exhibited an etch per cycle of 1.38 Å, near-ideal ALE synergy of 97%, and selectivity versus Si (**Figure 3**).

11:45am **AP+EL+PS+TF-WeM-16 Controlled SiO_2 Etch Rates Using a HF/H_2O Liquid-Layer in a Vacuum Environment: Dependence on H_2O and HF Pressures**, ***Samantha Rau,*** University of Colorado at Boulder*; Antonio Rotondaro, Hanna Paddubrouskaya, Kate Abel,* Tokyo Electron America, Inc.*; Steven George,* University of Colorado at Boulder

Our earlier research demonstrated SiO_2 etching by HF using a H_2O liquid-layer in a vacuum environment. The current work characterized the dependence of SiO_2 etch rate on the H_2O and HF pressures. We have observed a dramatic increase in SiO_2 etch rates at higher H_2O and HF pressures. This behavior suggests that the thickness of the HF/H_2O liquid-layer may be increasing rapidly at higher pressures.

SiO_2 etch rates may be sensitive to the HF/H_2O liquid-layer thickness when the thickness is close to the size the hydrated F^-, HF_2^- and SiF_6^{2-} ions that are involved during SiO_2 etching. For example, the size of the hydrated F^- ion is 7 Å. Lower SiO_2 etch rates may result from incomplete hydration of these ions. SiO_2 etch rates may approach the SiO_2 etch rates observed in solution for thicker liquid-layers.

Investigations were performed to determine the thresholds for HF/H_2O condensation versus H_2O and HF pressure. Spectroscopic ellipsometry was employed to measure the liquid-layer thickness, the mean squared error (MSE) in the thickness model, and the transmitted light intensity. Condensation was assumed to occur when the increase in liquid-layer thickness, the increase in MSE, and the decrease in light intensity all occurred rapidly at higher H_2O and HF pressures. Figure 1 shows that rapid changes in the liquid-layer thickness, MSE and transmitted light intensity are observed at a total pressure of 22.9 Torr (18 Torr H_2O and 4.9 Torr HF) at 30.4°C.

Experiments were conducted at initial H_2O pressures from 0-35 Torr and increasing HF pressures from 0-40 Torr to determine the threshold H_2O and HF pressures for condensation at 30.4°C. The resulting condensation points were then compared with the measured SiO_2 etch rates at various H_2O and HF pressures in Figure 2. Below the condensation curve in the ultrathin liquid layers, there were lower SiO_2 etch rates ranging from ~1-100 Å per 5 s HF exposure. These lower SiO_2 etch rates may result from incomplete hydration of the F^-, HF_2^- and SiF_6^{2-} ions. Above the condensation line, the measured SiO_2 etch rates of ~100-1000 Å per 5 s HF exposure were comparable with SiO_2 etch rates in bulk HF solutions with HF wt% values of 25-40%.

12:00pm **AP+EL+PS+TF-WeM-17 Thermal Selective Etching of $Si_{1-x}Ge_x$ in XeF_2**, ***Daniel Cho,*** *Yi Chen,* UCLA*; John Hoang, Nick Altieri, Ji Zhu, Samantha Tan,* Lam Research Corporation*; Jane P. Chang,* UCLA

In GAAFET fabrication, $Si_{1-x}Ge_x$ is etched selectively from Si. Wet, plasma, and thermal chemistries have been investigated to etch $Si_{1-x}Ge_x$ with a range of selectivity [1]. Thermal fluorine-based etch processes, including F_2 and XeF_2, show high selectivity with etch rates exhibiting a volcano-shaped dependence on x [2, 3].

In this study, we report $Si_{1-x}Ge_x$ (x = 0 to 1) etch by a XeF_2 beam. XeF_2 was sublimed into an expansion chamber to a target pressure, then pulsed into the reaction chamber. In each pulse, ΔP_{XeF2} was proportional to the XeF_2 dose. *Ex situ* x-ray photoelectron spectroscopy (XPS) identified the chemical bonding states on the $Si_{1-x}Ge_x$ surface from XeF_2, while scanning electron microscopy (SEM) measured the etch depth for etch rate (ER) calculations.

XeF_2 exposure on as-received $Si_{1-x}Ge_x$ samples showed no etch, confirmed by XPS and SEM. This was attributed to a native oxide which prevented XeF_2 from interacting with the underlying $Si_{1-x}Ge_x$. Prior to XeF_2 exposure, *in situ* Ar ion sputtering was used to remove the native oxide for all sequential etch conditions.

XPS results of XeF_2-processed $Si_{0.75}Ge_{0.25}$, Si, and Ge identified Ge-F, Si-F, and C-F bonding in the F 1s region at binding energies of 685.0 eV, 687.1 eV, and 689.6 eV, respectively, consistent with literature values [4-6]. Ge-F, Si-F, and C-F made up 20.8%, 37.4%, and 41.8% of the total fluorine content on the XeF_2-processed $Si_{0.75}Ge_{0.25}$. Quantitative analysis of fluorination by *ex situ* XPS was limited by air exposure between etch and measurement.

Synergistic etching, with Ar ions and XeF_2 simultaneously exposed, showed a Si ER of 6 nm/pulse at an ion beam voltage of 200 V and ΔP_{XeF2} =0.5 Torr, showing a higher ER than the sequential Si ER of 0.4 nm/pulse at the same ion beam voltage and ΔP_{XeF2}.

The peak sequential $Si_{1-x}Ge_x$ ERs for the following Ar ion beam voltage and ΔP_{XeF2} conditions, 100 V and 0.5 Torr, 200 V and 0.5 Torr, and 100 V and 0.2 Torr, were 7.8 nm/pulse, 9.9 nm/pulse, and 4.1 nm/pulse, respectively. For all conditions, ER increased from x = 0 to 0.1, followed by a decrease or plateau past x = 0.15. Higher pretreatment ion beam voltage and higher ΔP_{XeF2} both led to an etch rate increase for x = 0 to 0.25. The peak $Si_{1-x}Ge_x$/Si etch selectivity ranged from 20 to 30 under all conditions.

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Plasma Science and Technology
Room 315 - Session PS1-WeM

Plasmas for 3D Integration

Moderators: Hiroyuki Fukumizu, KIOXIA, **Dr. Jeffrey Shearer**, TEL Technology Center, America, LLC

8:00am **PS1-WeM-1 Challenges in Plasma Etching for 3D Interconnect Technology**, ***Violeta Georgieva,*** *Jeongsoo Kim, Eoin Jackman, Quyang Lin, Katia Devriendt,* IMEC, Belgium **INVITED**

Three-dimensional (3D) interconnect technology based on die vertical stacking has been attracting increasing attention recently as a key approach to extend system-level performance beyond conventional scaling limits [1]. Through-silicon vias (TSVs), through-dielectric vias (TDVs), and nano-TSVs (nTSVs) used in backside power delivery networks enable high-density vertical electrical signal or power transport in heterogeneous 3D integration.

3D interconnect performance depends not only on interconnect structures but also on upstream processes such as plasma dicing, which ensure die integrity and bonding yield. Reducing wafer thickness and downsizing dies have revealed the limitations of conventional mechanical and laser dicing methods, while plasma dicing offers precise and clean die singulation [2].

This work focuses on the challenges faced by the plasma etching community in delivering high-aspect-ratio processes with tight control of anisotropy at both the macroscale (TSV, TDV, and plasma dicing) and the nanoscale (nTSVs). In addition to profile performance, other important parameters such as high selectivity to photoresist (PR) and hard mask (HM), as well as endpoint detection in very small open areas with dense layouts, are addressed.

TSVs and nTSVs are both affected by etch-rate suppression and profile distortion due to aspect-ratio-dependent etching [3, 4]. For nTSVs, these challenges are exacerbated by the need for nanoscale precision, especially in TSV-last schemes, where extremely high silicon-to-oxide selectivity is required to preserve thin oxide liners [4].

TDVs introduce additional complexity due to the need to etch multilayer back-end-of-line dielectric stacks while maintaining uniformity and protecting underlying metallization [5]. Furthermore, intrinsically low

dielectric-to-PR selectivity and limited HM options remain critical constraints.

Plasma dicing combines many of these challenges, requiring precise etching of silicon, dielectric, and polymer layers within a single process [6].

This presentation reviews current process solutions and innovations addressing these issues and highlights remaining gaps and future directions in plasma etching for advanced 3D interconnect integration.

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8:30am **PS1-WeM-3 Low Global Warming Potential (GWP) Gases for Deep Si Etch for Through-Silicon Via (TSV) Applications**, ***Richa Agrawal,*** *Gloria Fraczak, Nathan Marchack,* IBM Research*; Yohei Takakura,* DAIKIN INDUSTRIES, LTD.*; Teodor Todorov, Martin M. Frank, Jaylynn Sheppard, Jose Daboin, Brian Pham,* IBM Research*; Kazunori Horiguchi,* DAIKIN INDUSTRIES, LTD.*; Yasuhiro Nojiri, Hisataka HAYASHI,* DAIKIN INDUSTRIES, LTD., Japan*; ERIC JOSEPH, ROBERT L. BRUCE,* IBM Research

Through-silicon vias (TSVs) are crucial components for three-dimensional (3D) integration technologies. Conventional Bosch processes typically rely on fluorinated gases such as c-C_4F_8 and SF_6, which exhibit high global warming potentials (GWPs) and are increasingly subject to environmental regulations. Given the criticality of deep-Si etch processes for packaging applications, it is of great interest to investigate alternative plasma chemistries to focus on sustainability for future technological node development.

In this work, the applicability of alternative with much lower GWPs for TSV applications at aspect ratios >10:1 with different integration routes, is investigated. The alternative gases show comparable etch profiles to the conventional C_4F_8-SF_6 processes – key performance indices including critical dimensions (CD), anisotropy, etch rates, mask selectivity are compared. Optical emission spectroscopy (OES) is used to assess gas phase species and compare plasma characteristics. Electrical characterization of the integrated TSVs shows similar resistance scaling for C_4F_8-SF_6 processes and alternative gases, with performance governed by TSV geometry, CD, and liner material properties. Exhaust sampling analysis using Fourier Transform Infrared Spectroscopy (FTIR) showed a two to three orders of magnitude reduction in high-GWP emission byproducts with the usage of alternative gases compared to C_4F_8 and SF_6. These results demonstrate a viable alternative pathway to reducing environmental impact while maintaining etch and electrical performance integrity for TSV fabrication.

8:45am **PS1-WeM-4 Multiscale Modeling Approach for Bosch Silicon Etching Process Coupled to Machine Learning, Toward a Fast Etching Process Optimization**, *Rim Ettouri,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel (IMN), France*; Fatima-Zahrae Hilal, Valeria Borodin,* IMT Atlantique, CNRS, Nantes Laboratory of Digital Sciences, LS2N, France*;* ***Ahmed RHALLABI,*** Nantes University, CNRS, Institut des Materiaux de Nantes Jean Rouxel, IMN, France

Deep silicon etching is a major challenge for the development of many electronic devices, such as DRAM memories, integrated 3D capacitors, and MEMS. Developing deep silicon etching processes with minimal morphological defects and a high degree of anisotropy, while avoiding empirical trial-and-error approaches, remains a significant scientific and technological challenge requiring substantial time and resources.

The Bosch process, based on an alternating discharge including an etching phase and a deposition phase, appears to be a particularly suitable solution for meeting these requirements depending on the targeted applications. However, its optimization generally requires long and costly experimental campaigns.

In this context, the development of etching simulators based on a multi-scale approach represents a promising alternative. Such tools could contribute in the understanding of plasma–surface interaction mechanisms and the optimization of the etching processes in a faster time.

In this context, we developed a multiscale approach for a deep silicon etching using the Bosch process with alternating discharges SF_6 for the etching step and C_4F_8 for the deposition step.The model is composed of three modules: a global kinetic model of SF_6 and C_4F_8 ICP plasmas, a sheath model based on the Monte Carlo method, and a 2D etching model based on the cellular Monte Carlo method.The simulator allows the prediction of the temporal evolution of the etched profiles, the surface chemical composition, and the etching rate.Well-known phenomena in the Bosch process, such as scalloping and undercut, are clearly demonstrated.

One of the disadvantages of our multi-physics models is its very long run time.Using machine learning to predict the evolution of silicon etch profiles as a function of the operating conditions (RF power, pressure, gas flow rates, ...) is a good way to significantly reduce the simulation times.The simulations from our multiscale approach serve as training data for the machine learning. This enables to move towards an AI approach that contributes to Bosch process optimization.

The data-driven analysis identified the relative importance of each parameter and their interactions for instance, quantifying how pressure and power jointly affect polymer deposition and SiF_x by-product formation.

9:00am **PS1-WeM-5 Feature-Scale Model of Si Plasma Etching in $SF_6/O_2/SiF_4$ Mixtures**, ***Maryam Khaji,*** University of Michigan, Ann Arbor*; Fatima Jenina Arellano, Kouta Kawahara, Noboru Yamaguchi, Taichi Suzuki, Tadamasa Kobayashi, Kenta Doi,* Ulvac Technologies, Inc., Japan*; Mark J. Kushner,* University of Michigan, Ann Arbor

High aspect ratio plasma etching of Si for TSV (through-silicon vias) and packaging applications is primarily performed in fluorine-containing plasmas with feedstock gases containing CF_4, NF_3 and SF_6 [1]. Si etching by F atoms is an isotropic process. Adding gases such as O_2 and SiF_4 produces sidewall passivation which, with moderate substrate biases, enables anisotropy. For comparable F-atom fluxes to the wafer, several studies have reported significantly higher Si etch rates in SF_6-containing plasmas compared to other F-containing plasmas [2]. This enhancement has been attributed to the possible catalytic role of S-containing species, surface sulfidization, which increases the efficiency of fluorination and increases etch yields [1,3]. In this work, results will be discussed from feature-scale modeling of Si HAR etching in an inductively coupled plasma (ICP) source sustained in $SF_6/O_2/SiF_4$ gas mixtures. With the goal of distinguishing the unique aspects of plasma etching in gas mixtures containing SF_6, the surface reaction mechanism includes fluorination, sulfidization, oxidation, and ion sputtering. Reaction probabilities were calibrated against experimental results obtained for different ICP powers, RF bias powers, gas compositions, and pressures. Reactor-scale simulations were performed with the Hybrid Plasma Equipment Model (HPEM), and feature-profile evolution was evaluated using the Monte Carlo Feature Profile Model (MCFPM) [4]. The consequences of plasma properties on feature evolution will be discussed. A brief update on the gas phase reaction mechanism for SF_6 containing plasmas will be provided.

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9:15am **PS1-WeM-6 Transport Gradient Model of Oxygen and Fluorine Flux Ratio in High-Aspect-Ratio Silicon Etching**, ***Kenji Ishikawa,*** *Shuto Tsuchioka, Trung Nguyen Tran, Kenichi Inoue, Takayoshi Tsutsumi,* Nagoya University, Japan*; Thi-Thuy-Nga Nguyen,* nagoya University, Japan

This study presents a quantitative investigation of the bowing mechanism observed in high-aspect-ratio (HAR) silicon etching using SF6/O2 inductively coupled plasmas through a multi-scale simulation framework. By integrating reactor-scale plasma modeling with feature-scale profile evolution analysis, we examine the dynamic balance of reactive radicals at the etch front and its role in profile formation. In contrast to previous studies relying on qualitative interpretations based on optical emission intensity ratios, this work provides numerical validation of the transport gradient model.

The model demonstrates that the localized oxygen-to-fluorine (O/F) flux ratio, rather than the global gas composition, governs sidewall passivation and etch stability. The local flux ratio incorporates transport physics, including Knudsen diffusion and surface sticking probabilities, which significantly modify reactant distributions. Consequently, gradients in

radical flux develop along trench depth, producing spatially varying surface reactions.

Parametric simulations identify a critical threshold in the local O/F flux ratio between 3.5% and 3.6%. Above this threshold, oxygen-rich coverage enables passivation and anisotropic etching. Below it, fluorine-dominant coverage induces a nonlinear increase in etch rate, causing rapid lateral etching and bowing.

This insight explains why a 30% O2 condition maintains verticality at shallow depths, whereas 20% O2 causes immediate bowing as the local O/F ratio falls below the threshold. These findings highlight the importance of transport-limited effects in HAR structures and provide a theoretical basis for optimizing radical flux control in advanced plasma etching processes.

9:30am **PS1-WeM-7 Effects of Discharge Frequency and Precursor Molecule on the Deposition Rate, Film Density, and Residual Stress of a-C:H Hard Masks**, ***Kazunori Koga***, *Shunpei Ohara, Soichiro Yoshida, Ryosuke Kinnami, Shinjiro Ono, Takamasa Okumura, Kunihiro Kamataki, Naho Itagaki, Masaharu Shiratani,* Kyushu University, Japan

Hydrogenated amorphous carbon (a-C:H) films are essential materials for hard masks in high-aspect-ratio (HAR) etching in semiconductor manufacturing. High-speed deposition of high-density and low-stress a-C:H films is strongly demanded for superior plasma etching resistance. Here, a-C:H films were deposited via plasma chemical vapor deposition (plasma CVD) where methane, acetylene, and cumene (C_9H_{12}) were used as precursor gases to evaluate their deposition rate, density, and stress. A parallel-plate plasma CVD system was used with 1 cm^2 Si substrates under Ar-diluted precursors. An RF voltage of 13.56 MHz or 400 kHz was applied. For 400 kHz, the concentration, flow rate, pressure, and Vpp were 5%, 100 sccm, 0.02 Torr, and 1600–2400 V. For 13.56 MHz, the flow rate was 100 sccm, concentration 5–50%, pressure 0.02–0.3 Torr, and Vpp 100 V or 250 V. At 13.56 MHz, acetylene and cumene yielded higher deposition rates than methane. Cumene achieved a 20 nm/min higher rate than acetylene with comparable density and stress (~1.0 GPa). Stress increased with density, reaching 3.8 GPa at 2 g/cm^3. Conversely, 400 kHz conditions—providing higher self-bias and incident ion energy—yielded high density (~2 g/cm^3) and low stress (~1.0 GPa), keeping stress constant independent of density. At 400 kHz, cumene deposited 10 nm/min faster than acetylene. Factors determining density were examined. Raman spectroscopy showed that hydrogen content and density are inversely correlated, independent of discharge conditions or precursors. To clarify ion energy effects, an ion energy index was defined as |Vdc|/pressure/Nc, where |Vdc| is self-bias voltage and Nc is the number of carbon atoms per molecule. Using this index, density peaked at ~5 regardless of precursors or frequencies. This indicates that the sub-plantation model, where incident ion energy is distributed among carbon atoms within a molecule to determine density, holds true even for high-carbon-number cumene. The Raman D/G peak ratio (sp^2/sp^3 bonding ratio) correlated well with density in the low-ion-energy region (13.56 MHz) but deviated in the high-ion-energy region (400 kHz). This deviation suggests a structural difference under high ion energy, explaining why stress remained decoupled from density. Etching measurements confirmed that higher density decreased the etching rate, proving that density governs etching resistance regardless of precursors or deposition conditions.

9:45am **PS1-WeM-8 Impact of HBr/H2 Gas Mixture on Etching of GeSexTe1-x Chalcogenide Thin Films for Reconfigurable and Nonlinear Photonics**, ***Giovanni BEDOUI***, CEA-LETI, France*; Aurélien TAVERNIER, Yoann BRULE, Jean-Baptiste DORY, Pierre MEILLEUR, Jules LAGRAVE, Clémence JAMIN-MORNET, Pierre NOE,* CEA-Leti, France

Chalcogenide materials are alloys composed of one or multiple chalcogen elements (S, Se, Te) and one or multiple alloying elements (Ge, As, ...). They demonstrate a wide transparency window and high linear and non-linear (NL) indices in the near and mid infrared. Some of them exhibit phase-change properties, transitioning reversibly from an amorphous to a crystalline state, with an unusual contrast between the electrical and optical properties of these two states [1,2]. As their properties makes them interesting for micro and nano-photonics applications, one issue impeding their widespread integration is the ability to pattern them without altering their optical properties.[3]

To address this issue, a plasma etching process with minimal impact over morphology and stoichiometry is needed for $GeSe_xTe_{1-x}$ destined to reconfigurable (1.55µm) and NL (2µm) applications. A focus will be made on HBr/H_2 etching gases and H_2/Ar Post-Etching Treatment (PET), expecting low impact on surface roughness (Rq), stoichiometry alteration and non-volatile compound (NVC) formation.[4]

This work involves unpatterned $Ge_{50}Te_{50}$ and $Ge_{50}Se_{50}$ thin film etching with HBr and HBr/H_2 both with and without PET in an ICP chamber. Characterization methods such as 2D Atomic Force Microscopy (AFM) for Rq and X-Ray Photoelectron Spectroscopy (XPS) for atomic composition were used. Figure 1 shows AFM measurement of Rq for both alloys at each gas composition. HBr/H_2 mix induces the lowest Rq and PET decreases Rq for both alloys. Figure 2 shows XPS measurement of both alloys with each gas composition. HBr and H_2 cause stoichiometric shifts by forming volatile GeH_x and NVC $GeBr_x$ in both alloys. For GeTe, PET seems to limit both NVC and volatile by-products. For GeSe, PET induces volatile SeH_x by-products generation.[5] We can conclude that HBr/H_2 + PET etching mix seems the most promising.

To go further, the impact of HBr/H_2 + PET mix over unpatterned and patterned $GeSe_xTe_{1-x}$ thin films will be studied. Characterizations techniques as 3D and 2D AFM for sidewall roughness and Rq measurement, XPS for atomic composition and Scanning Electron Microscopy (SEM) for sidewall angle analysis will be used. The addition of CH_4 gas into the etching mixture could be studied to improve sidewall angle control.[6]

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Plasma Science and Technology
Room 315 - Session PS2-WeM

Plasma Applications in Packaging and Wafer Bonding

Moderators: Prof. Kenji Ishikawa, Nagoya University, Japan, **Dr. Jeffrey Shearer**, TEL Technology Center, America, LLC

11:00am **PS2-WeM-13 Etch Opportunities in Advanced Packaging, Silicon, and Optical Photonics**, ***Brittany Hedrick***, Tokyo Electron America **INVITED**

Advanced Packaging grows more complex as the ever-increasing need for bandwidth, power, and memory persists and drives down feature geometries: from the transistor to the electrical routing line/space, and out to the assembled system through ever-finer plated interconnects and optical interconnects. Interconnect density pitches for conventional electrical interconnects are teetering between the realm of plated micropillars and Cu-Cu bonding down into D2W and W2W pitches enabled by direct Cu Hybrid bonding. Ever thinner HBM layers drive unique TSV integration for ultra thin die and singulation methods to handle these devices with high yield.

Meanwhile Si photonics features have been added to the mix to handle data for long haul and short haul tele-com/data-com and are finding traction in Quantum and AI applications as well.Introducing new materials into standard CMOS flows, Si photonics and Quantum computing devices are driving new tooling applications, novel processes, and research and development activities seeking advances in performance improvement.Waveguide materials and designs, for telecom and datacom, continue to be refined for improved propagation loss performance, and the optical interconnect features themselves are etched, milled, and engineered to reduce insertion loss to as close to 0 as possible.

In the consumer electronics sector personal devices are evolving from cell phones to AR glasses, with top makers looking to bring fashionable, functional, lightweight, and efficient devices to market for mass adoption. Optical photonics now drives glass and SiC wafer device fabrication across traditionally Si wafer/CMOS semiconductor tools.Depositing thin films on glass, litho, etch, and encapsulation to fabricate optical gratings for AR lenses provide new challenges the industry is rapidly rising to address.

Tokyo Electron (TEL) is working across these spaces to develop processes and equipment to keep pace with the ever-evolving packaging world. Throughout the presentation we will highlight recent process developments and practical adaptations in etch technology that respond to these growing industry applications.

11:30am **PS2-WeM-15 Impact of Surface Activation Plasma Chemistry on AlN - Oxide Wafer Bonding for BSPDN Applications**, ***Chetan Jois***, *Ryan Allen, Yusuke Suzuki, Andrew Tuchman, Christopher Netzband, Rinus Lee, Ilseok Son,* Tokyo Electron America, Inc.

In Backside Power Delivery Network (BSPDN) process flows, a carrier wafer is bonded to enable wafer thinning and backside access. When the carrier is retained for packaging, the bonding interface plays a dual role as both a mechanical support and a thermal transport pathway. Conventional oxide bonding dielectrics, such as SiO_2, introduce a thermally resistive layer between the carrier and device wafers, motivating the use of alternative bonding materials with improved thermal properties. Aluminum nitride (AlN) has emerged as a promising thermally conductive dielectric for carrier bonding. For integration, bonding interfaces must exhibit bonding energies greater than 1.5 J/m^2 to enable downstream processing and ensure mechanical reliability. However, achieving high bonding energy with AlN based films at low thermal budgets remains a key integration challenge. In this work, we investigate the bonding behavior of a thin AlN based bonding stack consisting of 30 nm PVD AlN capped with 5 nm ALD Al_2O_3, bonded to a thermally grown 100 nm SiO_2 carrier wafer. The surface activation plasma (SAP) process window is systematically studied with direct comparison between O_2 and N_2 plasma chemistries. Bonding energy measurements show a strong dependence on SAP gas chemistry, with O_2 plasma activation yielding higher bond strength than N_2 plasma under comparable process conditions, achieving a bond energy of 2.8 J/m^2 at optimized settings. Surface chemical analysis reveals that O_2 SAP results in a higher concentration of H_2O and hydroxyl related species compared to N_2 activated surfaces, indicating enhanced surface hydration that promotes stronger interfacial bonding. Post–anneal bond energy is found to correlate well with bond propagation speed and surface contact angle, suggesting that improved initial surface adhesion directly translates to increased final bond strength. Finally, the impact of SAP conditions on post–bond lithography overlay (PBLO) is evaluated for BSPDN integration.

11:45am **PS2-WeM-16 Optimization of Dielectric Plasma Activation for Wafer to Wafer Fusion Bonding**, ***Christopher Netzband***, Tokyo Electron America Inc.,*; Andrew Tuchman, Ilseok Son, Angelique Raley,* Tokyo Electron America, Inc.

As logic and memory scaling slows, the demand for higher interconnect density and speed has increased, especially among NAND and DRAM companies. Device performance gains are increasingly achieved in the back end of line using wafer-to-wafer (W2W) hybrid bonding for 3D NAND, CIS, 3D-SoC, and eventually bonded CFET architectures. One major hurdle to achieving bonded CFET structures is the strength and reliability of the bonding interface. If the mechanical strength of the bonding is low the wafers will come apart during grinding or etching, while if the chemical strength is low they will be etched apart during subsequent wet cleans. Most dielectric films have poor mechanical bonding strength as deposited they require plasma activation to enable bonding. This plasma activation breaks the surface bonds enabling hydrogen bonding and condensation to covalent bonds after a post-bond anneal. Unfortunately, just running this activation does not ensure good mechanical or chemical bonding strength as the results can vary based on your incoming film.

In this talk we will discuss what properties are most important for high quality bonding across a range of bonding materials. Examples of film properties that influence plasma parameter selection include exposed metal (hybrid bonding), thickness and density. In the case of hybrid bonding the plasma activation must be very low power and confined to the surface to eliminate the chance of leakage pathways along the bonding interface caused by Cu sputtering. Similar considerations are needed for thin oxides. If the interaction depth of the plasma is too deep can impact underlying layers or, if deposited directly on Si, cause hydrogen gas at the film/Si interface. While it is well known that SiO_2 performs better with N_2 plasma versus O_2 plasma, the degree of the difference between these activation gasses is directly correlated to the porosity of the films. In CVD TEOS the difference in bond strength between the two activation gasses is small and the interface after bonding is void free. Conversely, highly dense thermally grown SiO_2 has a 60% lower bond strength when using O_2 gas for the plasma activation and has small voids at the wafer edge caused by the plasma that further reduce the chemical and mechanical strength of the bond leading to quicker stress corrosion than the N_2 case. By understanding how to adjust plasma activation conditions to obtain high quality bonding with a wide range of materials even more opportunities for hybrid and fusion bonding will emerge in advanced packaging.

12:00pm **PS2-WeM-17 Plasma-Induced Surface Modification of Indium for Improved Bonding**, ***Kristen Steffens***, National Institute of Standards and Technology (NIST)*; Sujitra Pookpanratana,* National Institute of Science and Technology (NIST)*; Junyeob Song, Marcelo Davanco, Tammy Lucas, John Biesecker, Daniel Schmidt,* National Institute of Standards and Technology (NIST)

Bonding between materials plays an important role in advanced microelectronics integration and packaging by bringing together components and devices produced separately.Surface pretreatments on bonding materials have been consistently found to be crucial to achieving a high-quality bond, despite incomplete understanding of why certain treatments have greater success than others.Our project aims to improve understanding of atmospheric plasma pre-treatment effects to provide information to enable more efficient development of bonding protocols.

Indium is a critical material for conductive interconnects for the fabrication of cryogenic low-temperature electronics and optical detectors for infrared and microwave applications. Since indium is a superconducting material which retains its ductility and adhesion properties during thermal cycling, it sees particular use for Quantum Information and Quantum Sensor applications [1].Certain pre-bond plasma treatments increase the success of In-In bond adhesion.We have observed that plasma chemistries such as H_2/He, which do not include N_2 as a plasma gas, promote more successful In-In bonding.To understand why, we investigate the effects of atmospheric plasma exposure on indium surfaces for several plasma chemistries including He/H_2/N_2, He/H_2 and He/N_2.X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) are used to characterize indium surfaces prior to and after ambient pressure plasma treatment.All plasma treatments decreased the amount of carbon and increased both the amount of In-oxide present as well as the indium oxide/metal ratio as compared to an untreated film.N-$_2$-containing plasmas resulted in the appearance of an additional high binding energy peak in the N 1s XPS spectrum.We postulate that this may be due to nitrate species formed on the indium native oxide surface. Additional experiments were performed on indium foil both prior to and after Ar sputtering for comparison to treated samples.Nitrogen was found to be confined to the surface and reappeared after eleven weeks of exposure to air at room temperature.

UPS measurements showed that all plasma chemistry treatments lowered the work function compared to the non-treated control.Greater spatial variation in work function was observed for chemistries with high N_2 versus those with little to no N_2.This finding possibly correlates with poorer bonding for N_2 containing plasmas.

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Atomic Scale Processing Mini-Symposium
Room 316 - Session AP+2D+EL+EM+PS+TF-WeA

Atomic Scale Processing to Enable 2D Materials

Moderators: Dr. Robert Bruce, IBM Research, T. J. Watson Research Center, **Prof. Dr. Cristina Satriano**, University of Catania

2:15pm **AP+2D+EL+EM+PS+TF-WeA-1 Chemistry (and Some Physics) of Atomic Layer Deposition of Two-Dimensional Metal Dichalcogenides***, **Miika Mattinen,*** University of Helsinki, Finland **INVITED**

Two-dimensional (2D) materials are of interest for a range of applications from microelectronics to sensing to energy storage and production. One of the most prominent group of 2D materials are metal dichalcogenides, some of which are semiconductors, such as the prototypical MoS_2, while others are (semi)metals such as TiS_2 and TaS_2.[1] Deposition of 2D materials with desired properties on large, often temperature-sensitive, and complexly shaped substrates is a key challenge for practical applications. Atomic layer deposition (ALD) can fulfill these requirements, but unlocking the full potential of ALD requires understanding of precursor chemistry, nucleation, substrates, and film characteristics, among other factors.[1,2]

I will discuss chemistries for deposition of a range of 2D metal dichalcogenides including MoS_2,[3] SnS_2,[4] ReS_2,[5] WS_2,[6] HfS_2 and ZrS_2[7] using thermal ALD. I will cover precursor challenges related to reactivity, thermal stability, and etching reactions. Controlling crystallinity and morphology and continuity at low thicknesses are also key challenges encountered in ALD of 2D materials. To this end, I highlight the role of substrate choice and the use of a two-step SnS_2 process where the deposited amorphous film is crystallized with mild-post deposition annealing.[4,8,9]

Plasma-enhanced ALD (PEALD) can help overcome some of the challenges encountered in thermal ALD, such as limited reactivity of many precursors. For example, few thermal chemistries are available for direct deposition on low-cost plastic substrates for flexible applications (T ≤ 150 °C). To this end, I will discuss PEALD of TMDCs including MoS_2, TiS_2, and WS_2 at record-low temperatures down to 100 °C by controlling plasma chemistry[10] I will also describe advanced ABC type processes with two plasma steps, where both the plasma chemistry (reactive radicals) and physics (low-energy ions) are used to control film growth and properties.[11]

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2:45pm **AP+2D+EL+EM+PS+TF-WeA-3 First-Principles Survey of Molybdenum ALD Precursors for MoS_2 Thin Films***, **Ian Kerby,*** *Ashlee Riedinger, Lan Li,* Boise State University

Transition metal dichalcogenides, such as molybdenum disulfide (MoS_2), are promising candidates for various semiconductor applications. A crucial requirement for these applications is the controlled and conformal deposition of a monolayer film. Chemical vapor deposition (CVD) and atomic layer deposition (ALD) techniques are key to achieving thin films at commercial scale. Towards this end, the reactions of a variety of precursor chemicals with another variety of surfaces need to be understood. A reaction between a surface and a precursor can be difficult to study in-situ and ex-situ, making computational modeling a valuable tool for addressing this challenge. The work presented here is a survey of common and proposed molybdenum precursors for use in atomic layer deposition of MoS_2 films. Our work in modeling nucleation of these precursors includes various surfaces with the primary aim of determining the role of surface morphology and chemistry during deposition. We have conducted thermodynamic surveys using density functional theory (DFT) for spontaneity of proposed reaction pathways for the precursors to interact and nucleate on the surfaces. To generate and account for the inherent variability in the amorphous substrate, we have utilized ab-initio molecular dynamics (AIMD), enabling a more comprehensive exploration of the complex energy landscape. We have also investigated the formation of reaction residues on surfaces. Our studies lay the groundwork for future kinetic analyses. The stable intermediate states identified along the reaction pathways can be used in nudged elastic band (NEB) calculations to determine the associated energy barriers during nucleation. These insights may further help guide and inform experimental efforts.

3:00pm **AP+2D+EL+EM+PS+TF-WeA-4 Thermal and Plasma-Enhanced ALD of MoS_2 using $MoO_2(THD)_2$***, **Ryan Weiland,*** University of Michigan, Ann Arbor*; Ian Campbell,* IMEC*; Pierre Morin, Benjamin Groven,* IMEC Belgium*; Ageeth Bol,* University of Michigan, Ann Arbor

Field effect transistors (FETs) are foundational components of modern electronics. For these applications, scalability is as important as device performance. Two-dimensional MoS_2 exhibits a direct band gap and enables high fidelity electrostatic control due to its reduced dimensionality and the absence of dangling-bonds at the surface. MoS_2 is therefore an ideal channel material for future FETs. Atomic layer deposition (ALD) is a promising technique for scalable, conformal, and back-end-of-line compatible MoS_2 deposition. While promising, the electrical performance of ALD grown 2D MoS_2 does not meet expectations when compared to the electrical properties of mechanically exfoliated MoS_2, due its polycrystalline nature. Polycrystalline MoS_2 contains grain boundaries that act as scattering centers, trap-rich regions, and structural discontinuities, that degrade its desirable electronic properties. In this work, ALD processes were developed using a novel molybdenum precursor, $MoO_2(THD)_2$. $MoO_2(THD)_2$ contains bulky organic ligands, which could impose steric hindrance during surface reactions, thus limiting surface chemisorption density and favoring formation of larger crystal grains.

First, $MoO_2(THD)_2$ volatility and decomposition behavior were studied by thermogravimetric analysis (TGA). TGA showed sublimation beginning at 120°C with 100% mass loss at 300°C. Next, plasma and thermal ALD processes were developed at 400°C. A mixed H_2S/Ar co-reactant was used for both plasma and thermal ALD. The effects of precursor and co-reactant dosing times, co-reactant ratios, as well as purge conditions were systematically investigated using in situ ellipsometry. The growth per ALD cycle (GPC) was measured to be 0.07 Å/cycle for the thermal recipe and 0.15 Å/cycle for the plasma process. The resulting films were characterized by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and atomic force microscopy (AFM). XPS indicates near-stoichiometric MoS_2. Raman spectra confirm MoS_2 vibrational modes and film crystallinity for both processes, while AFM reveals smooth, continuous films without out-of-plane features, with an RMS roughness of ~0.5 nm.

Overall, this work establishes $MoO_2(THD)_2$ -enabled thermal and plasma-enhanced ALD at 400 °C as a scalable route to smooth, continuous, and crystalline MoS_2 thin films. These results lay the groundwork for integrating conformal, large-grain MoS_2 channels into back-end-of-line compatible process flows, with ongoing grain-size quantification and electrical testing expected to link microstructural improvements to device performance.

3:15pm **AP+2D+EL+EM+PS+TF-WeA-5 Low Temperature Magnetized Plasmas for Processing of Two-Dimensional Materials***, **Yevgeny Raitses,*** Princeton Plasma Physics Laboratory*; Stanislav Musikhin, Yerbolat Ussenov,* Princeton University Plasma Physics Lab*; Satya Butler, Saien Xie,* Princeton University*; Nirbhav Chopra,* Princeton University Plasma Physics Lab **INVITED**

Low-temperature magnetized plasmas generated by electron beams or non-thermal electrons offer new opportunities for atomic-scale materials processing relevant to microelectronics and quantum technologies.[1-3] Operating at low pressures (0.1–10 mTorr), the applied magnetic field enables spatial separation between a high-density plasma generation region (~10^{11}–10^{12} cm^{-3}, electron energies >10 eV) and a peripheral processing region characterized by lower plasma density (<10^9 cm^{-3}) and electron temperatures (<1 eV).[4] Substrates placed in this region are primarily exposed to low-energy ion fluxes (≲ a few eV), enabling damageless processing of two-dimensional materials or processing with a controllable defect formation of such materials. However, plasma instabilities can drive anomalous cross-field transport and increase ion fluxes and energies at the surface.[5] We present experimental results on instability mitigation in ExB plasma systems[4] and demonstrate improved low-damage processing of graphene and transition metal dichalcogenides. Quantitative defect characterization in plasma-treated monolayered WS_2 films is presented and benchmarked against conventional RF inductively coupled plasma processing. A focus will also be made on the effect of vacuum conditions in the plasma reactor chamber on the defect formation

(e.g. sulfur vacancies). Applications to hydrogen and nitrogen surface passivation of diamond for quantum devices are also discussed.[2]

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Acknowledgement

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4:15pm **AP+2D+EL+EM+PS+TF-WeA-9 Impact of Fluorination and Oxygenation Sources on the Thermal Atomic Layer Etching of Crystalline MoS_2***, **Spencer Smith**, Steven M. Hues, Elton Graugnard,* Boise State University

Atomic layer etching (ALE) has emerged as a transformative technique for atomic-scale processing of two-dimensional (2D) materials, including molybdenum disulfide (MoS_2), a promising semiconductor due to its high carrier mobility in monolayer form. Precise etching of MoS_2 films offers a pathway for tuning electrical and optical properties through controlled thickness. Previous studies have explored alternative fluorination and oxygenation chemistries for thermal ALE of amorphous MoS_2, including oxygen sources such as H_2O and O_3 and fluorine sources including HF/pyridine and MoF_6. In this work, we investigate the application of these alternative chemistries to the thermal ALE of MOCVD-grown and ALD-grown MoS_2 films. Preliminary work on ALE of crystalline MoS_2 indicates that etching occurs at defects and grain boundaries. This study aims to correlate etching behavior with changes in surface topography and defect density. Etching effectiveness will be characterized by atomic force microscopy, Raman spectroscopy, and photoluminescence spectroscopy. This study seeks to further expand the capabilities of ALE for precise processing of 2D materials relevant to next-generation semiconductor devices.

4:30pm **AP+2D+EL+EM+PS+TF-WeA-10 Atomic Layer Etching of Tungsten Disulfide in O2/Ar and BCl3/Ar Remote Plasmas***, **Jeremy J. Mettler**,* University of Houston*; Jaehong (Russell) Kwon, David. B. Graves,* Princeton University*; Vincent M. Donnelly,* University of Houston

Transition-metal dichalcogenides (TMDs) are a class of 2D materials consisting of covalently bonded sheets. Multi-layers are held together by cross-plane van der Waals forces. While these materials hold promise in future semiconductor applications, processes for manufacturing using TMDs are in the early stages of development. One challenge is obtaining uniform, monolayer growth of TMD films over large areas. Chemical vapor deposition results in the formation of multilayer islands. Etching of TMD films will also be required, if for no other reason than to thin multilayers to single layers. Atomic layer etching (ALE) is likely to be called upon for etching steps. TMDs are easily damaged by high temperature and energetic species bombardment, making thermal or plasma-assisted etching challenging. We have explored ALE of WS_2, a promising TMD 2D material. A remote plasma supplied reactive radicals. A switchable magnetic field allow low energetic ion bombardment to be turned on or off while having little effect on radical density. ALE of WS_2 was achieved in a two-step process. Vacuum-transfer x-ray photoelectron spectroscopy (XPS) was used to characterize the chemical composition and thickness of the remaining film at various stages in the process. Sulfur-terminated multilayer films of WS_2 were exposed to O atoms downstream of an Ar/O_2 inductively coupled plasma (ICP). Without ion bombardment thermal O atoms removed S from the surface and formed a tungsten oxide layer 1-2 monolayers thick, with a composition of roughly WO_4. These results agree favorably with parallel molecular dynamics simulations. In the presence of low energy ions (~15 eV) at a flux of ~3 x $10^{15}cm^{-2}$, the etching rate increased several-fold and the W-oxide stoichiometry was not changed. The Ar/O_2 plasma was followed by Ar/BCl_3 plasma to selectively etch the tungsten oxide layer relative to the underlying WS_2. This step required low energy ion bombardment to remove the WO_4 film and expose the next WS_2 layer. A detailed analysis of the film at various stages in the ALE process was carried out by using the high-resolution W(4f), S(2p), B(1s) and Cl(2p) in the film as well as the Si(2p) from the underlying substrate and O(1s) in the WS_2 film and underlying interfacial native oxide layer on Si. A complete picture of the stoichiometry of the film during ALE was obtained and will be presented.

This material is based upon work supported by the U.S. Department of Energy, Office of Science, Fusion Energy Sciences and Basic Energy Sciences, as part of the Extreme Lithography & Materials Innovation Center (ELMIC), a Microelectronics Science Research Center (MSRC), under contract No. DEAC02-09CH11466.

4:45pm **AP+2D+EL+EM+PS+TF-WeA-11 Investigation of Layer-by-Layer Etching of MoS_2 by Atomic Oxygen and XeF_2***, **Sei-won Chung**, Daniel Cho, Jane Chang,* University of California, Los Angeles

As semiconductor devices continuously scale down, the demand for channel materials of field effect transistors (FETs) with high mobility at low dimensions has increased. 2D transition metal dichalcogenides (TMDs) have gained interest due to relatively consistent mobility at 5 nm of body thickness compared to conventional silicon channel. However, non-uniform large area synthesis has been a challenge in integration. To improve device performance, non-uniform adlayers should be removed layer-by-layer to realize a uniform and large-area TMD films.

To investigate layer-by-layer etching of MoS_2, thermochemical analysis suggests thermodynamic feasibility of using oxygen and fluorine chemistries for MoS_2 etching. Individual and synergistic effects of Ar^+, O radical (produced by a coaxial waveguide microwave source) and XeF_2 (3Torr) were studied in the molecular beam where each species can be independently controlled in flux and energy. The as-received MoS_2 has S/Mo and Si/Mo ratios of 1.6 and 1.0. Neither O nor XeF_2 spontaneously reacted with the as-received MoS_2. Ar^+ ion beam (200V, 0.5mA, 10s) was used to remove surface contamination prior to etching, resulting S/Mo and Si/Mo ratios of 0.94 and 0.18 respectively. Following in-situ Ar^+ ion beam cleaning, O radical was shown to oxidize MoS_2 decreasing S/Mo from 0.94 to 0.46, while XeF_2 removes MoS_2 increasing Si/Mo from 0.18 to 7.1. It showed surface fluorination (~3%), corresponding to formation of $MoOF_x$ and CF_x.

Finally, the sequential process consisting of Ar^+ ion bombardment, O radical introduction, and XeF_2 vapor exposure (0.5T, 10 pulses) was applied which could enable surface activation, self-limiting oxidation and removal of modified layer by forming oxyfluorides. After XeF_2, O atomic composition decreased and S atomic composition increased indicating removal of MoO_3 with surface fluorination (~3%) of MoF_x and $MoOF_x$. Increasing number of pulses to 20 increases S/Mo from 1.1 to 1.4 while reducing the MoO_3 content. This research reveals the individual and combination effects of Ar^+ ion beam, O radicals and XeF_2 on MoS_2 etching and potentially applied to investigating mechanism of layer-by-layer etching of MoS_2.

This research is supported by the U.S. DOE, Office of Science, as part of the ELMIC MSRC through the Plasma-enabled 2D Materials project at PPPL, under contract No. DEAC02-09CH11466.

5:00pm **AP+2D+EL+EM+PS+TF-WeA-12 Width Reduction and Edge Smoothing of 2D MoS_2 Nanoribbons by Lateral Thermal Atomic Layer Etching***, **Janine Wyand**,* University of Colorado at Boulder*; Tara Pena, Eric Pop,* Stanford University*; Steven George,* University of Colorado at Boulder

Atomic layer etching (ALE) of 2D MoS_2 nanoribbons is important for the fabrication of MoS_2 channel transistors. E-beam lithography and conventional dry etching processes face problems when etching MoS_2 films. These disadvantages include delamination for nanoribbon widths < 25 nm and inability to control line edge roughness. ALE methods may bypass these limitations and produce narrower width MoS_2 channels with smoother edges that may have better electrostatic control and on/off switching.

Narrowing the width of 2D MoS_2 nanoribbons requires lateral etching in the 2D plane. Our earlier work on the thermal ALE of 2D MoS_2 showed that sequential exposures of O_3 and $SOCl_2$ produced lateral etching by either “outside-in” or “inside-out” mechanisms. In this study, the “outside-in” lateral etching of 2D MoS_2 crystalline nanoribbons was utilized to reduce the widths of 2D MoS_2 nanoribbons. O_3 (ozone) was used for MoS_2 oxidation to MoO_3 and $SOCl_2$ (thionyl chloride) was used for the volatilization of MoO_3 as MoO_2Cl_2. The studies were performed using high quality 2D MoS_2 nanoribbons on silicon coupons. The MoS_2 nanoribbons were prepared from monolayer 2D MoS_2 films using e-beam lithography and dry etching.

The etching of the 2D MoS_2 nanoribbons was examined by atomic force microscopy (AFM) at 150°C. The lateral etching could be quantified by returning to the same nanoribbon after various numbers of etching cycles

and measuring the nanoribbon width using AFM. **Figure 1** shows that the width of the nanoribbons decreases progressively versus number of etching cycles. The AFM images indicate that the etching cycles also smooth the nanoribbon line edge roughness.

The AFM images were consistent with lateral etching at the edges of the 2D MoS_2 nanoribbons. The AFM measurements determined that the 2D lateral etching rate was ~3.9 Å per etching cycle at 150°C as displayed in **Figure 2**. This lateral etch rate represents ~1 MoS_2 units removed per etching cycle at the step edge of the 2D MoS_2 crystalline domains. Additional AFM measurements revealed that nanoribbon widths < 25 nm were possible using this thermal ALE process.

Plasma Science and Technology
Room 315 - Session PS1-WeA

Machine Learning for Plasma Processes

Moderators: Dr. Robert Bruce, IBM Research, T. J. Watson Research Center, **Joseph Vella**, TEL

2:15pm **PS1-WeA-1 Machine Learning-Assisted Plasma Process Monitoring and Optimization***, **Fatima Jenina Arellano**, Kenta Doi, Fumito Ootake, Tadamasa Kobayashi, Kenta Tanino, Tzuan Chou, Yutaka Nishioka, Kouta Kawahara, Hanna Taku,* ULVAC, Inc., Japan **INVITED**

Advanced packaging is becoming an increasingly important part of AI-era semiconductor scaling alongside continued transistor scaling, as modern computing systems increasingly rely on heterogeneous integration, larger-format packaging, high interconnect density, and package-level thermomechanical reliability to achieve higher bandwidth, lower latency, improved power efficiency, and greater compute density. In both wafer and panel-level packaging, plasma-based etching must operate across increasingly diverse material systems including organic build-up films, dielectrics, polymers, metals, and deep silicon structures, while maintaining tight requirements in uniformity and reliability over larger substrates. In these systems, plasma nonuniformity and substrate warpage become major challenges that impact process stability and yield. To help address these challenges, we explore the use of machine learning techniques such as transfer learning, artificial neural networks, and Hidden Markov models alongside conventional plasma simulations, diagnostics, and process development tools. Target applications include correlating wafer-scale (often axisymmetric) plasma simulation behavior with panel-scale experimental results; improving endpoint detection and plasma process monitoring for the etching of organic materials and deep silicon structures; bridging experimental and prediction gaps in electron temperature and electron density estimation from optical emission spectroscopy; and accelerating plasma process and tool optimization.

2:45pm **PS1-WeA-3 Autonomous Determination of Plasma Reaction Rates Using Plasma-Physics-Informed Machine Learning***, **Yusuke Ando**, Takayoshi Tsutsumi, Kenichi Inoue, Kenji Ishikawa,* Nagoya University, Japan

The inherent complexity of plasma reaction fields has long hindered precise control of process outcomes. The lack of reaction databases often results in discrepancies between simulations and experiments and delays the implementation of new gas chemistries. The direct application of previously proposed methods for calculating reaction rates or cross sections, such as the transition state theory, remains challenging due to the vast number of reactions and nonequilibrium plasma fields where reactive species often deviate from the Maxwell-Boltzmann distribution. Consequently, data-driven approaches have recently attracted increasing attention as alternative analysis tools for process development [1]. In addition, previous studies have demonstrated that neural networks can virtually reproduce conventional liquid-phase chemical reactions [2].

In this study, we propose a plasma reaction neural network (PRNN) as a framework for the simultaneous analysis of plasma reactions. The neural network, designed based on plasma physics, consists of a single hidden layer with an exponential activation function and is capable of simulating the entire reaction network, where each node represents an elementary reaction. Given densities and temperatures of electrons, ions and neutral species at a certain time, the PRNN predicts the temporal evolution of each reactive species. This plasma-physics-informed machine learning architecture incorporates several physically meaningful parameters, particularly reaction rate coefficients. To validate the proposed model, time-resolved quadrupole mass spectrometry and Langmuir probe measurements were performed under various conditions with varied gas mixtures, pressures, and RF powers to train the PRNN. After fitting the model to the experimental dataset, the stoichiometric coefficients and reaction rate coefficients were extracted from the edge weights and node biases, respectively. The proposed methodology enables direct experimental acquisition of reaction rates with significantly reduced time and resources, regardless of the energy distributions of reactive species. Furthermore, the PRNN is applicable to other complex plasma systems, paving the way for efficient data acquisition for new gas chemistries and the realization of digital twins for plasma processes.

[1] Y. Ando et al., Diam. Relat. Mater. **151**, 111687 (2025) [2] W. Ji, S. Deng, J. Phys. Chem. A **125**, 1082 (2021)

3:00pm **PS1-WeA-4 Machine Learning Enhanced Kinetic Modeling of Plasma Processing Reactors***, **Andrew Tasman Powis**,* Princeton Plasma Physics Laboratory*; Alexander Khrabry,* Princeton University*; Melanie Huynh,* University of California Berkeley*; Salman Sarwar,* Princeton University*; Domenica Corona Rivera, Edward Startsev,* Princeton Plasma Physics Laboratory*; Ali Mesbah,* University of California Berkeley*; Igor Kaganovich,* Princeton Plasma Physics Laboratory

For plasma processing, there is a need to simulate large plasma devices via kinetic means, since the Electron Velocity Distribution Function in these devices is non-Maxwellian and therefore fluid treatment is insufficient to accurately capture the physics. Even on modern GPU accelerated high-performance computing systems, such simulations can take days or even weeks to deliver engineering relevant insights. Machine Learning (ML) offers many possibilities for accelerating kinetic plasma simulation or developing reduced order models which can provide insights at speeds that could enable rapid computer aided engineering of plasma reactors. We will discuss three recent approaches, including (1) using convolutional neural networks to provide improved initial conditions for PIC simulations which can reduce runtime by nearly 20x [1], (2) development of a hierarchical-embedding autoencoder with predictor (HEAP) architecture which can accurately model the multiscale nature of plasma dynamics [2], and (3) generalizable and interpretable symbolic regression models for ion flux within a capacitively coupled plasma discharge [3]. Together, these methods demonstrate how ML can bridge the gap between high-fidelity kinetic simulation and the fast, predictive modeling needed for practical plasma reactor design.

[1] A. T. Powis, D. Corona Rivera, A. Khrabry, and I. D. Kaganovich, Phys. Plasmas 33, 013902 (2026).

[2] A. I. Khrabry, E. A. Startsev, A. T. Powis, and I. D. Kaganovich, Phys. Fluids 38, 045138 (2026).

[3] M. T. Huynh et al., submitted to Mach. Learn.: Sci. Technol. (2026).

3:15pm **PS1-WeA-5 Machine Learning Applications and Challenges in Low Temperature Plasma Systems***, **Kallol Bera**,* Applied Materials, Inc.*; Abhishek Verma,* Applied Materials Inc.*; Sathya Ganta, Shahid Rauf,* Applied Materials, Inc. **INVITED**

Low-temperature plasmas (LTPs) are widely used in the semiconductor industry, where plasma modeling plays significant roles for chamber design and process optimization. However, physics-based plasma simulations are computationally expensive due to their multi-dimensionality, nonlinear behavior, multi-physics coupling, complex chemistry, plasma-surface interactions and wide spatio-temporal scales (nm to m, ns to s). These limitations hinder their use in applications requiring rapid and repeated computation. Machine learning (ML), particularly deep learning–based nonlinear model order reduction, is increasingly used to accelerate plasma modeling. ML enables fast design exploration, real-time control, and process optimization. Operator learning techniques help accelerate key solvers in multi-physics simulations. For complex plasma chemistries involving many species and reactions, methods such as principal component analysis, graph neural networks are used for mechanism reduction and identification of dominant pathways. Bayesian optimization is developed for real-time reactor control and multi-objective optimization. ML-based interatomic potentials further enable accurate and efficient modeling of plasma–surface interactions. Advances in machine learning for LTP systems are demonstrated through several examples. Deep neural networks trained on simulation data have been used to accurately predict plasma variables across operating conditions in inductively coupled plasmas. A neural network with long short-term memory (LSTM) predicts well the time evolution of electrode current from unseen voltage sequences in RF hollow cathode discharges using substantially lower computational cost within the training range and outside the range. Applications of Fourier neural operators (FNOs) and Physics informed neural network (PINN) for coupled PDEs describing capacitively coupled

plasmas are also illustrated. Despite these advances, key challenges remain. High-fidelity training data whether generated using computational plasma modeling or experimentation, is scarce and expensive. ML models typically interpolate well but struggle to extrapolate. Exploring different gas chemistries and new reactor configurations are extremely challenging. LTP systems, being multiscale and strongly coupled across multiple physics, are difficult to learn. Purely data-driven models may also violate physical constraints. Physics-informed approaches, such as PINNs, aim to incorporate conservation laws into ML, improving reliability. Such hybrid ML models, combined with experimental data, offer a promising pathway toward digital twins for plasma-based semiconductor processes

Plasma Science and Technology
Room 315 - Session PS2-WeA

Low Global Warming Potential and Sustainability in Plasma Processing

Moderators: Phong Nguyen, Air Liquide, **Prof. Dr. Necip Uner**, Middle East Technical University

4:15pm **PS2-WeA-9 Impact of Low-GWP GST Etch Chemistries on PCM Device Performance and Reliability**, ***Luxherta Buzi,*** IBM Research*; Yohei Takakura, Kazunori Horiguchi,* DAIKIN INDUSTRIES, LTD.*; Aya Kagimura,* DAIKIN INDUSTRIES, LTD., Japan*; Asit Ray, Amlan Majumdar, Lynne M. Gignac, Matthew BrightSky, Jaylynn Sheppard,* IBM Research*; Yasuhiro Nojiri, Hisataki Hayashi,* DAIKIN INDUSTRIES, LTD., Japan*; Eric Joseph, Robert L Bruce,* IBM Research

PCM is an emerging non-volatile memory technology for AI and Storage Class Memory applications due to its low power consumption, high density, and fast switching capability. Optimization of GST etch chemistry and process integration while minimizing structural and compositional damage is critical for reliable PCM device operation and long-term endurance. GST is commonly etched using halogen-based plasmas, where hydrofluorocarbons are often employed for sidewall passivation and profile control. However, due to the ongoing phase-out of high global warming potential (GWP) gases, development of low-GWP alternatives is becoming increasingly important for future PCM manufacturing.

In this work we report on the development and integration of GST reactive ion etch (RIE) processes using DIN01, a proprietary low-GWP chemistry, combined with Xe and Ar gas mixtures with and without passivating additives. DIN01/Xe and DIN01/Ar processes demonstrated good elemental composition and were successfully implemented on integrated PCM hardware. Electrical characterization showed excellent wafer yield, strong within-chip yield, fast SET speed, and high cycling endurance. PCM etch processes using DIN01/Xe gas mixtures exhibited superior electrical performance over DIN01/Ar mixtures.

Transmission electron microscopy (TEM) and chemical analysis were performed on DIN01/Xe etched devices and compared to a conventional PCM etch gas mixture. After approximately 20 programming cycles, similar electrical behavior and chemical evolution were observed for both process schemes without evidence of significant trace of gas residue. However, optimization is required to address poor etch selectivity to the SiN hard mask that leads to tungsten redeposition and oxidation in DIN01-patterned structures.

These results demonstrate that DIN01-based GST etch processes can successfully enable integrated PCM device operation and high yield while maintaining structural integrity and long-term device reliability.

4:30pm **PS2-WeA-10 A Low-GWP Molecule for High-Performance Plasma Etching**, ***Phong Nguyen****, Nathan Stafford, Xiangyu Guo,* Air Liquide

In recent years, several countries and semiconductor manufacturing companies have announced targets for net-zero carbon emission by 2050 or earlier. Plasma etch processes are responsible for a high percentage of a semiconductor manufacturer's scope 1 emissions. Dielectric plasma etch applications are pervasive in the manufacturing process, and are a significant contributor to these scope 1 emissions. These processes typically employ high global warming potential (GWP) fluorocarbon gasses such as C4F8. . Not only is C4F8 a high GWP gas, in addition hard to abate high GWP chemistries such as CF4 maybe formed in the plasma fragmentation process.

To address this challenge without sacrificing process capabilities, we introduce a novel low-GWP molecule (intrinsic GWP ~0) designed as a robust alternative to legacy etchants. This alternative chemistry is engineered to permit advanced plasma etch performance while providing a friendly abatement profile that substantially reduces overall direct CO2-equivalent emissions, whether evaluated post pump with no dedicated PFC abatement technology or post abatement systems designed to abate a portion of the PFC.

Characterization of the etch characteristics is done using an Ellipsometer for thickness and selectivity assessment. Furthermore, the plasma etch chamber emission gas stream is analyzed and quantified by Fourier Transform Infrared Spectroscopy (FTIR). Complementary to FTIR analysis, Quadrupole Mass Spectrometry (QMS), is implemented to help identify emission species in the chamber through studying the positive ion fragments present inside the plasma.

Results demonstrate that this novel molecule matches legacy etching rates while delivering improved selectivity to amorphous carbon (a-C) mask materials. The combination of analysis via QMS and FTIR gives us a better understanding of the etching process, confirming that this novel molecule yields beneficial deposition-promoting positive ions and crucially lacks the CF3 fragmentation pathways responsible for excessive CF4 generation. In addition, this novel chemistry has shown improved etch performance with lower CO2 equivalent emission than the current baseline.

4:45pm **PS2-WeA-11 Machine-Learning-Assisted Investigation of CF_3–X (X=H, I) Plasma Kinetics In Semiconductor Manufacturing for Etch Effectiveness and Environmental Sustainability**, ***Chi-Yun Lin****, Jane Chang,* UCLA

Hydrofluorocarbons (HFCs) gases are commonly used in semiconductor manufacturing to etch silicon dioxide, an essential insulator in integrated circuits, either from chamber wall deposits or patterned features. CHF_3 plasma is utilized for its high etch rate (ER), comparable to CF_4, and favorable anisotropic etching characteristics, though its high global warming potential (GWP_{100}) of 12400 and long atmospheric lifetime (LT) of 222 have prompted its phasedown by the EPA. CF_3I has a lower atmospheric lifetime (<0.005) and GWP_{100} (<1), which are 4-5 orders of magnitude smaller than those of HFCs, making it a promising alternative gas.

This work investigates CF_3X-based plasmas (where X = H, I) in etching SiO_2 with a focus on machine learning to extract meaningful kinetic parameters for modeling. $CHF_3/O_2/Ar$ plasma was first used to evaluate the reduce and abate strategies. O_2 serves a dual role: process-gas additive to reduce the usage of CHF_3 for improving SiO_2 etching and abatement reactant for reducing high-GWP fluorocarbon emissions. The experimental and modeled SiO_2 etch rate increased with measured emission of SiF_4 (kg-CO_2e) and the modeled ratio of fluorine flux to oxygen flux (Γ_F/Γ_O), reaching above 150 nm/min under selected conditions. The corresponding downstream composition was converted to $MMTCO_2e$ for CHF_3, CF_4, and C_2F_6. After introducing O_2 to downstream abatement, the modeled $MMTCO_2e$ decreased by approximately a few orders of magnitude relative to the untreated emission.

$CF_3I/O_2/Ar$ was evaluated as a lower-GWP alternative. A differentiable surface-kinetic model was developed to infer the unknown iodine adsorption and abstraction probabilities, using experimental SiO_2 etch rates as the ground truth, while modeled ion fluxes and etch rates served as known inputs. Descriptor information from CF_3X (X = F, Cl, Br, and I), including C–X bond dissociation energy, Si–X bond strength, and electronegativity, was used to define physically reasonable bounds for the unknown iodine-related surface kinetics. Automatic differentiation through the ODE solver reduced the average absolute percent error from 23% for the initial assumption to 12.5% after applying new surface kinetic by AI/ML inference. As the SiO_2 etch rate increases from 50–80 nm/min to above 100–130 nm/min, the corresponding measured and modeled emission for CF_3I and CF_4 decreases by an order of magnitude in $MMTCO_2e$.

Overall, selected $CF_3I/O_2/Ar$ operating conditions showed the SiO_2 etch rate increased by approximately 70% while the estimated emission impact reduce by an order of magnitude, indicating that higher etch performance can be achieved with lower greenhouse-gas-equivalent emissions.

5:00pm **PS2-WeA-12 A Low GWP and Low Emission Gas for Trench and Hole SiO_2 Etching**, ***Scott Biltek****, Nathan Stafford, Phong Nguyen, Angéla Christin,* Air Liquide

Over the past few years, numerous countries and semiconductor manufacturing entities have unveiled their commitments to achieving net-zero carbon emissions by 2050 or even sooner. A substantial fraction of direct emissions (as CO_2e) in semiconductor manufacturing stems from plasma etch processes. Standard gases for dielectric etching such as C_4F_8,

CH_2F_2, CHF_3 or CF_4 typically have high global warming potential (GWP) or emit high GWP byproducts after plasma fragmentation and recombination processes. While low GWP etch gases exist, it is challenging to find alternative gases that provide comparable etch process performance, with limited recipe development, that significantly decreases the direct CO_2e etch process emissions.

In previous work we have presented a novel low GWP etching gas as a replacement for C_4F_8 in high power, high aspect ratio etching[1]. In this work we revisit that gas as a replacement for C_4F_8 in lower power SiO_2 etches for both trench and contact hole applications. In both applications, we once again demonstrate matching etch performance with minimal recipe modification (simply replacing C_4F_8 flow with an appropriate replacement gas flow rate). Due to the high efficiency in the dissociation of the replacement gas, this etch performance is achieved at a significantly lower flow rate relative to C_4F_8. In addition to the low intrinsic GWP_{100} of the low GWP gas (<50) compared to C_4F_8 (~10,200), we also show significant (~80%) reduction in GWP_{100} of the final post plasma exhaust emissions as measured via fourier transform infrared spectroscopy (FTIR). In combination with past results, this strongly indicates the broad compatibility of this low GWP gas with current C_4F_8 plasma etch processes.

[1] - Biltek, Scott, et al. "Low GWP and Low Emission Gases for High Aspect Ratio Etching." AVS 70th International Symposium & Exhibition, Nov. 2024, Tampa, FL. Conference Presentation.

Atomic Scale Processing Mini-Symposium
Room 316 - Session AP+EL+MS+PS+TF-ThM

Advancing Spectroscopic Ellipsometry and Other in-Situ Techniques to Enable Atomic Scale Processing

Moderators: Prof. Dr. Marcel Junige, University of Colorado at Boulder, **Dr. Adrie Mackus**, Eindhoven University, Netherlands

8:00am **AP+EL+MS+PS+TF-ThM-1 Atomic Processes in Surface-Limited ALD Growth Studied by Real-Time Spectroscopic Ellipsometry**, ***Eva Schubert***, *Ufuk Kilic, Yousra Traouli, Mathias Schubert,* University of Nebraska - Lincoln **INVITED**

We employ in-situ spectroscopic ellipsometry (SE) to investigate the growth dynamics of ultrathin transition metal oxide films (ZnO, WO_3, TiO_2, and Ga_2O_3) during plasma-enhanced atomic layer deposition (PE-ALD). To analyze the dynamic optical response, we introduce a dual-box regression model in which the first box represents surface roughness using an effective medium approximation (EMA), while the second box captures cyclic variations in subsurface layer thickness associated with molecular rearrangements occurring during each ALD cycle. This approach provides a time-resolved and quantitative description of both surface roughness evolution and subsurface film growth dynamics, enabling accurate characterization of layer-by-layer deposition processes.

Accurate extraction of film thickness, density, and roughness at elevated substrate temperatures requires precise knowledge of the temperature-dependent dielectric function (TDF), which can differ substantially from room-temperature values. In this work, the TDFs of the transition metal oxides were determined through multi-sample analysis using optical data obtained from films of varying thicknesses measured at different stages of the growth process. The incorporation of experimentally verified dielectric functions enables the dual-box model to reliably describe the evolving optical response during high-temperature deposition, allowing detailed monitoring of sub-monolayer coverage, interface formation, and roughness evolution throughout the ALD process.

Post-deposition structural and chemical characterization using scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) corroborates the in-situ optical measurements and provides complementary insight into film crystallinity, morphology, and composition.

The capability of in-situ ellipsometry as a powerful tool for investigating growth dynamics will also be demonstrated for multilayer fabrication, ultra-precise thickness control, and monitoring of phase transitions in materials synthesized using physical and chemical vapor deposition techniques.

8:30am **AP+EL+MS+PS+TF-ThM-3 Tracking Critical Points: In Situ Ellipsometry for Rapid Assessment of Atomic Layer Processes on III-V Interfaces**, ***John Murphy***, *Glenn Jernigan, Michael Johnson, David Boris, Scott Walton, Jill Nolde,* U.S. Naval Research Laboratory

Plasma-enhanced atomic layer processing (PE-ALD, ALE) on semiconductor interfaces, especially III-V semiconductor interfaces, requires precise control of plasma–surface interactions to achieve oxide-free interfaces and low-defect dielectric interfaces. Conventional post-process characterization (XPS, AFM, CV profiling) is time-consuming and inefficient for navigating large, nonlinear plasma process parameter spaces. In this work, we demonstrate an *in situ* spectroscopic ellipsometry (SE) methodology that provides a real-time, model-light assessment of III-V surface quality by tracking high-energy critical-point amplitudes directly from the pseudodielectric function, without constructing full multilayer optical models. Notably, critical points in the 4–5 eV range have photon penetration depths of ≈10 nm in III-V semiconductors, making them highly sensitive to near-surface chemistry.

This methodology is illustrated on InAs (100) surfaces during remote Ar/H2 plasma treatments, aimed at reducing native oxides. In the case of InAs (100) surfaces the E_0' critical point (≈4.4 eV) is used as the primary surface-quality metric during plasma treatments. While second-derivative analysis of the directly measured pseudodielectric function provides temperature dependent energy positions for critical points and the magnitude of which are calibrated using chemically clean reference surfaces.

Variations in the normalized E_0' amplitude are monitored as function of various substrate temperatures (100–300 °C), plasma powers (100–500 W), and H_2 flow fractions (1.25–6.25%) to capture the interplay between oxide removal, metallic species formation, and plasma-induced disorder with greater sensitivity and immediacy than conventional XPS metrics. These variations can be used to rapidly define practical processing windows and enable efficient down-selection within large plasma parameter spaces. The results highlight a generally useful strategy for integrating in situ critical-point tracking into atomic layer processing of III-V materials and suggest straightforward extensions to other compound semiconductor and dielectric growth environments.

8:45am **AP+EL+MS+PS+TF-ThM-4 Intelligent Sustainable ALD Research Platform Integrating On-Demand Precursor Delivery with *in situ* Imaging Ellipsometry**, ***Takeshi Momose***, *Hiroshi Nishizato,* Kumamoto University, Japan*; Yugo Nakaya,* HORIBA STEC, Co., Ltd. / Kumamoto University, Japan*; Kanta Ishida, Shota Oda, Kinichi Nasu,* Kumamoto University, Japan*; Lianhua Jin,* University of Yamanashi, Japan*; Hiroshi Okajima,* Kumamoto University, Japan

The development of efficient and sustainable processes in atomic layer deposition (ALD) is becoming increasingly important for the fabrication of next-generation three-dimensional (3D) semiconductor devices. However, conventional run/vent precursor delivery systems are inherently inefficient, with precursor dosing durations reported to be only 1-10% of the total cycle time, resulting in over 90% of the precursor being discarded without contributing to film growth. Furthermore, the development of the ALD process, especially the conformality of high-aspect-ratio (HAR) features, typically relies on time-consuming offline characterizations. In this study, we developed an integrated intelligent ALD research platform that combines on-demand precursor delivery with *in situ* imaging ellipsometry for real-time conformality analysis.

The platform integrates two key technologies. First, to achieve stable and precise on-demand precursor delivery, we developed an in-house piezoelectric-valve system. By applying a machine learning (ML) and control engineering approach, we achieved feedforward valve control, thereby successfully compensating for the inherent hysteresis and nonlinear flow responses of the valve. This allowed the achievement of ideal step-wise gas pulses with a settling time of only 60 ms, compared with 2 s in the uncontrolled condition. This precise control significantly enhances the precursor utilization efficiency while maintaining rapid pulse operation. Second, an in-house lateral high-aspect-ratio (LHAR, AR = 300) test structure combined with imaging ellipsometry was employed to quantitatively monitor the temporal evolution of the precursor penetration depth (PD) during ALD. Sample imaging was enabled by installing an Offner optical system on our custom-built ellipsometer, which allowed us to determine the PD formed in a groove on the Si substrate. As this is currently in an offline setting, we plan to install it in an ALD chamber with on-demand precursor delivery for real-time PD monitoring.

The integration of these technologies enables the instantaneous evaluation of the effect of precise changes in the precursor dose and pulse duration on conformality within HAR features. Initial experiments using trimethylaluminum (TMA) demonstrated that PD evolution in LHAR structures could be tracked. The proposed platform concept leads to a foundation for data-driven, low-waste, and rapidly adaptive ALD process development, contributing to reduced precursor consumption, shorter development cycles, and more sustainable atomic-scale manufacturing.

9:00am **AP+EL+MS+PS+TF-ThM-5 Real-Time Insights into Plasma-Based Atomic-Scale Processing via Ellipsometry**, ***Gottlieb Oehrlein***, University of Maryland College Park **INVITED**

Single-wavelength ellipsometry (SWE) has been employed as an attractive diagnostic technique for real-time, non-invasive monitoring of thin-film evolution during semiconductor processing. Characterized by high temporal resolution and sub-angstrom sensitivity, SWE allows for the precise detection of surface modifications without disrupting the plasma environment. These aspects, combined with relative ease of integration into complex process chambers, make SWE a premier tool for tracking atomic-scale processing. Because of its rapid sampling capabilities, SWE is an invaluable tool for probing the primary kinetics of plasma-surface interactions. We will discuss several case studies where ellipsometric monitoring provides critical insights into complex surface mechanisms, including the achievement of high material etching selectivity for dielectric materials, semiconductors and metals, atomic layer etching (ALE), and the dynamics of electron-beam enhanced remote plasma processing.

While ellipsometry excels at tracking processes including endpoints across diverse materials, optical data alone cannot resolve complex surface chemistry. This talk emphasizes the methodological importance of coupling ellipsometric data with chemical analysis, e.g. X-ray Photoelectron Spectroscopy (XPS) or other materials characterization techniques, to

construct robust, chemically informative surface models. Integrating these complementary diagnostics bridges the gap between optical observations and fundamental chemical mechanisms.

Acknowledgements

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9:30am **AP+EL+MS+PS+TF-ThM-7 Spectroscopic Ellipsometry for Screening Chemical and Microstructural Properties of MoS_2 Thin Films Grown by Plasma Enhanced ALD***, **Douglas Heine,*** University of Michigan, Ann Arbor*; Paula Arellano,* University of Michigan*; Ageeth Bol,* University of Michigan, Ann Arbor

The two-dimensional layered semiconductor MoS_2 has attracted significant interest for applications in next-generation electronics, photonics and electrocatalysis due to its favorable electronic and optical properties. Plasma-enhanced atomic layer deposition (PEALD) provides a scalable route for the growth of MoS_2 thin films, offering excellent thickness control, conformality, and relatively low deposition temperatures, which are advantageous for integration into device architectures. However, PEALD grown MoS_2 films often exhibit complex microstructures, consisting of small and misaligned grains. Such structural disorder can adversely affect device performance due to the strong optical and electronic anisotropy of MoS_2[(1)].

In this presentation, we report the development of a model that rapidly estimates electronic and microstructural properties of PEALD-grown MoS_2 thin films from ellipsometry data. The influence of misaligned, out-of-plane oriented grains (“fins”) is described using a Bruggeman effective medium approach for intrinsically anisotropic inclusions[(2)], while local structural disorder is incorporated through modest variations in the intrinsic optical constants. The model is applied to a broad set of films grown under different deposition conditions, and the extracted parameters are correlated with independently measured film properties, including composition, crystallinity and roughness. By enabling rapid insight into the film microstructure and electronic properties, this ellipsometry-based analysis facilitates the development of PEALD processes that yield higher quality MoS_2 films.

(1) Toolbox of Advanced Atomic Layer Deposition Processes for Tailoring Large-Area MoS2 Thin Films at 150 °C. M. Mattinen et al. ACS Applied Materials & Interfaces, 2023 15 (29), 35565-35579.

(2) Bruggeman formalism versus “Bruggeman formalism”: particulate composite materials comprising oriented ellipsoidal particles. T. G. Mackay and A. Lakhtakia. Journal of Nanophotonics, 2012 6 (1), 069501-069501.

9:45am **AP+EL+MS+PS+TF-ThM-8 Monitoring Electron Beam-Assisted Atomic Layer Etching via Real-Time Ellipsometry and in-Situ XPS: Insights on the Early Stages***, **Vennela Vuruputuri,*** Department of Physics, and Institute for Research in Electronics and Applied Physics, University of Maryland*; Robert Bruce,* IBM TJ Watson Research Center*; Nathan Marchack,* IBM TJ Watson Center*; Marinus Hopstaken,* IBM TJ Watson Research Center*; Gottlieb Oehrlein,* Department of Material Science and Engineering, and Institute for Research in Electronics and Applied Physics, University of Maryland

Electron beam assisted etching of plasma functionalized materials has emerged as a novel approach to processing damage sensitive materials. This method employs synergistic interactions between low energy electrons and reactive neutral species to enable material removal while mitigating ion bombardment induced damage and achieving higher atomic precision. While this seems to be a promising approach, the influence of electron irradiation on surface chemistry, defect formation and bond scission are not well understood. Clarifying these mechanisms is essential to establishing electron beam-assisted atomic layer etching (EB-ALE) as a viable method for nanoscale fabrication. In this work, we investigate the EB-ALE of chlorinated single crystal silicon (c-Si) surfaces prepared using a remote plasma source with Ar/Cl_2 gas mixtures. The study examines the dependence of surface coverage, material modification and etching behavior on key parameters, including neutral exposure, and flood gun parameters like electron energy and dose delivery. ALE relies on self-limiting surface reactions, and one key question is if the EB-ALE process can maintain a constant etch depth per cycle as surface roughness, defect or byproduct accumulation evolve. The surface evolution is monitored in real time using in-situ ellipsometry, and it is further characterized using X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) to analyze changes in chemical composition and surface roughness respectively. Together, these measurements will provide a framework to better understand the mechanisms governing EB-ALE and ensure predictive control over low-damage atomic scale processing.

Acknowledgements

This material is based upon work supported by the National Science Foundation under the award number NSF CMMI – 2350338.

11:00am **AP+EL+MS+PS+TF-ThM-13 Building Intelligence Through in Situ Techniques for Atomic Layer Processes***, **Parag Banerjee,*** University of Central Florida **INVITED**

Note: This abstract was initially for TF, but I request that the talk be moved to Gary W Rubloff (GWR) Symposium as it is much more topically relevant.

Atomic layer processing, which consists of atomic layer deposition (ALD) and atomic layer etching (ALE), provides the ultimate processing toolbox for dimensional and compositional control of thin films. In this talk, I will first provide a historical perspective of how specifically, *in situ* techniques implemented for atomic layer processes have impacted our understanding of surface physical and chemical mechanisms that impart atomic layer processes their singular deposition and/or etching characteristics. For example, early work using *in situ* techniques such as, quadrupole mass spectrometry (QMS), Fourier transform infrared spectroscopy (FTIR) and quartz crystal microbalance (QCM) laid the foundation for understanding of the popular ALD chemistries of Al_2O_3 and ZnO. Next, I will showcase the use of *in situ* QMS and spectroscopic ellipsometry (SE) to rapidly screen new precursor molecules and deposit materials for a myriad of applications ranging from lasing fibers to passivation contacts for solar cells. The use of tandem *in situ* techniques will be highlighted which allows for unambiguous determination of both chemical and physical aspects of growth mechanisms during atomic layer processes. Last, due to the massive amounts of data obtained during *in situ* monitoring of processes, machine learning (ML) algorithms can now be successfully used to interpret process performance against process parameters, determining end points and establishing process – property causality. In summary, this presentation highlights the evolution of atomic layer diagnostics from foundational surface chemistry to modern, AI-driven process optimization.

11:30am **AP+EL+MS+PS+TF-ThM-15 Real Time Spectroscopic Ellipsometry and Passivation Studies of Ultra-Thin a-Si:H Films for C-Si / a-Si:H Heterojunction Solar Cells***, **Venkanna Kanneboina,*** *Prabin Dulal, Bishal Bishal Shrestha, Madan K. Mainali, Balaji Ramanujam, Ambalanath Shan, Nikolas J. Podraza,* University of Toledo

High passivation quality and excellent electronic properties of ultrathin hydrogenated amorphous silicon (a-Si:H) layers are essential to fabricate high efficiency crystalline silicon (c-Si) / a-Si:H heterojunction intrinsic thin layer (HIT) solar cells. The quality of the surface passivation of both undoped and doped a-Si:H layers deposited on c-Si are studied using minority carrier lifetime (τ_{eff}) measurements. Stacks of undoped a-Si:H / n-type c-Si / undoped a-Si:H, n-type a-Si:H / undoped a-Si:H / n-type c-Si / undoped a-Si:H / n-type a-Si:H, n-type a-Si:H / undoped a-Si:H / n-type c-Si / undoped a-Si:H / p-type a-Si:H are fabricated by radio frequency plasma enhanced chemical vapor deposition (RF-PECVD). Real time spectroscopic ellipsometry (RTSE) is performed to monitor growth during the deposition of the stacks to determine the structural and optical properties of the undoped and n- and p-type doped a-Si:H. To prevent epitaxial growth on the c-Si wafers, the first layer of undoped a-Si:H is deposited at relatively low temperature of 120ºC without hydrogen dilution followed by a second layer of higher quality undoped a-Si:H with hydrogen dilution deposited at 160ºC. The influence of additional hydrogen plasma treatment (HPT) on the passivation quality of a-Si:H layers on c-Si is studied by subjecting the undoped a-Si:H on both sides of the c-Si wafers to a hydrogen plasma. Passivation studies are performed on stacks of undoped a-Si:H deposited on both sides of c-Si, and then with an additional stack of doped a-Si:H. The symmetrically deposited bilayers of undoped a-Si:H effectively passivated the c-Si. The best τ_{eff} = 11.61 ms is obtained with HPT on undoped a-Si:H bilayers for 30 seconds at 200ºC. The sample is exposed to atmosphere for about 30 min before it is loading into PECVD chamber and the measured τ_{eff} is 8.25 ms prior to deposition of the n-type a-Si:H. The τ_{eff} is recovered about 3 ms with doped n-type a-Si:H stack, whereas 1 ms is recovered with the n- and p-type a-Si:H stack. The passivation quality of single layer of ~6 nm undoped a-Si:H is also studied with variation of temperature from 120 – 200ºC. In this case, the τ_{eff} decreased from 3.85 to 1.6 ms as the temperature increased from 120 – 200ºC. High efficiency c-Si / a-Si:H HIT solar cells are fabricated using these optimized, high quality ultrathin a-Si:H layers.

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11:45am **AP+EL+MS+PS+TF-ThM-16 Quantifying Interface Formation in InP/Al_2O_3: ALD Films Probed by XPS and MIS C-V**, ***Fabiano Borges,*** University of Campinas (Unicamp) and Federal Institute of Education, Science and Technology of São Paulo (IFSP), Brazil*; Cassio Almeida,* Semiconductor Laboratory (LabSem), Center for Telecommunication Studies (CETUC), Pontifical Catholic University of Rio de Janeiro (PUC-Rio), Brazil*; Ângela Albuquerque,* Brazilian Nanotechnology National Laboratory (LNNano, Brazilian Center for Research in Energy and Materials (CNPEM)), Brazil*; Gustavo Vieira,* Institute for Advanced Studies (IEAv), Department of Aerospace Science and Technology (DCTA), Brazilian Air Force, Brazil*; José Diniz,* University of Campinas (UNICAMP), Brazil

Abstract

Surface passivation of n-type InP was evaluated by X-ray Photoelectron Spectroscopy (XPS) depth-profile analysis after depositing an Al_2O_3 layer [1] with and without plasma treatments (oxidation (O2), nitriding (N2), oxidation followed by nitriding (O2N2), and nitriding followed by oxidation (N2O2)). To compare samples, we use the atomic fractions of Al2p, In3d, P2p, O1s, N1s, and C1s and two metrics [2]: top-film O/Al ratio at the first depth, with values near 1.5 indicating stoichiometric Al_2O_3; (ii) interface depth, the etch time where the sum of In+P≥20%.

The data show that O2 yields a stoichiometric surface (O/Al = 1.37) and the deepest interface (75s), consistent with a thicker interfacial oxide. N2 presents a very low O/Al (0.12) with detectable N and no interface onset within 120s, indicating a dense nitride/oxynitride barrier. N2O2 is intermediate (O/Al=1.42; interface 50s) with no residual N, suggesting oxidation of the nitride. The control sample shows oxidation (O/Al=0.51; interface 45s), while O2+sputtering produces the lowest O/Al (0.14) and the shallowest interface (35s), indicative of a less oxidized/less dense film.

Electrical C-V corroborates the chemical trends: the O2 sample exhibits a median flat-band voltage Vfb=0.00V (-0.30V for the control) and a donor density of the same order (2×10^{19} vs 1×10^{19} cm^{-3}), indicating a flatter band alignment without doping degradation. Altogether, O2 delivers the most stoichiometric Al_2O_3, a thicker/interfacial oxide and superior C-V metrics, pointing to improved passivation of InP compared with ALD on untreated surfaces; N2 forms a robust nitride that retards sputter breakthrough; and ALD delivers denser, more stoichiometric Al_2O_3 than sputtering.

References

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[2] A. G. Shard, "A step-by-step guide to X-ray photoelectron spectroscopy (XPS)," *J. Appl. Phys.*, vol. 131, no. 6, p. 061101, 2022.

Acknowledgments

This research is supported financially by IFSP, FINEP, CNPq and UNICAMP. This research used facilities of the Brazilian Nanotechnology National Laboratory (LNNano), part of the Brazilian Centre for Research in Energy and Materials (CNPEM), a private non-profit organization under the supervision of the Brazilian Ministry for Science, Technology, and Innovations (MCTI). The Spectroscopy and Scattering staff is acknowledged for the assistance during the experiment 20220304. The InP substrate weresupplied by LabSem of PUC-Rio. The author thanks the support of the Instituto de Estudos Avançados of the Brazilian Air Force.

Plasma Science and Technology
Room 315 - Session PS1-ThM

Advanced Ion and Reactant Control I

Moderators: Dr. Sebastian Engelmann, IBM T. J. Watson Research Center, **Prof. Dr. Christophe Vallee**, UAlbany

8:00am **PS1-ThM-1 Plasma Prize Talk: Drilling Really Tiny Holes in Glass: The Role of Ion Energy Control in Nano-Fabrication**, ***Steven Shannon,*** North Carolina State University **INVITED**

You would be amazed at how reliant our high technology economy relies on a process that at first glance sounds very straight forward... drilling holes in glass. Of course, this description simplifies things. These holes are as small as several hundred atoms in diameter and are as much as 200 times deeper than they are wide, and they are one of the most critical components in advanced interconnect layers for logic devices and the backbone of advanced memory devices.

Plasma assisted etching is used to fabricate these tiny holes. By combining the non-equilibrium chemistries and directed energetic ions formed in plasma systems, highly anisotropic holes can be cut into dielectric layers. This talk will focus on one aspect of these processes, the energetic ions that strike the surface. The role of these ions in anisotropic etching of these features and efforts to control and measure the direction and energy of these ions to further extend the capabilities of these processes will be discussed. Mechanisms for approximating and measuring the energy of ions that drive these processes will be discussed. Finally, current and future research paths for further extending the capabilities of these critical ion driven processes will be presented.

8:30am **PS1-ThM-3 Time-Domain RF Matching and Ion Energy Control in Pulsed Bias Capacitively Coupled Plasmas**, ***Yeon Geun Yook,*** University of Michigan*; Hyunjae Lee,* Samsung Electronics, Republic of Korea*; Mark J. Kushner,* University of Michigan

Pulsed-bias capacitively coupled plasmas (CCPs) are widely used in advanced semiconductor plasma etching processes to control ion energy, surface charging, and etch profiles. In practical RF systems, the voltage waveform produced by the generator is not necessarily delivered directly to the wafer electrode due to intervening impedances, including the match-box. Even when the impedance of the plasma reactor is well matched to the power supply though the match-box with continuous-wave (CW) excitation or late during the power-on phase of pulsing, a mismatch can occur during the power-on and power-off transitions. This mismatch is due to the finite transient response of the matching network, stored energy in circuit components, blocking-capacitor charge dynamics, and time-varying plasma impedance. These effects can distort the electrode voltage and self-bias waveform, thereby modifying the ion energy distribution delivered to the wafer.

In this work, the effects of time-domain RF matching transients on ion-energy control in pulsed-bias dual-frequency CCPs sustained in Ar/HF mixtures were computationally investigated using the Hybrid Plasma Equipment Model (HPEM). The bottom electrode is modeled with a π-type matching network and blocking capacitor through which the bias power is applied. First, the matching capacitors are tuned to minimize reflected power for long pulsed biases which have achieve a quasi-steady state. The effects of generator rise/fall times, pulse period, and blocking-capacitor value on plasma properties are analyzed, including time-dependent reflected power, network loss, stored energy, plasma absorbed power, and self-bias voltage.

The consequences of pulse power delivery on phase-resolved ion energy and angular distributions (IEADs) to the wafer during the rise, top-flat, fall, and off phases were investigated. Waveform compensation was explored as a possible strategy to mitigate matching-induced waveform distortion and improve ion-energy control. The plasma properties obtained from the HPEM were used as input to the Monte Carlo Feature Profile Model (MCFPM) to evaluate the impact of RF matching transients on etch profiles during cryogenic etching.

8:45am **PS1-ThM-4 Tailored Voltage Waveforms in Capacitively Coupled Plasmas: Effect of Voltage Transition Slope on Ion and Electron Dynamics in Argon Discharges**, ***Syed Zulqarnain****, Basak Bagci,* North Carolina State University*; Harutyun Melikyan, Ebony Mays,* Micron Technology*; Steven Shannon, Amanda Lietz,* North Carolina State University

Capacitively coupled plasmas (CCPs) are extensively employed in selective and anisotropic etching of semiconductor materials and deposition of thin films. Tailored voltage waveforms offer a promising approach to independently control ion energy and flux at the electrode surface, providing an additional degree of freedom for tuning the ion energy distribution function (IEDF). A square-shaped bias waveform is particularly attractive because its flat negative plateau maintains a near-constant sheath voltage, allowing ions to arrive at the substrate with narrow, well-defined energy. The negative phase must exceed the ion transit time across the sheath to ensure acceleration under a near-static potential, while the longer positive phase allows complete charge neutralization before the next pulse. This asymmetry makes the duty cycle a physically meaningful design parameter. At each polarity transition, the sheath boundary rapidly expands or collapses, transferring energy into electrons. The slew rate (dV/dt) sets the sheath expansion velocity, governing the intensity of this heating burst and the sheath potential during the transition. Ions crossing the sheath in this window experience a time-varying potential, shaping the tail of the IEDF. The slew rate is thus a fundamental control variable that simultaneously couples waveform shape to sheath dynamics, electron power absorption, and ion bombardment. In this study, a dual-frequency CCP discharge in pure argon at 10 mTorr is investigated using the Monte Carlo collisions-based particle-in-cell code, EDIPIC[1]. A 60 MHz sinusoidal

waveform on the upper electrode sustains the discharge and controls plasma density, while a 400 kHz asymmetric square voltage waveform on the lower electrode controls ion bombardment. The waveform uses a short negative phase (~0.5 µs) sufficient for ion transit and a longer positive phase (~2.0 µs) for full charge neutralization before each pulse. As the transition slope varies from near-instantaneous to gradual, its influence on sheath dynamics, electron heating, and power deposition is explored through time-resolved analysis over a single low-frequency cycle. The simulated IEDFs are compared against experimentally obtained IEDFs via retarding field energy analyzer, alongside comparisons of plasma density and sheath width. This investigation elucidates the interplay among the dual-frequency drive, waveform transition dynamics, and plasma response, providing insight into how square-wave tailored waveforms can control plasma dynamics in low-pressure CCP discharges*, with extensions to O_2 admixtures.*

1.https://pcrf.princeton.edu/capabilities/modeling-tools-and-computer-codes/edipic-code/

9:00am **PS1-ThM-5 Studies of Rf-ICP Source with a High Voltage Nanosecond-Tailored Voltage Waveform Biased Substrate***, **Yerbolat Ussenov**, Yevgeny Raitses,* Princeton Plasma Physics Laboratory

High-voltage substrate pulsing is a promising technique for tailoring peak ion energies and narrowing ion energy distribution functions (IEDFs) in high-aspect-ratio (HAR) plasma etching [1,2]. By utilizing a non-sinusoidal asymmetric bias (100–600 kHz) characterized by short positive pulses (~hundreds of ns) and extended negative phases, surface charge neutralization can be achieved while maintaining precise control over ion bombardment. In this study, we investigate the impact of pulsed substrate biasing [3] on a cylindrical inductively coupled plasma (ICP) source. Time-averaged axial distributions of plasma parameters and electron energy distribution functions (EEDFs) were characterized via Langmuir probe diagnostics and compared against steady-state (pristine) plasma conditions. To capture the transient discharge physics, time-resolved dynamics were analyzed through instantaneous floating potential measurements at different substrate to probe distance. Furthermore, the spatio-temporal evolution of optical emissions near the substrate was evaluated using phase-resolved optical emission spectroscopy (PROES) equipped with an ICCD camera and light emission filter. Also, the Doppler shift laser induced fluorescence (LIF) implemented to test the possibility of time resolved IEDF measurements. Our preliminary results demonstrate that the pulsing significantly alters the local plasma properties near the substrate. The underlying physical drivers are discussed.

This work was conducted at the Princeton Collaborative Research Facility (PCRF), which is supported by the U.S. DOE under Contract No. DE-AC02-09CH11466. The authors are grateful to Prof. Vince Donnelly for sharing ICP design, and Eagle Harbor Technologies, Inc. for providing their pulser.

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9:15am **PS1-ThM-6 Experimental Investigation of Tailored Voltage Waveforms in Dual-Frequency Ar/O_2 Capacitively Coupled Plasmas***, **Basak Bagci**, Syed M. Zulqarnain, Amanda M. Lietz, Steven C. Shannon,* North Carolina State University

Tailored voltage waveforms in capacitively coupled plasmas (CCPs) provide a powerful approach for controlling ion energy distributions and electron heating in semiconductor plasma processing. In low-pressure CCP discharges, waveform asymmetry and transition dynamics strongly influence sheath evolution, plasma potential, and ion acceleration, making waveform tailoring particularly attractive for applications requiring independent control of ion energy and ion flux. While these effects have been extensively investigated in noble gas plasmas, significantly less attention has been given to electronegative gas mixtures relevant to semiconductor manufacturing.

In this work, experimental measurements are performed in a dual-frequency and single-frequency CCP reactor operating in argon/oxygen mixtures at pressures near 10 mTorr. A 60 MHz sinusoidal waveform applied to the upper electrode sustains the plasma, while a low-frequency asymmetric pulsed waveform applied to the lower electrode controls ion bombardment dynamics. The influence of oxygen admixture and waveform transition characteristics on plasma behavior is investigated using synchronized plasma diagnostics. Ion energy distribution functions (IEDFs) are measured using a retarding field energy analyzer (RFEA), while electron density is obtained using a hairpin resonance probe. Simultaneous voltage measurements are acquired using VI probes to correlate plasma response with applied waveform dynamics.

The addition of oxygen significantly modifies the discharge through electronegativity-driven changes in electron density, sheath structure, and ion transport. Variations in waveform transition slope and duty cycle alter sheath expansion dynamics and electron heating during polarity transitions, producing measurable changes in the IEDF shape, energy spread, and high-energy ion population. Comparisons between pure argon and Ar/O_2 mixtures reveal how electronegative chemistry couples with tailored voltage waveforms to influence plasma stability and ion bombardment characteristics.

These measurements provide experimental insight into waveform-controlled plasma dynamics in electronegative CCP discharges and contribute to the development of advanced plasma control strategies for semiconductor processing applications.

9:30am **PS1-ThM-7 Passive Antenna Control of Ion Energy in Inductively Coupled Plasmas: Mechanism Study via Antenna Design Variation***, **Minsu Choi**,* Department of Physics, Chungnam National University, Republic of Korea*; Chulhee Cho,* Institute of Quantum Systems (IQS), Chungnam National University, Republic of Korea*; Inho Seong, Wonnyoung Jeong, Byeongyeop Choi, Seonghyun Seo, Isak Lee,* Department of Physics, Chungnam National University, Republic of Korea*; Youngseok Lee,* TEK R&D center, Tokyo Electron Korea*; Shinjae You,* Department of Physics, Chungnam National University, Republic of Korea

Ion energy is a critical parameter in plasma etching processes, governing etch rate, selectivity, and profile control. Conventional ion energy control requires an additional RF bias power source, which increases system complexity and cost. Passive antenna technology has recently been proposed as a bias-free alternative for ion energy modulation in inductively coupled plasmas (ICP), where ion energy is tuned through changes in the plasma potential. However, the mechanism by which a passive antenna modifies the plasma potential remains poorly understood.

In this work, we elucidate this mechanism through a systematic comparison of three antenna configurations: a closed-loop antenna, an open-ended antenna, and an open-ended antenna with an anodized surface. These designs were chosen to selectively suppress the two candidate pathways for plasma potential control —conduction current to the antenna and voltage generation at the antenna terminals. Plasma parameters, including electron density, electron temperature, and plasma potential, were measured using a Langmuir probe. Our results reveal two key contributions to passive antenna–driven ion energy control: (1) the collection of plasma electrons by the passive antenna, and (2) the voltage that develops at the open end of the antenna. Both effects act in concert to elevate the plasma potential and thereby increase ion energy at the substrate.

9:45am **PS1-ThM-8 Effects of Ar/O2 Gas Mixture Ratios on Ion Energy Distribution Functions in a Dual-Frequency CCP***, **Tanjina Akter**, Syed Zulqarnain, David Kanfer, Basak Bagci, Duncan Trosan,* North Carolina State University*; Chenyao Huang, Mark J. Kushner,* University of Michigan*; Amanda Lietz, Steven Shannon,* North Carolina State University

The investigation of ion energy distribution functions (IEDFs) formed by a powered sheath above a cathode can help optimize etching processes during the micro and nano fabrication. Capacitively coupled plasmas (CCP) have been routinely used to fabricate these structures. The coupling of ion flux and ion energy in a single-frequency CCP configuration limits its application for large-scale production. Hence, an independent control of ion flux and mean energy is required, which can be obtained by a multiple-frequency RF power configuration. Dual-frequency CCP can provide decoupled ion flux and ion energy, where the high-frequency component of the discharge produces charged particles and sustains the plasma, and the low-frequency component accelerates the ions to the surface [1]. A dual-frequency CCP configuration, with 60 MHz for the high-frequency (HF) and 13.56 MHz for low-frequency (LF), has been used in this experiment to observe the IEDF by placing a Retarding Field Energy Analyzer (RFEA) on the LF electrode. Bimodal IEDFs were found by the RFEA for the pressure range of 1-50 mTorr, electron densities of 10^9-10^{11} cm^{-3}, the sheath potential of 50-100 V, and the sheath thickness of 0.5-0.1 cm in the dual-frequency CCP using argon and argon-oxygen gas mixtures. The variations of IEDFs, electron density, and sheath thickness with different argon–oxygen gas mixture ratios were examined under constant HF and LF power conditions. The independent control of density and sheath voltage using a dual frequency configuration was also used to study the role of gas mixing under

identical density and voltage conditions that primarily dictate the IEDF to better understand the impact of molecular and electronegative effects on the evolution of IEDF's in these CCP reactors. A Particle-In-Cell (PIC) simulation has been performed to validate the experimental results.

This work is supported by the Department of Energy (DOE) grant DE-SC0024545.

Reference:

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Plasma Science and Technology
Room 315 - Session PS2-ThM

Advanced Ion and Reactant Control II

Moderators: Dr. Suman Bhaumik, TEL Technology Center, America, LLC, **Dr. Mingmei Wang**, Lam Research Corporation

11:00am **PS2-ThM-13 Energy-Resolved Angular Distribution of Ions Impinging on Biased Electrode in Dual-Frequency Capacitively-Coupled Ar Plasma**, ***Hirotaka Toyoda,*** Nagoya University, Japan **INVITED**

The ion angle distribution (IAD) on the biased electrode is one of the factors that determine the shape in high-aspect-ratio etching, and experimental insights into how the IAD varies with plasma parameters are extremely important as fundamental data for etching shape simulations. Therefore, we have developed a specially designed dual-frequency capacitively coupled plasma (CCP) source to measure the angular distribution of high-energy ions incident on the RF electrode. In this apparatus, particles are extracted from the plasma into a drift tube through a sampling orifice connected to the RF electrode, and after passing through the drift tube, they are detected by a microchannel plate (MCP) assembly with a fluorescent screen, offering angular resolution of less than 0.01 degrees. From Ar plasma experiment, it was revealed that the IAD consists of a intense Gaussian peak (angular width: <0.5°) and a weak tail component (angular width: >1°). The width of the main peak decreased with increasing LF power, indicating that sheath acceleration contributes to the narrowing of the angular width. To investigate the collision effect within the sheath in more detail, the pressure was varied while keeping the sheath thickness constant by controlling the plasma density. As a result, the width of the main peak deviated from the expected tendency at high pressure and high sheath voltage, suggesting that sheath collisions increase the angular width. To further investigate the behavior of ions within the sheath, energy-resolved IAD measurements were performed using the Time-of-Flight method. It is known that ions passing through an RF-oscillating sheath have an energy distribution from high to low energy, and similar results were obtained in our energy-resolved IAD measurements. Furthermore, the main peak width decreased with energy, and assuming that the width of the main peak is determined by the ion temperature and sheath acceleration energy, the ion temperature was found to be ~0.04 eV regardless of the ion energy. This indicates that the main peak is generated by high-energy collisionless-ions and low energy ions those experienced charge-exchange collisions without momentum transfer. The behavior of the tail component of the IAD was also investigated by varying pressure. With increasing pressure, a relative increase in the tail component was observed. Monte Carlo particle simulations within the sheath suggested that the tail component originates from small-angle scattering of background Ar neutral particles and Ar ions.

Acknowledgement

The author thanks K. Kurihara, H. Fukumizu and their colleagues from KIOXIA corporation for their support and discussion.

11:30am **PS2-ThM-15 Tailored Voltage Waveforms in Inductively Coupled Plasmas for Cryogenic Etching using Ar/HF Gas Mixtures**, ***Yifan Gui,*** *Yeon Geun Yook, Chenyao Huang, Mark J. Kushner,* University of Michigan, Ann Arbor

In microfabrication, fabricating high aspect ratio (HAR) dielectric features has relied on capacitively coupled plasma (CCP) reactors using fluorocarbon chemistries. In these systems, process parameters are tuned to optimize the production of C_xF_y fragments and ion energy distributions with the end goal of balancing polymer deposition and chemical sputtering to maintain profile control and etch rate. Inductively coupled plasmas (ICPs) have not been extensively used for dielectric etching due to the difficulty in controlling the fragmentation of the fluorocarbon gases. Cryogenic plasma etching of dielectrics typically uses HF based chemistries which rely on water-HF condensation and physisorption rather than the thickness and composition of the fluorocarbon polymer passivation layer. Consequently, the need to optimize C_xF_y dissociation is eliminated, which then makes ICPs more attractive for cryogenic etching systems. Decoupling plasma generation by the source power and ion acceleration by the bias power is also less difficult using ICPs.

In this presentation we discuss results from a computational investigation of the use of voltage waveform tailoring (VWT), specifically a rectangular bias (RB) waveform, in ICPs for cryogenic etching of dielectrics. RB waveforms generate a more mono-energetic ion energy distribution to the substrate compared to sinusoidal biases. This investigation was performed using, the Hybrid Plasma Equipment Model (HPEM), a modular simulator designed for low-pressure plasma systems. This study focuses on the evolution of incident fluxes and energy angular distributions (EADs) for electrons and ions onto wafers for ICPs operating at pressures of tens of mTorr with Ar/HF feed gas. We will discuss the impact of an expanded operational space (plasma source type, power/voltage scaling, and waveform) on the resulting EADs and flux uniformity across the wafer.

Work supported by Lam Research, Samsung Electronics and Department of Energy Office of Fusion Energy Sciences.

11:45am **PS2-ThM-16 Mechanisms of Si, SiCl, SiCl2, and Cl radical production and their role in isolated sidewall taper formation in pulsed Ar + Cl2 plasmas**, ***V S Santosh K Kondeti,*** Princeton University Plasma Physics Lab*; Leonid Dorf, Zihao Ding, Geuntak Lee, Sonam D. Sherpa, Takumi Yanagawa, Leonid Belau,* Applied Materials Inc.*; Yevgeny Raitses,* Princeton University Plasma Physics Lab

In chlorine-based plasma etching of silicon, sidewall taper in isolated features originates from the deposition of chemical by-products, which is governed by the generation and transport of reactive radicals. In this work, we investigate the mechanisms of Si, SiCl, $SiCl_2$, and Cl radical production and decay in a pulsed inductively coupled Ar + Cl_2 plasma with a pulsed bias voltage using time-resolved laser induced fluorescence diagnostics. The measurements show that SiCl radicals are produced predominantly in the gas phase through electron-impact dissociation of higher silicon chlorides ($SiCl_x$, x = 2–4), with $SiCl_2$ acting as a key precursor species. In contrast, $SiCl_2$ is generated primarily at the wafer surface and chamber walls through ion-assisted processes and desorption. The measured Si radical dynamics indicate that Si atoms are produced in the gas phase and sputtering of the wafer. Cl radicals are produced by the dissociation of the precursor Cl_2 gas during the plasma on-phase. $SiCl_2$ and Cl radicals increase in density in the afterglow after turning of all power suggesting that $SiCl_2$ is formed by this reaction SiCl + Cl_2 → $SiCl_2$ + Cl in the afterglow, before all species decay in density. The observed radical dynamics demonstrate that sidewall taper is governed by the buildup and decay of depositing species with a large sticking coefficient such as Si/SiCl, which can be controlled through modulation of plasma pulsing parameters. These results provide a mechanistic framework corelating plasma-phase chemistry to feature profile evolution and offer pathways to minimize by-product deposition for improved anisotropic etching.

This work is supported by Applied Materials and a Cooperative Research and Development Agreement (CRADA) between the Princeton Plasma Physics Laboratory and Applied Materials through the U.S. Department of Energy (contract DE-AC02-09CH11466).

12:00pm **PS2-ThM-17 Control of Electron Angular Distributions onto Substrates Using Non-Sinusoidal Low Frequency Biases in Capacitively Coupled Plasmas**, ***Max Kellermann-Stunt,*** *James Prager,* University of Michigan*; Josh Perry, Paul Melnik, Timothy Ziemba,* Eagle Harbor Technologies*; Mark J. Kushner,* University of Michigan

Independent control of ion and electron energy distributions onto plasma facing surfaces is an important challenge for high-aspect-ratio (HAR) semiconductor etching. In capacitively coupled plasmas (CCPs), ions are accelerated through the sheath toward the wafer with relatively narrow angular distributions, while electrons generally reach the wafer during limited portions of the radio frequency (RF) cycle and often have broader angular distributions. The difference between the ion energy angular distribution (IEAD) and electron energy angular distribution (EEAD) can contribute to asymmetric charging in HAR features, leading to notching, microtrenching and twisting. Non-sinusoidal bias waveforms are being developed to narrow, in in both energy and angle, IEADs delivered to the wafer. These voltage waveforms ideally have a short positive portion and

longer, constant negative. portion. A desired consequence of this waveform is an electric-field reversal in and near the sheath that will accelerate electrons towards the wafer with narrow angular distribution and high energies.

In this work we have computationally investigated EEADs and IEADs onto biased substrates in a CCP using non-sinusoidal waveforms. The investigation was conducted using the Hybrid Plasma Equipment Model (HPEM). Comparisons are made to experimental measurements of ion and electron energy distributions onto the substrate using an RFEA (retarding field energy analyzer).The experimental system consists of a CCP powered on the top electrode at 60 MHz with the bottom pedestal electrode biased by the non-sinusoidal waveform at 400 kHz. Measurements and simulations were performed for pure argon and argon-molecular gas mixtures with pressures ranging from 3 mTorr – 20 mTorr. The HPEM code was modified to enable simulation of electron energy distributions using very low frequency biases.

This work was supported by Eagle Harbor Technologies and the US Department of Energy Office of Fusion Energy Science under Award Number DE-SC0024861.

Atomic Scale Processing Mini-Symposium
Room 316 - Session AP+EL+MS+PS+TF-ThA

Advancing Atomic Scale Processing Through Novel Sources and Pulsing Methods

Moderators: Dr. Keren Kanarik, Lam Research Corporation, **Prof. Dr. Han-Bo-Ram Lee**, Incheon National University

2:15pm **AP+EL+MS+PS+TF-ThA-1 High-Throughput Silicon ALE via Rapid Matchless Power Modulation**, ***Banks Peete,*** North Carolina State University*; Jeremy Mettler,* University of Houston*; Paul Melnik,* EHT Semi*; Shreeyansh Rastogi, Zuhair Khan,* University of Houston*; Chris Bowman, James Prager, Timothy Ziemba,* EHT Semi*; Steven Shannon,* North Carolina State University*; Vincent Donnelly,* University of Houston

By leveraging rapid, multi-level power modulation, we have expanded the self-limiting window of continuous gas flow atomic layer etching (ALE) of silicon to higher chlorine flow rates enabling much quicker ALE cycle periods. ALE offers superb controllability, but it is limited in speed by the time it takes to purge and switch gases from the chamber. Previously, a continuous flow of argon and chlorine gases were injected into continuously-powered, inductively-coupled plasma (ICP) while the bias power to the substrate stage was pulsed on for 0.2 s and off for 1 s. When the chlorine flow was kept in a narrow window, the silicon chloride surface layer was removed by argon ions faster than the surface can re-chlorinate. At higher chlorine flow rates, this process collapsed into traditional reactive ion etching.

In this work, we expand this “ALE window” by modulating the ICP power in sync with the bias-on period. This was accomplished using a matchless power generator (EHT Semi “Orion”), capable of rapidly changing power levels by an order of magnitude in microseconds. The matchless capabilities ensure that power is still delivered efficiently during the large change in plasma impedance. Time-resolved hairpin probe measurements confirm electron density transition times between power states in the hundreds of microseconds time-scale, far faster than would be possible with a traditional matching network based power delivery system. By operating the ICP at 300W during the bias-off period and at higher powers (600 W to 1.5 kW) during the bias-on period, the ALE window can be expanded to higher chlorine flow rates. During the bias off phase, the higher chlorine flow rates re-chlorinate the surface faster, decreasing the total ALE cycle time. Time-resolved optical emission spectroscopy of the SiCl (280.75 nm) line was used as a real-time monitor of the relative etching rates. At higher chlorine flows, the line exhibited a “spike and decay” profile indicative of ALE, unlike the previous work with constant 300 W power, which showed a square wave-like response to the bias turning on that is associated with simple pulsed reactive ion etching. This confirms that syncing the bias with a higher level ICP power enables higher chlorine flow rates while still outrunning re-chlorination.

2:30pm **AP+EL+MS+PS+TF-ThA-2 Etching Commercially-Relevant Materials Using Tailored Waveform Biasing**, ***Benjamin Harris,*** *Daryl White, Kate Stokes, Matthew Loveday, James Ellis, Geoffrey Hassall,* Oxford Instruments Plasma Technology, UK

Control of the ion energy distribution function (IEDF) in a plasma is essential for optimising etch processes, such as atomic layer etching (ALE) and reactive ion etching (RIE). If the ion energy is too low, ions will fail to etch the surface of a material. If the ion energy is too high, ions may induce subsurface damage by sputtering material below the surface layer. Between these two boundaries lies the optimal range for ion energies, where ion utilisation is maximised and subsurface damage is minimised. Historically, a radio-frequency, sinusoidal bias is applied to the wafer table to control the IEDF near the wafer surface. This produces bimodal IEDFs with characteristic widths on the order of tens of eV, which is often wider than the optimal window for etching industrially-relevant materials [1]. Tailored waveform biasing (TWB) provides an alternative to radio-frequency biasing that offers enhanced control over the width and mean energy of the IEDF.

In this study, TWB is used to sputter etch commercially-relevant materials. A retarding field energy analyser is used to measure IEDFs, and on-wafer outcomes are investigated with a suite of metrology tools, including atomic force microscopy and scanning electron microscopy. The results are compared with radio-frequency biasing, showing the benefits of TWB for enhanced process control.

[1] Faraz, T., Verstappen, Y.G., Verheijen, M.A., Chittock, N.J., Lopez, J.E., Heijdra, E., van Gennip, W.J., Kessels, W.M. and Mackus, A.J., 2020. Precise ion energy control with tailored waveform biasing for atomic scale processing. *Journal of Applied Physics*, *128*(21).

2:45pm **AP+EL+MS+PS+TF-ThA-3 Precise Ion Energy Control Using Advanced Pulse Modulation for Thin Film Deposition and ALD**, ***Yejin Shin,*** WONIK IPS CO., LTD., Republic of Korea*; Junghoon Kim, Tae Cho,* WONIK IPS CO., LTD.*; Hyun-Joug Woo, YongBaek Jeon, GyuTai Kim, TaeJoon Kim,* WONIK IPS CO., LTD., Republic of Korea

As semiconductor device dimensions continue to shrink, advanced thin film deposition processes increasingly require precise control of ion energy and ion flux to achieve void-free filling in narrow-pitch and high aspect ratio structures. In particular, lateral gap-fill processes for next-generation semiconductor architectures demand highly controlled plasma-surface interactions to improve bottom coverage, suppress seam and void formation, and maintain film uniformity within confined geometries. Conventional RF plasma technology often provides limited flexibility for controlling ion bombardment conditions, motivating the development of advanced waveform engineering approaches.

In this work, an advanced pulse modulation was adapted to precisely control ion energy characteristics during RF plasma deposition processes through tailored voltage waveform. To enable this capability, the bottom components of a system were extensively modified, including the integration of a redesigned junction module and an optimized RF grounding architecture. The modified structure was specifically designed to improve transient voltage response, reduce parasitic effects, and support consistent pulse modulation under plasma load. Particularly, the hybrid junction module was designed to have minimized reflected power fluctuation and enabled more stable waveform delivery to the substrate electrode, which is critical for precise ion energy control during deposition processes. These hardware enhancements enabled more accurate control of sheath voltage evolution and allowed dynamic tuning of ion bombardment energy at the substrate surface. Using the developed platform, various pulse modulation conditions were investigated to evaluate their influence on plasma stability, ion energy distribution, and deposition characteristics. Experimental observations which were made using the advanced PEALD tool manufactured by Wonik IPS expects that advanced pulse shaping can significantly influence ion acceleration dynamics and plasma-surface interactions without substantially perturbing bulk plasma stability. In particular, the ability to manipulate transient sheath behavior enabled improved control of ion-assisted deposition compared with conventional continuous-wave RFs as a 13.56 or 27.1MHz.

This work establishes a hardware and process framework for future investigation of advanced deposition applications, focused on evaluating the effectiveness of this approach for next-generation conformal film deposition. The presented approach provides a promising pathway toward plasma processing for advanced semiconductor manufacturing applications requiring precise control of plasma-surface interactions.

3:00pm **AP+EL+MS+PS+TF-ThA-4 Characterizing Inductively Coupled Plasmas in Ar/N2/H2 Mixtures for Plasma Enhanced Atomic Layer Deposition of Crystalline Films**, ***David Boris,*** *Jeffrey Woodward, Virginia Wheeler, Michael Johnson, Mackenzie Meyer, Scott Walton,* U.S. Naval Research Laboratory

Low temperature plasmas containing mixtures of Argon, Nitrogen, and Hydrogen are widely used in the plasma enhanced atomic layer deposition of crystalline metal nitrides (e.g. AlN) at low temperatures (<500C).Generally, the addition of H_2 is beneficial in that it facilitates the removal of precursor ligands and leads to films with low carbon content (<1%). In addition, if the process conditions are properly chosen, highly crystalline metal-nitride films can be grown in $Ar/N_2/H_2$ mixtures.However, the effects of H_2 addition on the downstream plasma properties near the substrate are not well understood in remote, inductively coupled plasma (ICP) geometries.As such, a better understanding of the downstream plasma properties in this gas chemistry will be the focus of this presentation.

In this work, we use a combination of Langmuir probes, a retarding field energy analyzer, and optical emission spectroscopy (OES) to examine the effects of varying process parameters on the physical characteristics of $Ar/N_2/H_2$ plasmas generated in a remote, ICP geometry.In particular, a range of applied RF powers, gas flows, and pressures are explored with a focus on the resulting changes in atomic species density, plasma density, plasma potential, and the energy and flux of ions at the substrate.Of particular interest is the effect H_2 has on the ion flux and ion energy

distribution at the substrate. These changes in plasma properties are then tied to changes in the characteristics of AlN thin films grown via plasma-enhanced ALD using a remote ICP employing $Ar/N_2/H_2$ gas mixtures. This work was supported by the NRL Base program through the Office of Naval Research.

3:15pm **AP+EL+MS+PS+TF-ThA-5 Direct Atomic Printing of High-K Dielectric Thin Film Oxide Materials** *, **Tesfalem Welearegay**, Nandan Singh Ruhela, Simone Santucci, Mira Baraket, Maksym Plakhotnyuk,* ATLANT 3D Nanosystems, Denmark

The rapid scaling up of CMOS microfabrication combined with growing demand for wide- and ultrawide-bandgap power electronics (GaN, SiC, β-Ga_2O_3), and the integration of high memory and neuromorphic devices have placed high-k dielectric thin films at the centre of modern semiconductor technology. High-k dielectric oxide thin films such as HfO_2, ZrO_2, Al_2O_3, Ta_2O_5, Nb_2O_5, and Ga_2O_3 are predominantly as-deposited by conventional atomic layer deposition (ALD) and spatial ALD techniques. Although ALD offers sub-nanometre control and excellent conformality, its low throughput, vacuum-based batch operation, high precursor consumption, and lack of in-line patterning have become major bottlenecks for the development and scale-up of next-generation high-k materials. These limitations become significant when device roadmap require sub-nm equivalent oxide thickness, and ultralow defect density to fine tune the film's intrinsic properties required for rapid materials screening with high throughput and precision..

We, therefore, present Direct Atomic Layer Processing (DALP®) technique — a spatial, atmospheric-pressure ALD technology platform that enables direct atomic printing of oxide thin films with monolayer-level precision and higher throughput while significantly reducing precursor waste. By spatially separating the precursor and oxidant zones under inert-gas exposures, DALP® technology combines the self-limiting surface chemistry of ALD with the speed and selective-area capability of a direct-write process. The platform offers unique versatility in fine-tuning the film composition, property and and structure, thereby enabling to control over the targeted properties of the film. The capability is demonstrated on two selected high-k oxide materials. GaOx deposited from its spatial precursor Galai™ (air liquide) with H_2O at relatively low temperatures of 150–240 °C under open atmosphere conditions. The as-deposited oxide films follows an ALD-like deposition window at 180–210 °C with growth per pass (GPP) of 0.35–0.5 Å/pass. Moreover, NbOx (Nb_2O_5) thin films were grown from its spatial precursor Nautilus 2™ (Air liquide) with H_2O at relatively low-temperature ALD window of 180 - 240 °C with GPP of 0.41 - 0.43 Å/pass, producing high-purity amorphous films suitable for different applications including DRAM capacitors, Mott memristors, and high-index optical coatings. These results establish DALP® technology as a versatile, sustainable, and high-throughput platform for the rapid development and manufacturing of high-k dielectric thin films for power electronics, memory, and quantum-device applications.

3:30pm **AP+EL+MS+PS+TF-ThA-6 Plasma-Enhanced ALD of $TaCxN_{1-x}$ Tailored for Superconducting Quantum Technologies Through Ion Energy and Other Plasma Control Knobs** *, **Silke Peeters**, Arthur De Jong, Adrie Mackus, Erwin Kessels,* Eindhoven University of Technology, Netherlands*; Harm Knoops,* Oxford Instruments Plasma Technology, Netherlands

Tantalum nitride compounds are emerging materials for superconducting quantum circuits due to their reduced surface oxidation compared to Ta, which is used in state-of-the-art devices. However, the synthesis of electrically conductive tantalum nitride compounds is challenging. Moreover, these circuits require sharp material interfaces with minimal impurities to achieve state-of-the-art performance.

Ar-H_2 plasma has enabled the preparation of superconducting TaC_xN_{1-x} through atomic layer deposition using the metalorganic $Ta[N(CH_3)_2]_3[NC(CH_3)_3]$ precursor. In previous work[1,2], we have shown that the quality of TaC_xN_{1-x} and $Nb_xTi_{1-x}N$ films can be substantially improved through ion-energy control, achieved via application of a radiofrequency (RF, 13.56 MHz) substrate bias during low-pressure, remote plasma exposure. In this work, we explore the novel method of tailored-waveform (TW, 200 kHz) biasing[3,4] and variation of the Ar-H_2 plasma composition to tune film properties for application in superconducting quantum devices.

Compared to RF biasing, TW biasing offers more precise control over the ion energy. Consistent with earlier RF-bias results, application of TW biasing up to an ion energy of 140 eV enhances grain growth and grain boundary quality through increased adatom mobility and preferential removal of weakly-bonded surface species. As a result, room-temperature electrical resistivity is improved from $(9.6 \pm 0.5)*10^4$ μΩ cm for an 11 nm film to $(3.8 \pm 0.2)*10^2$ μΩ cm for a 7 nm film. A decrease of the H_2-dilution in the Ar-H_2 gas mixture supplied to the plasma further enhances TaC_xN_{1-x} electrical conductivity and crystallinity, and promotes (111) texturing. A decrease in blistering, which can occur at high-stress, H-containing interfaces, is observed at the Si(100) substrate interface. The balance between Ar and H species significantly affects crystal grain growth. Ar species more effectively stimulate near-surface atomic rearrangement through physical bombardment, while H species act as reducing agents. However, H species can also reduce adatom mobility through over-passivation of dangling bonds and accumulate in the film.

This work shows that accurate understanding and control of plasma properties is necessary to tailor TaC_xN_{1-x} films to superconducting quantum technologies. Using the developed toolbox, we demonstrate successful integration of TaC_xN_{1-x} thin films in superconducting quantum technologies.

[1]S. A. Peeters et al. *Appl. Phys. Lett.* 123, 132603 (2023)

[2]S. A. Peeters et al. *AVS Quantum Sci.* 7, 026801 (2025)

[3]T. Faraz, A. A. De Jong et al. *J. Vac. Sci. Technol. A* 44, 033004 (2026)

[4]A. A. De Jong, S. A. Peeters et al. *to be published*

3:45pm **AP+EL+MS+PS+TF-ThA-7 Direct Atomic Layer Processing (DALP®): Spatially Localized, Multi-Material Fabrication for Next-Generation Devices from Discovery to Manufacturing** *, **Mira Baraket**,* ATLANT 3D Nanosystems, Denmark

Progress in next-generation advanced electronic and functional devices, based on complex heterostructures and advanced materials integration, is increasingly constrained by the rigidity of conventional thin-film processing and patterning workflows. While these approaches deliver high material quality and uniformity, they offer limited flexibility for spatially localized, multi-material fabrication, three-dimensional thickness engineering, and rapid experimentation at the nanoscale within a single process flow.

ATLANT 3D introduces Direct Atomic Layer Processing (DALP®), a nanofabrication technology enabling digitally controlled, spatially localized deposition of multiple materials with atomic-scale precision. DALP allows different materials to be deposited sequentially and locally in a unified workflow, enabling manufacturing of complex material stacks, heterostructures, interfaces, and thickness gradients without intermediate lithographic patterning steps.

This presentation describes the DALP process architecture and its role in both combinatorial materials discovery and targeted device manufacturing for next-generation devices. By enabling programmable material placement, controlled thickness variation, and repeatable execution within a single platform, DALP supports accelerated materials exploration while also enabling the direct production of device-ready structures as part of broader manufacturing flows. Representative examples include multi-material nanoscale structures for advanced semiconductor and functional material applications, where precise interface control, spatial selectivity, repeatability, and manufacturability are critical. DALP expands the accessible design space of nanoscale fabrication and provides a a direct pathway from materials discovery to device-ready, manufacturable structures.

4:00pm **AP+EL+MS+PS+TF-ThA-8 From Plasma to Process: Understanding Dielectric Barrier Discharges for Spatial Atomic Layer Deposition** *, **Ralph Houben**, Antoine Salden, Jente Wubs, Richard Engeln, Erwin Kessels, Julian Held, Bart Macco,* Eindhoven University of Technology, The Netherlands

Atomic layer deposition (ALD) is a thin-film deposition technique based on sequential, self-limiting reactions. Plasma-enhanced ALD (PE-ALD) extends this concept by leveraging non-equilibrium plasmas to enable low-temperature processing, wider choice in materials, and enhanced film properties. Advancing PE-ALD requires a detailed understanding of plasma chemistry and the role of reactive species from the plasma in driving surface reactions.

Spatial ALD (SALD), in which precursor and reactant zones are separated in space rather than time, enables high-throughput and large-area processing, making it attractive for low-cost and high volume applications such as photovoltaics and batteries. SALD often operates at atmospheric pressure in linear slit geometries, making dielectric barrier discharges (DBDs) a natural plasma source. However, the high-pressure environment introduces strong collisionality that fundamentally alters plasma chemistry compared to low-pressure PE-ALD. For example, for O_2 plasmas, rapid three-body reactions favor ozone (O_3) formation over atomic oxygen (O). The gas temperature plays a crucial role here, as it directly affects the rate coefficients of the ozone-forming reactions. Furthermore, power dissipation occurs through filamentary microdischarges rather than a uniform glow —

both aspects that have no direct analogue in conventional low-pressure PE-ALD.

The oxidative species composition governs surface chemistry in oxide ALD. Quantifying O_3 and O with absolute densities — and linking them to plasma parameters through models — is essential for process control, yet such data for atmospheric DBDs in an ALD context are scarce.

In this work, ozone densities have been determined using broadband UV absorption spectroscopy, yielding absolute concentrations on the order of 10^{15} cm^{-3} under typical operating conditions. The density depends on dissipated power, gas temperature, and O_2 input in the gas mixture. We further present cavity ring-down spectroscopy (CRDS) as technique for probing the forbidden transition of atomic oxygen near 630 nm, providing calibration-free, absolute quantification of atomic oxygen densities. These measurements are supported by plasma chemistry modeling, which shows that the O_2/N_2 ratio governs whether ozone or atomic oxygen dominates — a critical distinction for ALD surface reactivity.

Furthermore, the species generation predicted by the model is directly tied to how power is dissipated in the discharge. Power dissipation analysis reveals the filamentary nature of the discharge and how it governs species generation. These insights are essential for rationally designing plasma-assisted SALD processes.

Plasma Science and Technology
Room 315 - Session PS-ThA

Simulation for Plasma Processes

Moderators: Nobuyuki Kuboi, Sony Corporation, **Dr. Yu-Hao Tsai**, TEL Technology Center, America, LLC

2:15pm **PS-ThA-1 A Multi-Scale Simulation Methodology for Recipe Design in Semiconductor Etch Processes***, **SeungMin Lee**,* Samsung Electronics, Republic of Korea **INVITED**

As semiconductor device scaling approaches sub-nm regime and beyond, the synergy between plasma-surface interactions and feature-scale topography evolution has become increasingly non-linear and difficult to predict. Conventional technology computer-aided design (TCAD) and Monte Carlo-based topography simulations, while physically robust, often face a trade-off between computational cost and predictive accuracy, especially when accounting for complex plasma chemistries. This gap between theoretical precision and practical processing speed necessitates a fundamental shift in how we approach process modeling and feature-scale evolution.

To address these limitations, this presentation introduces a robust hybrid framework that integrates plasma physics, topography simulation, and artificial intelligence (AI). By bridging AI with domain-specific physics of plasma reactions and surface kinetics, we accelerate the coupling between equipment-level plasma distributions and feature-scale profile evolution. This methodology allows for the rapid prediction of etching and deposition profiles with maintaining the rigor or Monte Carlo-based transport models. Furthermore, we explore how AI-driven features extraction can identify hidden correlations between plasma reaction transitions and structural defects, providing insights that were previously inaccessible through traditional TCAD-based methods.

Ultimately, the fusion of AI with physical modeling provides a new paradigm for "Digital Twin" environments in semiconductor manufacturing. We demonstrate how this integrated methodology enables autonomous TCAD calibration and real-time optimization of process conditions to improve etching outcomes. This science-based AI approach not only enhanced our fundamental understanding of plasma process but also significantly accelerates the development cycle for the next generation of logic and high-density memory devices.

2:45pm **PS-ThA-3 GPU-Accelerated AMR Simulation of Charging-Driven Instability in Ion-Assisted Etching***, **Takumi Ohmura**, Satoshi Nakamura, Hisashi Kotakemori, Taishi Ikeda, Kenta Yashima, Yasuyuki Kayama,* Samsung Device Soltuions R&D Japan*; YunTae Lee,* Samsung Electronics, Republic of Korea*; Yukihide Tsuji,* Samsung Electronics, Japan*; Jaehoon Leem, Jaeyong Lee, Shinwook Yi, Moon-Hyun Cha, Jaehoon Jeong,* Samsung Electronics, Republic of Korea

Predictive modeling of high–aspect–ratio contact etching requires resolving three–dimensional geometries that involve surface reactions, surface charging, and long–timescale evolution, which remain computationally challenging.Our simulator combines adaptive mesh refinement (AMR) with GPU acceleration for both the Poisson solver and particle transport. The Poisson solver is accelerated by more than an order of magnitude (>10×) using an AMR–based multi–level multigrid solver on GPUs. Moreover, both charged and uncharged particle transport are further accelerated by more than 2× through hierarchical voxels. This advance enables high–resolution, long–term simulations.

Using a simplified ion–assisted etching model, we demonstrate that charging–induced electrostatic fields can cause morphological instability. Parametric studies indicate that striation formation is primarily driven by the low–energy ion population. These ions are reflected by a potential barrier that increases approximately linearly with feature depth and grows with higher electron temperature. We find that striations appear when the low–energy ion energy is comparable to the potential barrier, within a factor of two. In this regime, ion trajectories are strongly perturbed by the electrostatic fields. Meanwhile, when ion energies significantly exceed the potential barrier, striation formation is suppressed. However, lateral broadening is observed due to the angular spread of ion trajectories.

This work shows that GPU–accelerated AMR is suitable for feature–scale simulations incorporating surface charging, and it provides physical insight of interpreting charging–driven pattern formation. In addition, our finding is expected to provide useful guidance for realistic processing conditions and improve process-parameter optimization.

3:00pm **PS-ThA-4 Particle in Cell Monte Carlo Collision Simulations of Capacitive Ar/Cl_2 Discharges***, Bahram Mahdavipour, **Jon Tomas Gudmunsson**,* University of Iceland

Reactive gases mixed with rare gases in capacitively coupled discharges are often used in etching and deposition processes in microelectronic device fabrication. The chlorine discharge and its mixtures are frequently applied in the etching of semiconductors and metals. Here, capacitive discharges in Ar/Cl_2 mixture driven by sinusoidal rf voltage at 13.56 MHz with 2.54 cm discharge gap are explored using one-dimensional particle-in-cell/Monte Carlo collisional (PIC/MCC) simulations. The discharge model includes excited argon species and secondary electron emission, due to electron, ion and excited species impact on the electrodes. Chlorine is a highly electronegative discharge gas, whereas argon forms an electropositive discharge. By adding chlorine to an argon discharge, the plasma discharge can be transformed from being electropositive to become electronegative, and the electronegativity can be varied over a wide range. For pressure of 10 Pa the electronegativity can be varied from 0 - 107, while the electron energy distribution varies from bi-Maxwellian to Druyvesteyn like, as the Cl_2 fraction in the admixture is varied from 0 - 100 %. We will discuss how the electron power absorption mechanisms, the electronegativity, the electron energy distribution function, the reaction rates, and the composition of the discharge vary with the addition of chlorine to the argon discharge. Furthermore, we explore how the electron power absorption mechanisms, the electronegativity, the electron energy distribution function, and the discharge composition evolve with changes in pressure and driving voltage amplitude. In particular, we identify the discharge conditions where the electron power absorption transitions from the alpha-mode to the drift-ambipolar (DA) mode to a combined DA and striation mode, as the pressure, and the Cl_2 fraction in the feedstock are increased.

3:15pm **PS-ThA-5 Verification and Validation of the Open-Source Code PICLas for Capacitively Coupled Plasma Discharges in Etching Applications***, **Paul Nizenkov**, Asim Mirza, Stephen Copplestone, Julian Beyer,* boltzplatz - numerical plasma dynamics GmbH, Germany*; Marcel Pfeiffer,* Institute of Space Systems, University of Stuttgart, Germany

Capacitively coupled plasma (CCP) discharges are widely used in plasma etching and surface treatment processes. Predictive simulation of such discharges is essential for reactor design, process optimization, and the development of new etching chemistries. In this contribution, we present the verification and validation of PICLas (https://github.com/piclas-framework/piclas), an open-source Particle-in-Cell with Monte Carlo Collisions (PIC-MCC) code released under GPLv3, for radio-frequency CCP discharges in argon relevant to plasma etching applications. PICLas provides a framework for kinetic plasma simulation using Particle-in-Cell, Direct Simulation Monte Carlo (DSMC), Bhatnagar-Gross-Krook (BGK), and Fokker-Planck methods, enabling detailed modelling of electron kinetics, plasma chemistry, and plasma-surface interactions in low-pressure processing environments. First, the 1D benchmark by Turner et al. (Phys. Plasmas 20, 013507, 2013) is employed for a systematic code-to-code comparison of argon CCP discharges at multiple operating conditions. Second, a 2D axisymmetric simulation of the Gaseous Electronics Conference (GEC) reference cell, a standardized reactor geometry representative of industrial

etching tools, is performed and compared with available numerical results and experimental measurements. Key outputs include species- and time-resolved ion energy and angular distributions at the substrate and chamber walls, surface-charge tracking on dielectric boundaries, and secondary electron emission fluxes. These quantities can directly feed feature-scale etch models and surface chemistry frameworks. The verified simulation capability provides a foundation for predictive modelling of etching plasmas and plasma-surface interactions, supporting reactor-scale process development and optimization.

3:30pm **PS-ThA-6 Fully Kinetic Full-Chamber Modeling of ICP Discharges**, ***Daniel Main***, Silvaco, Inc.*; Seth Veitzer, Tom Jenkins, John Cary,* Silvaco Inc.

Low-temperature kinetic plasma simulations using particle-in-cell (PIC) and Monte Carlo methods (DSMC/MCC) for the chemistry can provide many advantages over fluid simulations, including self-consistent collisional heating at low pressure and correctly modeling sheaths without ad hoc assumptions. In addition, a fully kinetic approach can move beyond common assumptions made in fluid models, such as local conductivity or Maxwellian distributions of the plasma species. In this talk we present kinetic modeling results of inductively coupled plasmas (ICPs) in a 2D cylindrically symmetric geometry using the VSim[1] software package. We demonstrate how implicit methods can make these challenging simulations feasible, reducing compute times by factors of 20-200. We also demonstrate a method of providing constant power to the plasma, which further decreases the runtime needed to achieve steady-state discharges. We present several case studies which are based on process parameters discussed in Godyak et al. (2002)[2], showing good agreement with experimental measurements including plasma potential, plasma density, and electron temperature. Finally, we demonstrate the importance of a fully kinetic approach at low pressure (<~ 10 mTorr) to correctly model collisionless heating. We show that the simulated electron energy probability function compares well with experimental results, including the tri-Maxwellian features observed in Godyak et al.

1.www.txcorp.com

2. Godyak, Valery A., R. B. Piejak, and B. M. Alexandrovich, *Plasma Sources Science and Technology* 11.4 (2002): 525-543.

3:45pm **PS-ThA-7 Generalized RF Breakdown Surfaces and Avalanche Regimes in Dual-Frequency Argon CCPs: A 2D PIC/MCC Study**, ***Junesuk Kang***, KWT Solution, Republic of Korea

Single-frequency RF breakdown in argon capacitively coupled plasmas has often been represented as a breakdown curve versus pressure or *pd*. In dual-frequency CCPs, however, the breakdown boundary is inherently multidimensional because the high-frequency voltage, low-frequency voltage, frequency ratio, relative phase, and electrode surface properties can all modify the balance between electron multiplication and wall loss. In particular, the low-frequency field is not merely an additional contribution to an effective RMS voltage. Depending on the operating condition, it may increase electron drift loss to the electrodes and raise the required high-frequency breakdown voltage, or it may enhance ionization and surface-emission feedback and lower the threshold.We investigate these effects using a two-dimensional electrostatic PIC/MCC model of voltage-driven argon CCP breakdown. The simulations track electrons and Ar^+ ions, include electron-neutral elastic, excitation, and ionization collisions, Ar^+ collisions, and configurable surface reflection and secondary-electron-emission models. For each pressure, LF voltage, frequency pair, phase, and surface condition, the HF breakdown voltage is obtained by bisection using a growth-rate criterion based on $d(\ln N_e)/dt$, together with density-threshold crossing and self-sustained-growth confirmation. The resulting data are analyzed as generalized breakdown surfaces, $V_{HF,br}(p, V_{LF}, f_{HF}, f_{LF}, \theta, \text{surface})$. Ionization sources, electron wall fluxes, J·E, electron energy distributions, and secondary-electron-induced ionization are used to classify RF-avalanche, LF-loss-dominated, LF-assisted, surface-assisted, and mixed avalanche regimes. This framework provides a kinetic benchmark for RF startup windows and ignition-margin control in dual-frequency plasma processing reactors.

4:00pm **PS-ThA-8 Stochasticity in Advanced Plasma Etching**, ***Xingyi Shi***, *Han Luo, Jason Kenney, Shahid Rauf,* Applied Materials

As feature dimensions continue to scale, variability in plasma etching increasingly limits pattern fidelity. While intra-feature etch variations have traditionally been attributed to variations in incoming mask critical dimensions, emerging process regimes introduce additional sources of variability. Highly constrained plasma operating conditions can lead to ion-flux-limited etching, where stochastic effects become significant even for nominally uniform feature geometries. Under such conditions, measurable intra-feature variations may develop during etching despite minimal geometric nonuniformity at the start of the process.

In this work, we investigate the role of ion-driven stochasticity in governing intra-feature etch depth variations using feature-scale modeling. The study examines how process conditions and feature characteristics influence the evolution of etch front variability in ion-limited regimes. By comparing cases with different etching conditions and feature opening areas, the analysis highlights general trends linking stochastic transport and surface reaction processes to observed etch nonuniformity. Ongoing and forthcoming simulation results will be used to quantify these effects and to establish a qualitative framework for understanding and mitigating stochastic-induced variability in advanced plasma etching processes.

4:15pm **PS-ThA-9 Influence of Nitrogen Addition on Metastable Dynamics in a 2.45 GHz Ar-N_2 Plasmas**, ***Nafisa Tabassum***, *Duncan Trosan,* North Carolina State University*; Abdullah Zafar, Timothy Chen, Kelvin Chan,* Applied Materials, USA*; Steven Shannon,* North Carolina State University

A microwave-driven plasma operating at 2.45 GHz was studied using OES, LAS, probe diagnostics, and the plasma simulation package Zapdos [1]. The working gas was an Ar/N_2 mixture with a N_2 partial pressure range from 0 % to 25 % of total gas pressure (mTorr range) and a delivered power density (0.30 W/cm^3 -1.2 W/cm^3 range). Spatially resolved diode laser absorption spectroscopy of the Ar 696.7 nm transition $1s_5 \rightarrow 2p_2$ was used to probe the plasma. The line-integrated density and gas temperature were determined from the integrated absorption and broadening of the measured line shape. Relative concentrations of molecular N_2, ionized molecular N^+_2 and atomic N as well as bright Ar emission lines were obtained through optical emission actinometry as a function of N_2 partial pressure. The electron density and electron temperature were measured using Langmuir and hairpin probes. The metastable density decreases with increasing pressure, likely due to enhanced collisional quenching and reduced electron excitation out-weighing the production. In pure argon, it also decreases with delivered power, whereas the addition of N_2 leads to an opposite trend, with the metastable density increasing with power. The opposite power dependence likely results from modified plasma chemistry and surface interaction processes. Additionally, the experimental findings are compared with simulations conducted using CRANE and ZAPDOS plasma simulation applications in the Multiphysics

Object-Oriented Simulation Environment (MOOSE) platform.[1] PSST 32 (4), 044006

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Atomic Scale Processing Mini-Symposium
Room Ballroom A - Session AP+EL+PS+TF-ThP

Atomic Scale Processing Mini-Symposium Poster Session

AP+EL+PS+TF-ThP-1 Design of Gas Flow Field for a Slip Flow ALD Processing Chamber, ***Kyung-Hoon Yoo***, Korea Institute of Industrial Technology, Republic of Korea; *Geun-Soo Song,* The KUMYOUNG Inc., Republic of Korea; *Chun-Sik Kim,* TNG Co., Republic of Korea; *Jun-Young Hwang, Sang-Ho Lee, Jeong-Jin Kang, Shin-Ae Song, Kyung-Tae Kang,* Korea Institute of Industrial Technology, Republic of Korea; *Hyeong-Cheol Lee,* Hanyang University, Republic of Korea; *Kun-Hyung Lee,* SAMSUNG DISPLAY, Republic of Korea

As semiconductor feature sizes reach the nanometer scale, ALD processing equipment has become indispensable for atomic-layer control. However, conventional ALD processes face significant challenges regarding economic and environmental feasibility due to the excessive consumption of precursors and energy. [1,2] To address these issues, it is essential to establish sustainable manufacturing technologies through the development of high-efficiency ALD processing chambers. In the present study, we propose a slipflow based ALD chamber designed to optimize the process space and minimize resource waste. The nitrogen flow fields within the chamber were numerically investigated using Computational Fluid Dynamics (CFD) for process gap sizes of 1, 10, and 100 mm at 400 °C. Under an inlet static pressure of 1 Torr and a mass flow rate of 4.233×10^{-5} kg/s, the Knudsen number (Kn) and flow Reynolds number (Re) were evaluated as 0.0137 and 0.822, respectively for the 10 mm gap. These values confirm that the flow resides within the slip flow regime, where rarefaction effects at the surface wall become significant. Accordingly, the steady-state compressible laminar flow field was simulated by solving the continuity, momentum, and energy equations.[3,4]

Acknowledgment

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AP+EL+PS+TF-ThP-2 Nucleation and Evolution of Dislocations and Extended Faults in Complex Perovskite Oxides, ***Rishi Raj***, *K. Andre Mkhoyan,* University of Minnesota, USA

The stoichiometric flexibility of a perovskite oxide (ABO_3) results in several unique properties due to the presence of three elements in the crystal structure. This allows it to host a variety of defects across all dimensions. 1D primitive edge dislocations with varying terminations, screw dislocations as well as 2D structural faults like Ruddlesden-Popper, elastic distortions, and BO_3 octahedral tilts are commonly observed and studied. Even though structure and electronic properties of some of these defects have been reported, the nucleation and growth of such defects and dislocations is still unclear. Analytical STEM study of perovskite oxide thin films of $BaSnO_3$ and $SrSnO_3$ show the existence of two kinds of edge dislocations: single ([001]/(100)-type) and dissociated ([001]/(110)-type) edge dislocation each with two half planes missing. Six different types of such dislocations are possible and observed due to the terminations of the perovskite half planes. Similarly, 2D Ruddlesden-Popper faults are also observed to result from missing planes of atoms, suggesting a correlation with 1D dislocations. Apart from such conventional topological defects, complex perovskite oxides also showcase several line defects and dislocations with reconstructed cores. This suggests we can selectively populate the material with defects by altering the terminations of crystal half planes. Strain tuning during growth by swapping substrates or decorating the surface morphology can effectively allow termination control. This would allow certain defect and dislocation structures to be more favorable than others. By establishing this correlation between 1D and 2D faults, this work provides a potential pathway to transition from passive extended defect management to intentional, termination-controlled defect engineering.

AP+EL+PS+TF-ThP-3 Atomistic Study of the Effect of Moisture-Modified Amorphous SiO_2 Interfaces on Gas-Phase Clustering in LPCVD, ***Minseung Cha***, Seoul National University, Republic of Korea

Particle formation is a critical issue in LPCVD processes because nanoscale contaminants can cause film defects, pattern failure, yield loss, and process instability. Although particle generation is often explained by precursor decomposition and homogeneous gas-phase reactions, the chemical state of quartz-glass components used in LPCVD equipment has not been sufficiently considered. In particular, amorphous SiO_2 surfaces are widely exposed in parts such as process tubes, chambers, boats, injectors, and nozzles, and these surfaces can be modified by moisture during air exposure.

In this study, we investigate the role of moisture-modified amorphous SiO_2 interfaces in gas-phase clustering using molecular dynamics and density functional theory calculations. Dry SiO_2, hydroxylated SiO_2 surface models are constructed to represent different surface states. H_2O adsorption and dissociative chemisorption are first examined to evaluate silanol formation. The interaction between reactive molecules or cluster precursor species and each SiO_2 surface is then analyzed in terms of adsorption stability, residence behavior, and desorption tendency.

We propose that hydroxylated SiO_2 surfaces can act as reactive boundaries rather than inert walls in LPCVD environments. Surface silanol groups may temporarily stabilize reactive species through hydrogen bonding and electrostatic interactions, increasing local molecular concentration near the interface. These stabilized species can subsequently return to the gas phase and enhance molecular aggregation, thereby increasing the probability of cluster and particle formation.

This study provides an atomistic interpretation of how the moisture exposure condition of quartz-glass parts can influence gas-phase clustering in LPCVD processes. The results suggest that controlling moisture exposure and the hydroxylation state of amorphous SiO_2 interfaces in components such as nozzles, chambers, and boats may be important for particle suppression and process stability.

Keywords: LPCVD, amorphous SiO_2, H_2O vapor, hydroxylation, silanol, molecular dynamics, MD, density functional theory, DFT, gas-phase clustering, particle formation, quartz glass, semiconductor, process

AP+EL+PS+TF-ThP-4 Low Temperature Atomic Layer Deposition of ZnO for Optoelectronic Applications, ***Anil Yadav***, *Aditya Sadhanala,* Indian Institute of Science, India

This work demonstrates the ultra-low-temperature atomic layer deposition (ALD) of ZnO thin films at 50 °C and 70 °C using a 1 M diethylzinc (DEZ) solution in hexane and water as precursors. This was achieved in a custom-built ALD chamber with precise control over the process parameters. Despite the ultra-low deposition temperatures, the resulting ZnO films demonstrated excellent uniformity. This approach not only solves the problem of substrate compatibility by enabling ultra-low-temperature growth but also demonstrates the use of solvent-diluted pure precursors. The X-ray diffraction (XRD) patterns of as-deposited ZnO films deposited at 50 °C and 70 °C as a function of the number of ALD cycles from 50 to 250 were measured. As the ALD deposition cycles increased to 100, distinct diffraction peaks corresponding to (100), (002), and (101) planes emerged. When the deposition temperature increased from 50 °C to 70 °C, the (002) peak became more intense and sharper, indicating improved crystallinity.

To evaluate the electronic properties of ZnO thin films deposited at ultra-low temperatures of 50 °C and 70 °C, we integrated them as the active layer in field-effect transistors (FETs). The fabricated devices demonstrated exceptional electrical characteristics, exhibiting an I_{ON}/I_{OFF} ratio exceeding 10^8 with the saturation mobility of 0.85 cm^2/V.s. These results clearly confirm the applicability of solution-based precursors for ultra-low-temperature ALD depositions in electronic device applications.

AP+EL+PS+TF-ThP-5 Oxidation-Assisted SF_6 Remote Plasma Etching for Surface Roughness Reduction of TiN, ***Min Kyun Sohn***, *Subin Heo, Seong Hyun Lee, Sun Kyu Jung, Jeong Woo Park, Dongwoo Suh,* Electronics and Telecommunications Research Institute, Republic of Korea

Titanium nitride (TiN) is widely used as a conductive diffusion barrier and work-function metal in advanced semiconductor devices. As device dimensions continue to scale down, controlling not only the etch amount but also the post-etch surface morphology becomes increasingly important, because nanoscale roughness can directly affect electrical reliability,

interface quality, and subsequent film deposition. In the present study, we investigate the effect of SF_6 remote plasma-based etching on the surface morphology of TiN thin films, with particular emphasis on the role of a pre-oxidation step.

Three TiN surface conditions were compared: as-deposited TiN, TiN exposed to SF_6 radicals only, and oxidized TiN followed by SF_6 radical exposure. The etch per cycle (EPC) increased from 0.16 Å/cycle for the SF_6-only process to 0.38 Å/cycle for the oxidation-assisted SF_6 radical process, indicating that surface oxidation enhanced the fluorine-radical-driven removal of TiN. Atomic force microscopy measurements showed that the as-deposited TiN exhibited an RMS roughness of 1.313 nm, which modestly decreased to 1.117 nm after direct SF_6 radical exposure. In contrast, when the TiN surface was oxidized prior to SF_6 radical exposure, the RMS roughness further decreased to 0.850 nm, corresponding to an approximately 35% reduction compared with the as-deposited TiN surface, demonstrating a clear surface-smoothing behavior.

This difference suggests that the oxidation step plays a critical role in modifying the TiN surface before fluorine-radical exposure. The smoothing behavior is attributed to the formation of a TiO_x or TiO_xN_y surface layer during oxidation, followed by its conversion into volatile TiF_x species during SF_6 radical exposure. The higher EPC and lower RMS roughness obtained after oxidation-assisted SF6 exposure suggest that the modified surface layer can be removed more efficiently and uniformly than the native TiN surface. This oxidation-assisted pathway provides a chemically controlled route for reducing TiN surface roughness without relying on ion-driven physical sputtering.

These results indicate that surface pre-oxidation can be an effective strategy for controlling the morphology of TiN during radical-based etching. The proposed oxidation-assisted SF_6 radical process offers a potential strategy for morphology-controlled TiN etching in nanoscale device integration.

AP+EL+PS+TF-ThP-6 Development of in-Situ Laser Diagnostics Measurements of CH_3 Radical Concentrations for Study of Thin Film Depositions Using Organo-Metallic Precursors, ***Mruthunjaya Uddi***, Advanced Cooling Technologies Inc.*; Prawal Agarwal, Devon Jensen,* ACT*; Anatoli Morozov,* Princeton University*; Arthur Dogariu,* Texas A&M University

Many environmentally friendly non-halogen precursors contain CH3 structure component. Plasma chemical vapor deposition of pure metallic thin films using these precursors is challenging and requires better understanding of the gas phase and surface reaction mechanisms. We present a novel, time and spatially resolved, in-situ femtosecond laser diagnostics method to measure CH3 radicals in a non-equilibrium plasma environment. The CH3 radicals are predissociated to CH2 and H radicals using a 275 nm femtosecond laser pulse, followed by a 205 nm probe beam to measure the H radical concentrations. A single femtosecond laser is used to generate the required 275 nm and 205 nm beams. Measuring and knowing the dissociation cross section of CH3 radical by 275 nm pump beam, allows the quantification of CH3 radical concentrations with spatial and time resolution.

AP+EL+PS+TF-ThP-7 Hybrid Electrospun ZnO Nanofiber and ALD ZnO Electron Transport Layers for Near-Infrared Organic Photodiodes, ***Anna Leonard***, *Neha Chaturvedi, Veena Misra,* North Carolina State University

Organic photodiodes (OPDs) require efficient electron transport layers (ETLs) to achieve charge-selective extraction while minimizing recombination and dark current impacts. In this work, hybrid ZnO ETLs consisting of electrospun ZnO nanofibers and atomic layer deposited (ALD) ZnO were investigated for integration into near-infrared OPDs with a PTB7-Th:IEICO-4F active layer. The inclusion of the electrospun ZnO nanofibers increases the interfacial area between the ETL and active layer and provides enhanced electron transport pathways while the ALD ZnO layer provides film continuity and assists in passivating traps to mitigate defect states introduced by the nanofibers.

Three ETL architectures were investigated: ZnO fibers beneath ALD ZnO, ZnO fibers above ALD ZnO, and ALD ZnO control devices. ZnO nanofibers were fabricated through electrospinning of a zinc acetate dihydrate/polyvinylpyrrolidone (PVP) solution followed by calcination to oxidize the fibers and remove excess PVP. Device performance was evaluated through dark current density vs. voltage (J_{Dark}-V) and external quantum efficiency (EQE) measurements. Devices utilizing hybrid nanofiber/ALD ZnO ETLs exhibited reduced initial dark current compared to control devices indicating suppression of leakage pathways and trap-assisted recombination. Enhanced EQE response was observed in devices with fibers deposited above the ALD ZnO layer, suggesting improved interface quality and charge extraction.

These results demonstrate that combining electrospun ZnO nanostructures with ALD ZnO provides a promising method to engineer ETLs for high-performance OPDs and other optoelectronic devices.

AP+EL+PS+TF-ThP-8 Site-Specific and Temperature-Dependent Hydration of Faceted Hematite, ***Asare Dua***, Illinois Institute of Technology*; Luke Pretzie,* Purdue University*; Ashley Bielinski,* Argonne National Laboratory*; Yue Li,* Argonne National Lab*; Valentine Novosad, Cong Liu, Alex Martinson,* Argonne National Laboratory*; Adam Hock,* Illinois Institute of Technology

Alpha hematite (α-Fe_2O_3) is an abundant metal oxide whose surfaces and interfaces control key processes in catalysis, sensing, and photoelectrochemistry. While the more stable α-Fe_2O_3 (001) surface is well studied, less stable facets such as (012) and (104) which are more relevant in the aforementioned applications due to higher surface activity remain least studied. Surface sites of α-Fe_2O_3 (012) and (104), as well as their distinct stability were identified through temperature-dependent hydration by combining in situ infrared reflection absorption spectroscopy (IRAS) with density functional theory (DFT) vibrational analysis. For α-Fe_2O_3 (012), we found sites that promoted the dissociative and molecular adsorption of D_2O. Dissociatively adsorbed D_2O were either terminal or bridging. In both cases the hydroxyls were either isolated or interacting with nearby species. Protons of bridging hydroxyls (μ3a-OD (isolated); μ3b-OD (interacting with nearby hydroxyls)) are bound to triply coordinated surface oxygens while terminal hydroxyls (μ1a-OD (interacting with nearby hydroxyls)) were bound to octahedral surface Fe atoms (Fe_{oct}^{3+}). Similar to dissociatively adsorbed D_2O, molecularly adsorbed D_2O was either isolated (D_2Oa) or interacting with nearby hydroxyls (D_2Ob). α-Fe_2O_3 (104) on the other hand exhibited an isolated doubly coordinated bridging hydroxyl (μ2a-OD) and an interacting bridging species (μ2b-OD) rather than triply coordinated bridging hydroxyls. This preference is backed by our DFT calculations which shows triply coordinated bridging hydroxyls were highly unstable on α-Fe_2O_3 (104). Results from IRAS showed two isolated terminal hydroxyls, μ1a-OD and μ1b-OD, were present on the surface of α-Fe_2O_3 (104). This indicates two types of undercoordinated surface atoms existed with the first being undercoordinated tetrahedral Fe atoms (Fe_{tet}^{3+}) since they're the surface atoms of α-Fe_2O_3 (104), while the second is from the second layer of Fe atoms which have octahedral geometry. The undercoordination of Fe_{oct}^{3+} atoms however suggests oxygen vacancies (V_o) were present and some of these might migrate from surface to the second lattice of α-Fe_2O_3 (104). Our temperature dependent studies support this hypothesis since the population of μ1a-OD, μ1b-OD, and μ2a-OD increased with increasing temperature when under vacuum (0.8 torr). The distinct local environments of the sites on α-Fe_2O_3 (012) and α-Fe_2O_3 (104) and changes in properties with respect to temperature revealed through this work provide a fundamental tool that may be used to engineer the surface of alpha hematite through site- or facet-selective atomic layer deposition.

Plasma Science and Technology
Room Ballroom A - Session PS-ThP
Plasma Science and Technology Poster Session

PS-ThP-1 CO_2 as an Alternative Oxidant to N_2O in Plasma–Enhanced CVD Oxide Deposition, ***Lipeng Qian***, Micron technology, Singapore

Silane–based oxide and oxynitride films are widely deposited using plasma–enhanced chemical vapor deposition (PECVD) with silane (SiH_4) as the silicon precursor and nitrous oxide (N_2O) as the oxidant. Due to the high global warming potential and limited abatement efficiency of N_2O, alternative oxidants are being evaluated. In this study, a PECVD process is developed in which carbon dioxide (CO_2) replaces N_2O as the oxidation gas.

A schematic comparison of the conventional N_2O–based process and the CO_2–based process is shown in Figure 1. The primary technical challenges associated with this transition arise from the intrinsically lower reactivity of CO_2 relative to N_2O, which results in reduced oxidation efficiency during plasma activation. The higher bond energy of CO_2 limits its dissociation and oxide–forming capability with SiH_4, necessitating extensive process tuning to achieve acceptable film formation.

Significant differences in film composition are observed between the two processes, leading to challenges in matching key optical properties, including refractive index (n) and extinction coefficient (k), as shown in Figure 2. In addition, the CO_2–based process exhibits a shifted and narrower

process window, with substantially degraded defect performance relative to the N_2O baseline. Defect sensitivity is strongly process–region dependent and requires targeted optimization to achieve manufacturable performance.

Integration impacts are also observed, as the CO_2–based films demonstrate different wet and dry etch behaviors, requiring adjustments to downstream photo and etch processes to maintain compatibility. Despite these challenges, successful implementation of an N_2O–free PECVD process is achieved through systematic optimization and process innovation. Representative film performance is summarized in Table I, showing reduced surface roughness, slower wet etch rate, and reduced dry etch rate compared to the N_2O reference process.

This work demonstrates the technical feasibility of CO_2–based PECVD oxide deposition for semiconductor manufacturing, providing a viable pathway toward N_2O–free deposition processes while maintaining film property control and integration compatibility.

PS-ThP-2 Effect of Electrode Configuration on Plasma Discharge Characteristics and PVDF Film Properties Using Atmospheric Pressure Plasma Jets, ***Eun Young Jung***, The Institute of Electronic Technolog, Kyungpook National University, Republic of Korea*; Heung-Sik Tae,* School of Electronic and Electrical Engineering, Kyungpook National University, Republic of Korea*; Choon-Sang Park,* Department of Electrical Engineering, Milligan University

The development trends of piezoelectric nanogenerators (PENGs) will be flexible light weight and wearable self-poweredelectronics for an industrial application. For this reason, polyvinylidene fluoride (PVDF) for piezoelectric polymer materials seem to be attractive candidates for flexible PENGs owing to mechanical flexibility and good properties of the piezoelectric and ferroelectricity [1,2]. Recently, these PVDF-basedpolymers are used to produce films using the various plasma techniques such as low-pressure and atmospheric pressure plasma (APP). In particular,the APP process is the appropriate method to deposit the polymer film on the point of view a simple and low cost process. ThisAPP process are effective method for polymer deposition under ambient air due to easy, simple process, and room temperature[3]. There are few research on the piezoelectric polymers using the APP process [1,4].However, there are some problems such as low deposition rate, loss of monomer precursor, and small deposition area of the APP processes. Thus, to resolve these problems, the structural improvement of plasma reactor is essential for enhancing the efficiency of deposition rate and deposition area.Accordingly,this study investigates the plasma discharge characteristics and structural properties of PVDF thin film deposited by using APP reactor in terms of two different electrode configurations (metal-mesh and planar-type). The characteristics of PVDF thin films investigated using field-emission scanning electron microscope (FE-SEM), Fourier transforms-infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and LCR meter. Through new APP plasma reactor electrode configurations, the thickness of PVDF thin film was increased by using a planar-type electrode compared to that of a metal-mesh type electrode at room temperature using a mixed polymer solution composing of PVDF nano powder and dimethylformamide solution. FE-SEM results show that PVDF nanoparticles are clearly observed and uniformly coated. In the FT-IR spectra, two types of chemical bonds (α and β phases) were observed in the deposited PVDF thin film. Based on these experimental results, we may expect that a new APP plasma reactor will be a great attractive method in order to synthesis the PVDF thin film under atmospheric pressure.The APP with new APP plasma reactor, FE-SEM, FT-IR, XRD, LCR meter, and related mechanism of PVDF thin film are studied and will be discussed in detail.

PS-ThP-3 Time Stability of Hafnium Nitride Thin Films Deposited by Plasma-Enhanced Atomic Layer Deposition, ***Sandra Schujman***, NY Creates*; Natalya Tokranova, Christophe Valleé,* University at Albany*; Vidya Kaushik,* NY Creates

Transition metal nitrides are sought for semiconductor device applications due to their low electrical resistivity and because they can be excellent diffusion barriers for copper and oxygen. Such films prepared by Atomic Layer Deposition (ALD) have the additional advantage of spatial conformability to structured surfaces and tight thickness control.

In particular, for the ALD deposition of hafnium nitride there have been a number of studies demonstrating tunable electrical properties by controlling the process chemistry (varying the precursor and co-reactant), using thermal ALD versus Plasma-Enhanced ALD, using different plasma compositions, and by varying the deposition parameters (substrate temperature, plasma pressure, plasma composition, etc.). Even though very low electrical resistivity values have been reported, it has also been observed that over time, the resistivity of the layers tends to increase.

In this work, we concentrated on the analysis of electrical resistivity stability as a function of time for HfN thin films deposited on Si or SiO_2 substrates. Various ionic compositions of the plasma, different external RF bias of the substrate, and ALD cycle parameters, were used in order to obtain low electrical resistivity. The layers were characterized by X-ray Photoelectron Spectroscopy, Grazing Incidence X-ray Diffractometry, X-ray Reflectrometry, and Atomic Force Microscopy, and four-point probe measurements were done to determine resistivity.

The samples were kept under regular atmospheric conditions and remeasured over time to understand composition and crystallinity variations and their effect on layer resistivity.

PS-ThP-4 Study on Cryogenic SiO_2 Etching Mechanisms in High Aspect Ratio Contacts Using CF_3I-Based Plasmas with C_4F_6 and WF_6 Passivation, ***Junyeob Lee***, *Mingyu Kim,* Daejeon University, Republic of Korea*; Hyunjun Kim,* Daejeon university, Republic of Korea*; Woongsun Lim, Changhwan Kim, Sanghee Gwak, Sungin Kim,* Korea Advanced Nano Fab Center, Republic of Korea*; Jeongwoon Bae, Kyongnam Kim,* Daejeon University, Republic of Korea

As 3D NAND flash memory integration increases, securing High Aspect Ratio Contact (HARC) etching technology capable of penetrating multi-layer dielectric stacks of hundreds of layers has become essential. Conventional fluorocarbon (C_xF_y) processes are prone to defects such as etch-stop and bowing as aspect ratios increase. Recently, cryogenic etching has gained significant attention as a solution due to its ability to form precise sidewall passivation layers. In this study, a cryogenic SiO_2 etching process was investigated using a Capacitively Coupled Plasma (CCP) system with a base gas chemistry of CF_3I and $H_2/Ar/O_2$, while incorporating C_4F_6 and WF_6 as passivation gases to elucidate the cryogenic etching mechanism. An Amorphous Carbon Layer (ACL) was used as a hard mask, and the substrate temperature was varied from 20℃ to –90℃ to investigate the effects of temperature on passivation and etching mechanisms. In the gas chemistry, the H_2/O_2 flow rate ratio was selected as a key variable to analyze the effect of hydrogen radical concentration on ACL mask protection and sidewall stability. Furthermore, the etching process was performed under various conditions, including the individual and simultaneous injection of C_4F_6 and WF_6, to systematically investigate the effects of CFx polymers and tungsten-containing compounds on cryogenic etching.

Changes in the etch profile were evaluated through cross-sectional SEM analysis. Additionally, XPS analysis was conducted to examine the content and chemical bonding states of Iodine (I), Carbon (C), and Tungsten (W) within the formed passivation layers. Through these analyses, this study aims to verify and propose the correlation between the multi-layer passivation mechanism and etch profile formation.

PS-ThP-5 Impact of Secondary Electrons on Scaling Wafer Bias to High Power, ***James Prager***, *Josh Perry, Paul Melnik, Timothy Ziemba,* Eagle Harbor Technologies, Inc. (dba EHT Semi)*; Max Kellermann-Stunt, Mark J. Kushner,* University of Michigan

The semiconductor market demands high-aspect-ratio (HAR) features that can be produced at high etching rates. This requires a high ion current to the wafer surface to increase the etch rate. Simultaneously, the aspect ratio of these features is increasing towards 100:1. To achieve high aspect ratios, the ion angular distribution must be well controlled to reduce the sidewall damage to the feature. To accomplish this, tool manufacturers are requesting tailored waveforms wafer bias power systems that can operate at higher voltage. As the wafer bias voltage increases, the secondary electron effects also increase.In this work, we investigate the effect of secondary electrons on the power scaling of a tailored waveform wafer bias power system as the voltage increases. This experimental work was conducted with a capacitively coupled plasma, whose top-side electrode is driven by a 60 MHz radio frequency generator. The bottom-side electrode is driven by a high-voltage tailored waveform generator (Perseus) operating at 400 kHz. Plasma measurements made with a retarding field energy analyzer will be presented along with power system measurement. The experimental results will be compared with modeling results from the Hybrid Plasma Equipment Model. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Fusion Energy Science under Award Number(s) DE-SC0024861.

PS-ThP-6 An RF Generator Without a Matching Network for Capacitively Coupled Plasma and Bias Applications, ***Timothy Ziemba***, *Josh Perry,* Eagle Harbor Technologies, Inc. (dba EHT Semi)*; Paul Melnik, Chris Bowman, Connor Liston, Stephanie Geeson, James Prager,* Eagle Harbor Technologies Inc. (dba EHT Semi)

Capacitively coupled plasma (CCP) sources are used throughout the semiconductor and thin film industries. CCPs are driven by a radio frequency (RF) generator with a fixed output impedance that must be impedance matched to the plasma. However, matching networks increase the cost, complexity, thermal management requirements, and response times of CCPs, which all scale with power of the RF generator. EHT Semi has developed a new RF generator that eliminates the need for a matching network while driving a capacitive load. This RF generator is being tested on a CCP for plasma generation and bias applications across a range of experimental parameters (power, neutral pressure, and gases). EHT will present the output and electrode waveforms of this new type of RF generator as well as plasma measurements.

PS-ThP-7 Modeling Atomic Wall-Catalyzed Recombination Kinetics and Weakly Bound Surface Species, ***Jonathan Tran***, *David Graves,* Princeton University

Radical surface recombination kinetics are important in plasma reactors, but mechanisms are still poorly understood. Improving the models for these processes is the main goal of this work. This requires a better understanding of weakly-bound species, but how to handle them in surface kinetics models remains an open question. Understanding the dynamics of non-chemisorbed species will also provide valuable insight into other important problems in plasma-surface reactions, for example, cryogenic etching.

In this work, we use molecular dynamics (MD) simulations to identify fundamental mechanisms of weakly-bound chlorine on chlorinated silicon surfaces. The reactive empirical bond-order (REBO) potential form is used. Insights from these simulations can be leveraged to develop reduced-order models (ROMs). The model parameters are then fit to MD results and combined with nudged elastic band (NEB) REBO calculations. Finally, the ROM results are compared to experimentally observed radical surface recombination kinetics. We identify plausible surface recombination mechanisms, propose models for how we may treat weakly-bound species in plasma surface systems, and suggest future experiments and computational studies that are necessary to clarify the role of weakly-bound species in these systems.

PS-ThP-8 Low Thermal Budget Dopant Activation via Spike Plasma Enhanced Annealing, ***Zhihao Ma***, University of Texas at Dallas*; Mahsa Shekarnoush, Yuanning Chen, Malcolm Bevan, Harvey Stiegler,* MicroSol Technologies Inc.*; Lawrence Overzet,* University of Texas at Dallas

The formation of highly activated ultra-shallow junctions remains a critical challenge for advanced semiconductor device scaling, where dopant activation must be achieved while suppressing thermal diffusion and preserving structural integrity. Conventional annealing approaches, including furnace annealing and rapid thermal annealing (RTA), typically require temperatures above 800 ℃, resulting in undesirable dopant redistribution, junction broadening, and degradation of thermally sensitive device structures and materials.

Plasma Enhanced Annealing (PEA) has demonstrated strong potential as low thermal budget annealing approach through localized and controllable energy delivery from plasma ions, which significantly reduce substrate temperatures (300-500 ℃) by adjusting ion kinetic energy, flux, dose, and species. In this work, a spike plasma enhanced annealing (spike-PEA, millisecond scale) process was investigated for phosphorus-, arsenic- and B-implanted silicon wafers and the post-process properties were systematically characterized by four-point probe measurement, Raman spectroscopy, and secondary ion mass spectrometry (SIMS). Compared with conventional thermal annealing (TA) and RTA under identical temperatures, spike-PEA demonstrated substantially enhanced dopant activation, producing significant reductions in sheet resistance across all implantation profiles, together with improved crystallinity. The effective activation fractions as high as 105% relative to 800 ℃ RTA reference were achieved at only 400 ℃ with minimal junction broadening.

The results demonstrate that spike-PEA enables efficient dopant activation through selective near-surface ion energy deposition while minimizing dopant diffusion. These findings establish spike-PEA as a promising low-temperature annealing strategy for next-generation semiconductor manufacturing and advanced ultra-shallow junction integration.

PS-ThP-9 Effect of Thin Dielectric Layer Boundary Conditions on Electronegative Plasmas in Capacitively Coupled Plasma Reactors, ***Jeong-hoon Son***, KWT Solution Inc., Republic of Korea

As semiconductor processes become increasingly precise, simulation-based plasma analysis is attracting growing interest due to the inherent limitations of direct experimental measurement. However, a persistent challenge remains the discrepancy between simulation predictions and experimental results, often arising from insufficient representation of actual experimental conditions in plasma simulations.

One commonly overlooked condition is the dielectric coating applied to electrode surfaces in real equipment. In industrial plasma reactors, electrodes are routinely coated with materials such as Al_2O_3 or Y_2O_3 to prevent plasma-induced corrosion and contamination. These coatings modify the effective sheath voltage through surface charge accumulation, yet most simulation studies continue to model electrodes as bare conductors.

In this study, we analyze the effect of dielectric electrode coatings in a capacitively coupled plasma (CCP) reactor using the thin dielectric layer boundary condition provided by a commercial fluid simulation software. Particular attention is given to electronegative plasmas, in which the presence of negative ions (O^-) fundamentally alters the discharge structure. Simulations are performed at 250 mTorr and 13.56 MHz with an applied voltage of 100 V, while the Ar/O_2 gas composition is systematically varied to examine how the influence of the coating changes as the negative ion fraction increases relative to the electropositive baseline.

As the O_2 fraction increases, the negative ion density rises and the overall plasma density distribution undergoes a significant transition. At low O_2 fractions, the radial electron density profiles with and without coating show little difference. However, as the O_2 fraction increases, the coating boundary condition produces a pronounced change in the radial electron density distribution. These results indicate that in highly electronegative plasmas, accurate representation of electrode surface coatings is not a minor modeling detail, but a physically significant factor that substantially affects simulation fidelity.

Given the growing use of electronegative gases in plasma processing, proper treatment of surface coating effects will be an essential element for obtaining reliable simulation results.

PS-ThP-10 Implementation of a Surface Coverage Module in K-PLASMA(0D) and Validation Against a C4F8 Inductively Coupled Plasma Global Model, ***Yongil Lee***, KWT Solution, Republic of Korea*; Deuk-Chul Kwon,* Korea Institute of Fusion Energy, Republic of Korea*; Dong-Hun Yu,* KWT Solution, Republic of Korea

In spatially-averaged plasma simulations, surface reactions are often represented as interactions with a single, time-invariant wall state characterized by fixed sticking or recombination probabilities. This simplification cannot capture the evolving surface state during etching or deposition processes, where adsorbed species progressively modify the wall composition and thereby change the probability of each subsequent wall reaction. To address this limitation, the wall must be resolved into multiple surface states whose fractional coverages are coupled with gas-phase kinetics. We report the implementation of a surface coverage module in K-PLASMA(0D), a 0D global plasma simulator currently under development and commercialization, and its validation against a reference C_4F_8 global model and inductively coupled plasma (ICP) measurements.

The new module couples gas-phase kinetics with a heterogeneous wall reaction set that distinguishes bare, fluorinated, and ion-activated sites of the fluorocarbon (fc) film. F atoms adsorb on the fc film and form a fractional surface coverage θ_F that blocks fc-radical deposition on bare sites and enables $CF_x + F(s) \rightarrow CF_{x+1}$ recombination (x = 0–3), including CF_4 formation. Ion-induced site activation and ion-enhanced etching releasing CF_2 are also incorporated. The reaction probabilities and the C_4F_8 gas-phase reaction set, comprising electron impact, ion recombination, autodetachment, neutral recombination, and associative detachment, follow the reference formulation.

Simulations were performed for a C_4F_8 ICP reactor at 200 sccm C_4F_8 / 10 sccm Ar, pressure of 9.7 mTorr, T_gas = 305 K, and source power of 500–2,000 W. Using the reference global model as a benchmark, K-PLASMA(0D) successfully reproduces the F, CF_2, and CF density trends and the surface coverage evolution, with θ_F reaching ~0.19 at 2,000 W[1]. The agreement confirms that the surface coverage module, including F-blocking and surface recombination pathways, has been correctly implemented in K-PLASMA(0D).

In this work, only the fractional coverages of three surface states — bare site, F-adsorbed site (θ_F), and ion-activated site — were considered during polymer formation. As a next step, the surface reaction rates obtained here can be aggregated to derive the macroscopic polymer deposition rate, enabling the present module to be applied to PECVD process modeling. The framework will also be extended to other surface chemistries, in particular SiO_2 etching.

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PS-ThP-11 Positive Pulse Biasing for Directional Electron Extraction in Capacitively Coupled Plasma*, Kyoung-Jae Chung,* ***Junbeom Park****, Daehyun Kim,* Seoul National University, Republic of Korea

In high aspect ratio (HAR) etching, ions are directionally accelerated through the sheath, whereas electrons cross the sheath mainly by thermal motion. This difference causes positive charge accumulation near the bottom of narrow structures, which can distort the etching profile. Our previous work demonstrated through simulations that positive pulse biasing can extract directional electrons from capacitively coupled plasma (CCP) and transport them into HAR structures. In particular, the simulations showed that a shorter pulse rise time produces more directional electrons by enhancing the transient electron extraction process. However, experimental validation is needed to determine whether this pulse-induced electron extraction can be realized in an actual CCP system. In this work, positive pulse biasing is applied to a CCP system to observe directional electron extraction and to experimentally examine the correlation between pulse parameters and electron extraction behavior suggested by the simulations. The influence of plasma density on the extraction process is also analyzed, and the results provide guidance for the development of pulse bias waveforms that mitigate charge accumulation and improve profile control in advanced plasma processing.

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PS-ThP-12 Plasma Impedance Monitoring of SiNx Etching Processes with Different Grounding Conditions*, **hyun kyu Choi**, Heeyeop Chae,* Sungkyunkwan University (SKKU), Republic of Korea

Plasma impedance variations at the RF grounding interface were monitored to assess the system status in this work. The experiment was conducted in a 300 mm ICP chamber using Ar/CF_4 plasma at 30 mTorr. A 13.56 MHz source power and a 2 MHz bias power were applied to the inductive coil on a quartz window and to the electrostatic chuck, respectively. The grounding conditions were controlled by mechanically tightening the inner liner bolts using a torque driver. The bolt torque was adjusted from 1 to 15 torque levels, and the 15 torque condition was served as the reference for comparison. A VI probe captured the electrical variations of the plasma response to grounding status. The electrical resistance at 15 torque exhibited a standard deviation of 29.04% compared to the 1 torque condition, and the reactance showed a standard deviation of 21.06% under the same conditions. Theoretical analysis using the CMY models (Int. J. Heat Mass Transfer, 1969) and Greenwood models (Proc. R. Soc. Lond. A, 1966) was performed to predict the interface mechanics. These models show that increased torque expands the effective contact area and enhances the surface conductance.In addition, SiN etching experiments were performed under different torque conditions. The etch rate at 1 torque was 2.495% lower than the value at 15 torque. These results indicate that the bolt contact status alters the grounding stability of the chamber.

PS-ThP-13 Particle-in-Cell Simulation of the Synchronous Effect in Pulsed Dual-Frequency Capacitively Coupled Plasma*, **Jun Hee Mun**,* KWTSolution, Republic of Korea

This study investigates the synchronization effects between high-frequency (HF) and pulsed low-frequency (LF) voltages in a dual-frequency capacitively coupled plasma (DF-CCP) system, which is widely utilized in semiconductor processing and advanced plasma-based manufacturing. Dual-frequency operation enables independent control of plasma density and ion energy; however, the introduction of pulsed LF biasing introduces temporal complexity whose underlying mechanisms remain poorly understood. In particular, pulsed LF excitation has been proposed as an effective approach to tailor ion energy distributions for high-aspect-ratio etching, but the role of its phase relationship with HF excitation in determining plasma characteristics remains largely unexplored.

In this work, a two-dimensional particle-in-cell (PIC) simulation is performed to systematically analyze these synchronization effects. A 20 MHz sinusoidal HF voltage and a 400 kHz pulsed LF voltage are applied, with the LF duty cycle fixed at 50%. Two representative control strategies are considered: (1) varying the HF duty cycle from 50% to 100% to modulate the overall temporal overlap, and (2) maintaining a 50% HF duty cycle while introducing a controlled phase delay in the HF waveform within the LF pulse-on period. These approaches allow precise adjustment of the overlap ratio between HF excitation and the LF active phase, providing a consistent framework to isolate synchronization-driven phenomena.

The simulation results demonstrate that the degree of temporal overlap strongly affects the spatiotemporal evolution of plasma potential, sheath dynamics, and electron heating mechanisms. In particular, changes in overlap modify the phase-resolved electron power absorption and lead to distinct electron density distributions and potential structures. As a result, ion acceleration dynamics within the sheath are also altered, indicating that ion energy control is closely linked to waveform synchronization rather than solely to individual frequency components.

These findings highlight that synchronization between HF and pulsed LF voltages is a key operational parameter in DF-CCP operation. The results provide practical insight into waveform engineering strategies for precise control of plasma characteristics, provide pathways toward optimizing etching performance in next-generation semiconductor fabrication processes.

PS-ThP-14 3D PIC-MCC Simulation for Plasma Nonuniformity in off-centered DC Magnetron Sputtering*, **Yu Gyeong Suh**, Hae June Lee,* Pusan National University, Republic of Korea

DC magnetron sputtering (DCMS) remains a cornerstone of thin film deposition and is widely used for metal gap fill in semiconductor packaging processes. However, plasma nonuniformity arising from the closed E×B drift loop continues to limit target utilization and film uniformity. Nowadays, intentionally asymmetric magnet topologies offer an underexplored route to control plasma spatial structure and ion bombardment. This study utilizes a self-consistent 3D particle-in-cell with Monte Carlo collision (PIC-MCC) simulation to investigate a DCMS discharge driven by a non-circular off-centered magnet. Using an in-house-developed code, an Ar discharge at 5 mTorr with a planar Cu target has been investigated using a fully kinetic analysis under a realistic, azimuthally nonuniform magnetic field. We quantify how this non-circular topology reshapes the spatial distribution of electron and ion densities through the competition among E×B, ∇B, and diamagnetic drifts. Preliminary calculations confirm that the off-centered topology breaks the azimuthal symmetry of the trap region, inducing localized weakening of the curvature-driven gradients along the racetrack. These features drive azimuthally varying ion flux and measurable shifts in the IEAD high-energy tail. This work establishes a 3D kinetic framework for magnet design optimization, providing a physics-based basis for tuning film growth conditions in large-area, high-performance coatings.

PS-ThP-15 Two-Dimensional Particle-in-Cell Simulation of Electronegative Plasmas in Chlorine Capacitively Coupled RF Discharges*, **Dongmin Lee**, Hae June Lee,* Pusan National University, Republic of Korea

Capacitively coupled plasmas used in the etching process of advanced semiconductor fabrication include negative ions and reactive radicals. Unlike electropositive discharges, electronegative plasmas contain a large amount of negative ions, depleted electron densities, and enhanced bulk electric fields. It has been reported that these features modify sheath dynamics, electron power absorption, radical generation, and charged-particle motion. However, ion dynamics near the bulk–sheath boundary remain insufficiently understood under RF-driven etching conditions. In this work, frequency-dependent charged-particle dynamics in chlorine capacitively coupled plasmas are investigated using a two-dimensional particle-in-cell Monte Carlo collision (PIC MCC) simulation. Chlorine is selected as a representative electronegative etching gas, where dissociative attachment and negative-ion confinement can lead to an ion-dominated bulk plasma. By changing the RF driving frequency, different degrees of electronegativity are obtained, enabling comparison of charged-particle motion. At lower driving frequencies, the discharge becomes highly electronegative. The bulk electron density is low because negative ions are confined in the plasma bulk, while positive ions are accelerated toward the electrodes through the RF sheath. This separation produces a localized space-charge density peak near the bulk–sheath boundary, thereby enhancing the local electric field. The resulting field perturbs the relative motion of positive and negative ions, generating a low-frequency ion-scale response that extends from the sheath edge into the plasma bulk. This ion motion is coupled to the electron power absorption, suggesting that the bulk–sheath boundary acts as an active region for energy exchange and charged-particle dynamics. As the driving frequency increases, the plasma becomes less electronegative, the localized space-charge peak weakens,

and the ion-scale response near the sheath edge decreases. These results suggest that the localized electric field structure is governed by the balance among negative-ion confinement, ion inertia, and RF sheath motion. The results provide a kinetic interpretation of ion dynamics in electronegative chlorine CCPs and clarify how RF frequency can influence electronegativity and sheath-edge field formation. Understanding these mechanisms is important for high-aspect-ratio and profile-sensitive etching because the spatial distribution of ions, radicals, and energy deposition affects etch rate, selectivity, sidewall control, and process uniformity.

PS-ThP-16 Electrified C–N Coupling in Ethylene Glycol Using Nitrogen DC Plasma-Liquid Interactions, ***José Balena***, *Mikhail Vasilev,* University of Notre Dame*; R. Mohan Sankaran,* University of Illinois Urbana-Champaign*; Caue Ribeiro,* Embrapa Instrumentation, Brazil*; David Go,* University of Notre Dame

Direct-current (DC) plasma–liquid interactions have emerged as a promising strategy for electrified chemical transformations under mild conditions. Plasma systems are particularly attractive for nitrogen activation because cleavage of the N≡N bond is thermodynamically and kinetically challenging using conventional methods. Industrial nitrogen fixation still relies mainly on the energy-intensive Haber–Bosch process, and electrochemical and photocatalytic N-transformation often need highly active substrates, while suffering from low efficiencies and limited N_2 solubility in liquids. In this work, a nitrogen plasma generated directly over liquid ethylene glycol (EG) was employed to promote nitrogen incorporation into organic molecules. EG was selected as both solvent and carbon source due to its low cost, low volatility, biodegradability, and availability from biomass valorization, plastic recycling, and CO_2-derived routes. Reaction products were investigated by GC–MS using direct injection and silylation derivatization methods. The major nitrogen-containing product identified after derivatization was (2-hydroxyethyl) carbamate providing evidence for incorporation of nitrogen in the organic substrate. Total nitrogen analysis indicated a nitrogen fixation rate of approximately 370 μmol h^{-1} in EG. This rate was not significantly affected by either the reaction volume or reaction time, provided that the electrolyte concentration and gas flow rate were maintained constant at 0.17 M $NaClO_4$ and 50 sccm N_2, respectively. Control experiments using hydroxylamine (NH_2OH) and ammonium hydroxide (NH_4OH) under argon plasma yielded the same compound, suggesting NH_2• radicals as key intermediates. Comprehensive analysis of the samples revealed a broader distribution of nitrogen-containing compounds. GC-MS detected traces of amino acids after derivatization, while direct injection identified cyclic nitrogen compounds such as piperidinoacetonitrile. Ongoing studies are being performed to further elucidate reaction pathways and reactive intermediates. These findings demonstrate the potential of plasma-liquid systems for sustainable nitrogen fixation and electrified synthesis of value-added nitrogen-containing chemicals from abundant feedstocks.

PS-ThP-17 Effect of H_2O Additive Gas on Sio_2 and Si_3N_4 Films in C_4F_8 Self-Bias Plasma, *Heeyeop Chae,* ***Haegeon Jung***, Sungkyunkwan University (SKKU), Republic of Korea

Fluorocarbon (FC) layer formation affects surface reactions and profile evolution in low-temperature plasma processing. This study investigates the effect of H_2O addition on FC layer formation on SiO_2 and Si_3N_4 films in C_4F_8 self-bias plasma. An inductively coupled plasma chamber generates C_4F_8/Ar plasma without external RF bias. Substrate temperature ranges from 20 °C to −60 °C. FC layer thickness is evaluated by ellipsometry and VSEM, and surface bonding structure is analyzed by XPS. Low substrate temperature increases FC layer thickness on both SiO_2 and Si_3N_4 films due to enhanced polymer accumulation and reduced desorption. SiO_2 surfaces exhibit thicker FC layer formation than Si_3N_4 under identical plasma conditions. XPS analysis confirms increased C–C and C–CF bonding fractions at low temperature, indicating stabilization of carbon-rich FC structures. H_2O addition further increases FC layer thickness in C_4F_8 plasma, particularly on Si_3N_4 surfaces, while O_2 addition suppresses carbon accumulation through oxidation-related reactions. These results indicate that H_2O addition modifies FC surface chemistry and temperature-dependent polymer stabilization behavior in C_4F_8 self-bias plasma. The study suggests material-dependent FC layer formation behavior in low-temperature fluorocarbon plasma processing.

PS-ThP-18 Aqueous Electron Yields for Non-thermal Plasma in Contact with a Water Cathode: Effects of Plasma Gas Composition, ***Mikhail Vasilev***, *David Bartels, David Go,* University of Notre Dame

Nonthermal plasmas in contact with liquids present a unique plasma–surface interaction challenge: the liquid surface acts as the cathode and must supply electrons to sustain the discharge and maintain charge balance. Despite this fundamental role, the mechanism of secondary electron emission from the liquid cathode remains poorly understood. Proposed mechanisms include photoionization, field emission, and ion-induced emission. One candidate process involves plasma-generated reactive species producing free conduction-band electrons in the liquid, with a small fraction escaping into the plasma while the majority thermalize and solvate to form aqueous (solvated) electrons[1]. The probability of electron emission from the liquid surface is extremely low, with only ~10^{-6} of conduction-band electrons estimated to escape into the plasma, making direct measurement difficult and mechanistic assignment challenging.

Water has an ionization energy of ~10 eV, yet the average kinetic energy of ions impinging on the liquid surface through the plasma sheath is estimated at only ~1 eV for argon systems. This energy gap argues against simple ion-induced ionization of water and suggests that alternative interfacial processes, such as proton-transfer pathways or metastable-driven reactions, contribute to electron generation. Prior work using argon plasma–liquid systems and chloroacetate reduction as a liquid-phase electron dose probe has estimated apparent electron yields on the order of unity. In this work, we quantify how different gas ions affect electron generation at the plasma–liquid interface using in situ chloride ion measurements produced by the reaction of aqueous electrons with chloroacetate. By varying plasma gas composition (H_2, He, Ar, Kr, Xe), this work investigates how ion mass, metastable energy, and chemical reactivity govern electron generation pathways at plasma–liquid interfaces, with implications for secondary electron emission modeling in plasma–liquid systems.

PS-ThP-19 Plasma Monitoring for Chamber Conditioning Steady-State Detection Using He-Normalized SiF Saturation in Inductively Coupled Plasma, ***Suyoung Ko***, *Heeyeop Chae,* Sungkyunkwan University (SKKU), Republic of Korea

The He-normalized SiF Saturation Index (SSI) was developed as a real-time chamber wall condition indicator. SSI monitored chamber wall stabilization during post-preventive maintenance (PM) chamber conditioning in inductively coupled plasma etchers with Y_2O_3-coated walls. Optical emission spectroscopy (OES) monitored full-spectrum emission in situ during plasma cleaning cycles on a 300 mm ICP etcher with Y_2O_3-coated walls across three PM events. Partial least squares variable importance in projection (PLS-VIP) analysis identified SiF (440.1 nm) as the wall-state-sensitive emission line. SSI was defined as the cycle-averaged I(SiF)/I(He) ratio, using He (706.5 nm) as the normalization reference. Blanket oxide etch rate was measured to validate SSI. He normalization reduced the CV of SiF emission from 17.6% to 3.8%. This reduction isolated the wall-state-dependent SiF signal from plasma source fluctuations, enabling SSI to track chamber wall condition independently. SSI converged to a ±2% stability band at the 7th conditioning wafer across three PM events, indicating faster chamber stabilization than the conventional fixed 24-wafer chamber conditioning protocol. SSI correlated with blanket oxide etch rate at $r = 0.965$ ($p < 0.001$), confirming SSI as a process-relevant chamber wall condition indicator. SSI identified the chamber stabilization point in real time, replacing the conventional fixed-count chamber conditioning protocol. This work demonstrated that SSI is a practical in-situ wall condition indicator applicable to production ICP etchers.

PS-ThP-20 Time-Resolved Langmuir Probe Measurements of Pulsed RF Argon Plasmas, ***Collin Clay***, *Kylan Herring, David Ruzic,* University of Illinois

Pulsed RF plasmas are a powerful tool for etching and other plasma processes. The pulsing of the RF plasma provides a number of variables to control the plasma treatment process such as pulse repetition rate and duty cycle. While computational models have provided insight into the fundamental physics of pulsed RF plasmas, there is still a significant lack of experimental validation of these models. In this we work, we present progress on measuring the time-resolved evolution of the electron energy distribution function (EEDF) in a pulsed RF argon plasma. The energy distribution of electrons in pulsed plasmas is unique because the electrons are constantly adjusting to the on- and off-states of the RF plasma. Models have predicted that the electrons at the beginning of a pulse have a low density with a high electron temperature, and over time, the density increases while the temperature decreases. This work uses time-resolved Langmuir probe measurements with a sub-nanosecond temporal resolution to experimentally determine the evolution of the EEDF in a pulsed plasma system. We present initial work measuring the IV traces of argon plasmas under pulsed RF ignition conditions at pressures from 30 – 100 mTorr. We explore the impact of pressure and pulse parameters on the EEDF. We will

also discuss how the time-evolution of the EEDF can impact the application of pulsed RF plasmas for industrial processes.

PS-ThP-21 Optical Emission Diagnostics of Electron Temperature and Density in Argon ICP Assisted by Collisional-Radiative Modeling, ***JiHyun Park,*** Samsung Electronics Co., Republic of Korea

Optical emission spectroscopy (OES) is a useful non-invasive diagnostic technique for low-temperature plasmas, but measured emission intensities are governed by coupled collisional and radiative processes. Consequently, direct estimation of electron temperature (Te) and electron density (Ne) from emission intensities alone requires a collisional-radiative (CR) model. In this study, Te and Ne in argon inductively coupled plasma (Ar ICP) were estimated using OES combined with a CR model.

Ar I emission spectra were measured in a cylindrical quartz-tube ICP reactor operated at 13.56 MHz. RF power was varied from 30 to 50 W and gas pressure from 200 to 400 mTorr, giving nine operating conditions. For each condition, five repeated OES measurements were performed to evaluate repeatability. The spectra were corrected by wavelength-dependent and spectral-response calibration, and Ar I emission lines selected from the 696–978 nm range were used for analysis.

The CR model included the Ar ground state, four 4s metastable/resonance states, and ten 4p excited states. Electron-impact excitation and de-excitation, ionization, collisional quenching, diffusion loss to the wall, radiative transitions, and radiation trapping were considered. The diagnostic procedure was performed sequentially. First, Te was determined by minimizing the root-mean-square error between measured and CR-model-predicted line-intensity ratios. The 763.51 nm line was used as the reference, and five lines at 750.39, 772.38, 801.48, 826.45, and 912.30 nm were used to construct the ratio vector. Next, Ne was estimated by scaling the CR model intensity to match the experimental intensity at the determined Te. The Ar I 811.53 nm intensity at 300 mTorr and 40 W was used as the normalization reference.

The estimated Te ranged from 1.604 to 1.814 eV, while Ne ranged from 2.84 × 10^{12} to 8.07 × 10^{12} cm^{-3}. Te decreased with increasing pressure and showed a slight decrease with increasing RF power, whereas Ne increased with both pressure and RF power. The relative standard deviation was 0.14–0.96% for Te and 2.14–7.27% for Ne, indicating good repeatability. Comparison with a 0D global model showed that Te agreed within ±5%, while Ne showed larger quantitative deviations but reproduced the trends with operating conditions.

These results demonstrate that the sequential CR-OES approach provides physically consistent, non-invasive estimates of Te and Ne in Ar ICP, and is applicable to conditions where probe insertion is impractical or may perturb the plasma.

PS-ThP-22 ReaxFF Development by Latent Space Exploration for Plasma Etch Modeling, ***George Arsnow,*** *David Graves,* Princeton University

Extension of molecular dynamics (MD) etching simulations to industrially relevant plasma etching systems including silicon (Si), fluorine (F), chlorine (Cl), sulfur (S), and oxygen (O) necessitates the development of new interatomic potentials with suitable accuracy, transferability, and computational cost. These criteria can be balanced by the ReaxFF potential, which has sufficient flexibility and physicality to handle the highly non-equilibrium atomic environments replete in plasma etching simulations. Growing use of data-intensive machine learning interatomic potentials has spurred the creation of systematic and user-agnostic protocols for training set generation [1]; such active learning algorithms can also be harnessed to produce data sets for ReaxFF parameterization.

We demonstrate an active learning algorithm to sample an atomic configuration set's latent space, which comprises the first few principal components of the set's atomic descriptors. Latent space exploration enables efficient interpolation between user-defined boundary configurations, allowing the user to institute limits on the resulting potential's transferability [2]. We use this latent space exploration–based active learning algorithm to parameterize ReaxFF potentials for elemental subsets of the Si/F/Cl/S/O system. Parameterization is performed with version 2 of the JAX-ReaxFF global optimization software [3]. Validation entails comparison of ReaxFF-predicted energies and forces on a test data set to those calculated by density functional theory (DFT) and comparison of experimental etch rates and etch product selectivities to those manifested in MD etching simulations.

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PS-ThP-23 Enhanced Catalytic Performance in Plasma-Assisted Dry Methane Reforming via Ferroelectric Perovskites, ***Shanza Baig,*** University of Oklahoma

Non-Thermal Plasma technology holds significant potential for activating CH_4 and CO_2 molecules, enabling their conversion into H_2 and other valuable chemicals under mild conditions. However, conventional thermal catalysts which are primarily heat responsive often lack compatibility with non-thermal plasma environment, where reaction mechanisms and dominant species differ considerably. Moreover, as CO_2 has a higher bond dissociation energy than CH_4, there is a necessity to design a catalyst that can enhance CO_2 dissociation kinetics to improve overall DRM efficiency. This study integrates ferroelectric materials into plasma catalytic systems enhancing energy transfer to reactant molecules, increasing electron density in discharge regions, and elevating average electron energy – key factors critical to increasing the conversion rates of both CH_4 and CO_2 in plasma-assisted DRM. Perovskite oxides synthesized via the Pechini method were categorized into three classes: titanates ($BaTiO_3$, $CaTiO_3$, $SrTiO_3$), zirconates ($BaZrO_3$, $CaZrO_3$, $SrZrO_3$), and niobates ($KNbO_3$, $NaNbO_3$, $KNaNbO_3$), each exhibiting distinct curie temperatures and ferroelectric properties. Niobate-based ferroelectric catalysts, particularly $KNbO_3$ and $NaNbO_3$, demonstrated the highest CH_4 conversions of 71.7% and 71.9%, CO_2 conversions of 62.4% and 60.5%, H_2 yield of 33.6% and 33.3%, and CO yield of 33.5% and 32.9%, respectively. $KNbO_3$ resides in its orthorhombic ferroelectric phase at 800 V and 5 kHz enabling sustained polarization and enhanced surface charge effects. To further enhance performance and stability of traditional supports, ferroelectric $KNbO_3$ was incorporated into Al_2O_3 and SiO_2 using a co-precipitation method. This integration further improved CH_4 and CO_2 conversions to 75.5% and 54.6% with Al_2O_3, and 81.7% and 64.6% with SiO_2. To study the effect of loading active metal, nickel was introduced via incipient wetness impregnation. However, its addition to ferroelectric catalysts such as $KNbO_3$-Al_2O_3 and $KNbO_3$-SiO_2 led to reduced CH_4 and CO_2 conversions and a shift in product selectivity towards CO, highlighting the pivotal role of spontaneous polarization in directing plasma induced reaction pathways. In contrast, paraelectric perovskites exhibited poor catalytic performance due to their inability to maintain polarization under plasma conditions either due to inherently non-ferroelectric structures or low curie temperatures. Overall, among all tested catalysts, ferroelectric $KNbO_3$ based catalysts demonstrated superior control over electric field interactions at the catalyst surface, promoting localized micro-discharges, enhancing CO_2 dissociation, and reducing energy losses.

PS-ThP-24 Plasma-Enhanced CO_2 Dissociation for Chemical Synthesis: Modeling and Experimental Verification, ***Andrew Herschberg,*** *Nathan Bartlett, Jameson Crouse, Emily Greene, Jaime Robertson, David Ruzic,* University of Illinois at Urbana-Champaign

The conversion of carbon dioxide into carbon monoxide using non-equilibrium plasmas is of growing interest for carbon utilization, syngas generation, and plasma-assisted chemical synthesis. Radio frequency inductively coupled plasmas are attractive for this application due to stable operation, high plasma density, and efficient power coupling. In this work, a combined modeling and experimental study of CO2 dissociation in an intermediate-pressure RF ICP reactor is presented. A physics-based numerical model is being developed to simulate electromagnetic power deposition, plasma transport, and reaction pathways relevant to CO2 conversion. Parametric studies examine the influence of applied power, pressure, residence time, and feed composition on predicted dissociation behavior and energy utilization.

Experimental validation is being conducted using an RF ICP reactor operated under comparable conditions. A combination of mass spectrometry and remote OES actinometry methods are used to measure species concentrations in the reactor effluent. Comparison of experimental measurements with model predictions will be used to refine the simulation framework and identify operating conditions for efficient plasma-assisted

CO2 conversion. This work supports the development of scalable plasma reactors for chemical synthesis and carbon utilization applications.

PS-ThP-25 Effect of Steric Hindrance and Precursor Reactivity on Aluminum Oxide Area-Selective Atomic Layer Deposition*, **Sharmistha Bhattacharjee**, Nicholas C. Strandwitz,* Lehigh University

Area-selective atomic layer deposition (AS-ALD) offers a promising route for bottom-up fabrication of advanced nanoscale devices by enabling deposition only on targeted surfaces while suppressing growth on undesired regions. However, maintaining selectivity during deposition remains a major challenge, particularly for highly reactive precursors that can penetrate blocking layers and nucleate on non-growth regions. In aluminum oxide AS-ALD, precursor properties such as molecular size, ligand structure, and reactivity play a critical role in determining interactions with self-assembled monolayer (SAM) blocking layers, surface defects, and precursor diffusion pathways. Small and highly reactive precursors such as trimethylaluminum (TMA) can readily infiltrate non-growth surfaces, leading to faster selectivity loss. Therefore, tailoring precursor chemistry is important for improving blocking efficiency and sustaining selective growth.

In this study, the influence of precursor molecular size and reactivity on Al_2O_3 AS-ALD was investigated using TMA, aluminum tri-sec-butoxide, and tri-i-butylaluminum with H_2O as the co-reactant. Dodecanethiol SAM deposited on copper substrates was employed as a blocking layer, and deposition behavior was examined over a temperature range of 100–160 °C. Film thickness and density were analyzed using spectroscopic ellipsometry and X-ray reflectivity, while blocking performance was evaluated through X-ray photoelectron spectroscopy measurements of Al atomic concentration. Compared with TMA, the larger precursors demonstrated substantially improved resistance to precursor infiltration and enhanced selectivity. Aluminum tri-sec-butoxide maintained 100% selectivity at low temperature, while tri-i-butylaluminum preserved selectivity above 90% after 100 ALD cycles of Al_2O_3. These findings highlight the importance of precursor design in AS-ALD and demonstrate that combining bulkier, lower-reactivity precursors with well-ordered SAM blocking layers provides an effective pathway for improving long-term selectivity performance.

PS-ThP-26 Evolution of Ion Energy Distribution Functions in High Aspect Ratio Features*, **David Kanfer**,* North Carolina State University*; Krista Morris, Rex Anderson,* Micross*; Tanjina Akter,* North Carolina State University*; Chenyao Huang, Mark Kushner,* University of Michigan, Ann Arbor*; Steven Shannon,* North Carolina State University

The growing demand for High Aspect Ratio (HAR) features in micro and nanoscale devices motivates an understanding of the evolution of the ion energy distribution function (IEDF) as ions travel down a HAR feature. As the aspect ratio (AR) increases, features undergo bowing, tapering, and notching, deviating from the expected HAR geometry; these are largely attributed to AR dependent changes in the IEDF. By combining a retarding field energy analyzer (RFEA) with capillary plates (CPs) of varying ARs, the evolution of IEDFs as a function of depth into an HAR feature can be directly measured. This method has been previously demonstrated in inductively coupled plasmas.

Industry often uses capacitively coupled plasmas (CCPs) to perform the HAR etch. A CP design has been developed with feature diameters from 20 um to 90 um, and thicknesses from 200 um to 450 um, yielding features with ARs ranging from 2-22. The CPs are fabricated on backlapped silicon wafers. Copper is sputtered onto the back of the wafer as an etch-stop. A mask with an array of holes is exposed onto the wafer. The subsequent etch step varies, with larger diameter holes requiring a longer etch. The copper is then removed. Finally, dry thermal oxidation is used on some samples, forming a thin layer of SiO2 throughout the feature. An argon / oxygen / nitrogen dual-frequency CCP is used to test the fabricated CPs. The CCP is powered by a 60 MHz high frequency to sustain sufficient density, and a 13.56 MHz low frequency for sheath control.

By varying the AR of the CP used, power ratio of the dual-frequencies, pressure, and gas, the IEDF through the HAR can be measured with the RFEA. Additionally, by comparing the SiO2 HAR features to the non-oxidized features, the effect of insulating sidewalls is determined. These results provide insight into how IEDFs evolve within HAR features in dual-frequency CCPs.

This work is supported by Department of Energy grant DE-SC0024545.

PS-ThP-27 Complex Transient Processes Observed During in-Plasma Nanocalorimetry*, **Carles Corbella**,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; Caroline Adam, Holger Kersten,* Kiel University, Germany*; Feng Yi, Andrei Kolmakov,* National Institute of Standards and Technology (NIST)

Nanocalorimetry is a promising diagnostics tool to measure and analyze the energy fluxes from plasma discharges used for surface processing, such as film deposition, etching, and cleaning. Nanocalorimeter sensors consisting of silicon dies usually include a Pt thin film microstrip acting as a resistor, deposited on an ultrathin, free-standing SiN_x membrane. Recently, a two-timescale temperature profile upon plasma ignition has been observed: (1) initial fast sensor heating associated with the heat dissipation to the ultrathin SiN_x supporting membrane, followed by (2) slow heating of the silicon die in contact with the aluminum envelope. The reduced thermal mass of the membrane-supported Pt sensor enables a rapid temperature response down to the millisecond resolution. Nanocalorimeters' characteristic short response times, together with their sensitivity and selectivity, make such devices ideal for transient thermal processes' analysis during plasma processing. From plasma ignition to pulsed discharges, plasma-surface physics and chemistry are governed by transition processes where plasma parameters rapidly evolve. The energy fluxes during such non-stationary conditions can now be studied with nanocalorimetry sensors, whose thermal responses are validated using an array of independent plasma monitor techniques, such as electrical and optical probes. The time evolution of sensor temperature is correlated with RF discharge parameters (gas pressure, power, and residence time) and electrode materials (aluminum, copper, gold) to provide a unified description of the substrates' heating mechanisms. The roles played by the gas phase conditions and chemistry on the electrodes are discussed, as well as the separate contributions of gas, ions, electrons, and photons heat fluxes in the global heating of the nanocalorimeter.

PS-ThP-28 Three-Dimensional Kinetic Plasma Simulations for Predictive Modeling of ExB Plasma Processing Devices*, **Andrew Tasman Powis**,* Princeton Plasma Physics Laboratory*; Jian Chen,* Sun Yat-sen University, China*; Igor Kaganovich,* Princeton Plasma Physics Laboratory

Three-dimensional kinetic plasma simulations are emerging as an essential tool for first-principles modeling of low-temperature plasmas used in materials processing. In many plasma sources, including partially magnetized discharges relevant to etching, deposition, surface functionalization, and ion-beam-assisted processing, device behavior is controlled by kinetic electron transport, self-consistent sheath formation, wave–particle interactions, and plasma–surface coupling. These effects are often reduced or parameterized in lower-dimensional models, but they can depend sensitively on the third spatial dimension, boundary conditions, and nonlinear instability dynamics. This talk highlights recent progress in high-performance 3D3V particle-in-cell simulations as a pathway toward predictive modeling of processing-relevant plasmas.

Two recent studies illustrate this point. In Hall-thruster-like crossed-field plasmas, 3D kinetic simulations show that radial boundary conditions can qualitatively alter density, temperature, electric-field structure, instability spectra, and cross-field electron transport [1]. In beam-generated partially magnetized plasmas, 3D PIC-MCC simulations reveal a transition from quasineutral lower-hybrid spiral arms to non-neutral diocotron-driven helical rotation, demonstrating that structures appearing spoke-like in projection may be intrinsically three-dimensional [2]. Together, these studies show that fully 3D kinetic simulations are not merely computational refinements, but necessary tools for connecting fundamental plasma instabilities to transport, wall interaction, and ultimately process control in advanced plasma technologies.

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PS-ThP-29 PICLas: An Open-Source Kinetic Simulation Framework for Plasma Science and Technology*, **Paul Nizenkov**, Asim Mirza, Stephen Copplestone, Julian Beyer,* boltzplatz - numerical plasma dynamics GmbH, Germany*; Marcel Pfeiffer,* Institute of Space Systems, University of Stuttgart, Germany

PICLas (https://github.com/piclas-framework/piclas, GPLv3) is an open-source, massively parallel kinetic simulation framework combining Particle-in-Cell (PIC), Monte Carlo Collisions (MCC), and Direct Simulation Monte Carlo (DSMC), Bhatnagar-Gross-Krook (BGK), and Fokker-Planck methods for rarefied gas and plasma dynamics. This poster demonstrates its versatility through three applications spanning plasma processing, beam physics, and radiation transport. First, reactive magnetron sputtering of

titanium in an O_2/Ar atmosphere is simulated within an industrial coating chamber using DSMC. A reactive wall model (Tonneau et al. 2018, J. Phys. D 51, 195202) couples target surface coverage to incoming particle fluxes and sputter emission. Gas distribution, sputtered particle transport with configurable emission distributions, and deposition rates are analyzed under varying reactive gas inflow conditions, capturing the characteristic racetrack erosion pattern and the poisoning transition from metallic to compound target mode. A parametric racetrack model is introduced, enabling the simulation of rotating substrates by rotating the racetrack position accordingly, providing a computationally efficient approach for industrial coating geometries. Second, electron beam propagation in a PVD system is modelled with coupled PIC-MCC. Ionization of the background neutral gas, self-fields of charged species, and a superimposed magnetic field are included. The ionization-induced self-focusing of the beam is shown, and simulated beam widths are validated against burn-in diameter measurements within the beam generator. A species-specific time step bridges the different timescales of electrons and ions. Third, PICLas is bidirectionally coupled with a line-by-line radiation solver and a photon Monte Carlo transport method. The capabilities are demonstrated for an atmospheric entry plasma, a strongly non-equilibrium environment that shares key physical characteristics with high-power industrial plasma processes, enabling prediction of radiative transport properties and spectroscopic signatures in flow regimes inaccessible to continuum-based CFD. Together, these cases establish PICLas as a versatile kinetic simulation platform freely available to the plasma science and technology community.

PS-ThP-30 Time-Resolved Ion Energy Distribution Function Study of High Power Impulse Magnetron Sputtering with Positive Cathode Reversal using a Linear Magnetron for Cu and Ti, ***Collin Jeckell****, Tag Choi, Matt Egly, Ricky Pickering, David Ruzic, Dren Qerimi,* University of Illinois at Urbana Champaign

High-Power Impulse Magnetron Sputtering (HiPIMS) is a physical vapor deposition (PVD) technique that, through short voltage pulses with high peak currents, is able to achieve higher density plasmas compared to traditional DC magnetron sputtering. This higher density leads to a significant increase in the ionization fraction, which leads to higher quality films by improving their adhesion, density, and roughness. A recent area of study has been how changing the polarity of the cathode affects the energies of the deposited ions. This work seeks to show how changing different parameters of the HiPIMS pulse with the positive cathodic reversal, and the position of the magnetron affects the time-resolved Ion Energy Distribution Function (IEDF). This data was collected using a Plasma Sampling Mass spectrometer (PSM) from Hiden Analytical Inc. For each experiment the IV trace was also collected allowing us to verify that the plasma is stable. By understanding how changing these parameters leads to changes in the IEDFS we can better design HiPIMS plasmas to obtain the desired film. For this both copper (Cu) and titanium (Ti) targets were studied changing 9 parameters to see how each of them affects the IEDF. Parameters such as main pulse length between 10 – 30 µs, peak current between 100 – 300 A, positive pulse length between 50 – 150 µs, with/without positive voltage of the cathode, angles of the PSM to target, etc. are varied. By testing all of these parameters we are able to see how they affect the behavior of the plasma. Secondarily by comparing the results between the two materials, we are able to observe if changing material properties has a large impact on the trends observed.

PS-ThP-31 Neural-Network Based Reconstruction for Limited-Line-of-Sight CT-OES Plasma Diagnostics, ***Jiseong Nam****, Kyoung-Jae Chung, Sang Yoel Park,* Seoul National University, Republic of Korea

Computed-tomographic optical emission spectroscopy (CT-OES) is a non-invasive diagnostic technique for reconstructing the spatial distribution of local optical emissivity in plasmas from line-integrated emission signals. In practical plasma devices, however, the number and angular coverage of available lines of sight (LOS) are often limited by chamber geometry, viewport configuration, and optical-access constraints. Under such limited conditions, the reconstruction problem becomes highly ill-posed, and different non-axisymmetric emissivity distributions may produce similar projection signals. In this work, we propose a neural-network-based reconstruction model for CT-OES under limited-LOS conditions constrained by chamber structure and optical access. The model is designed to infer local emissivity distributions from sparse LOS signals while capturing non-axisymmetric and localized plasma emission structures. By learning physically plausible emissivity patterns from training data, the proposed model acts as an implicitly regularized inverse solver, enabling robust reconstruction from sparse LOS measurements with reduced dependence on manually tuned regularization parameters.

PS-ThP-32 Stannane Decomposition and Sticking Coefficients under Different Sample Conditions, ***Emily Greene****, Jameson Crouse, Nathan Barlett, Eric Mushrush,* University of Illinois at Urbana-Champaign*; Niels Braaksma,* ASML*; David Ruzic,* University of Illinois at Urbana-Champaign

This is a placeholder abstract. I will update with the real abstract as soon as I receive sponsor approval. Thank you again for your patience and understanding!

PS-ThP-33 Plasma Torch Method for Silicon Carbide (SiC) Dopant Implantation, ***Victor Veltmeyer****, Renato Beraldo, José Pissolato Filho, José Diniz, Marcos Puydinger dos Santos,* State University of Campinas, Brazil

Silicon Carbide (SiC) has been shown to be a capable semiconductor for power electronics applications, as it supports high forward currents whilst blocking high reverse voltages, while switching up to MHz frequencies. Those properties are enabled by an exceptionally durable crystalline lattice that allows it to withstand remarkably high temperatures, enabling it to sustain transient power regimes that would otherwise destroy standard silicon semiconductors.

This exceptional crystal lattice, however, also represents the main challenge in fabricating large SiC power electronics, as it is extremely difficult to dope (or alter in general) with standard fabrication techniques, whether it be thermal diffusion or ionic implantation. The former requires heating the substrate to temperatures as high as 2100 K for several minutes, while the latter requires 100-300 keV per µm of implant depth for aluminum, the standard p-dopant for SiC, while also requiring substrate heating up to temperatures between 500-1100 K during the entire process.

Our study aims to evaluate a novel method of dopant implantation, adapting an innovative plasma torch device to perform both thermal diffusion and ionic implantation concurrently by using accelerated ions within a thermal plasma discharge. The main source of ion energy are Lorentz electromagnetic forces, which also increase the plasma plume's temperature via magnetic self-confinement, a process which has been experimentally shown to reach temperatures to extremes of 4000 K in the original device.

This plasma torch, which originally operated at atmospheric pressure, was fitted with a fused-quartz high-vacuum (10-5 Torr) chamber to reduce the beam's temperature while also boosting ion energies by increasing their mean free path. A silicon carbide wafer coated on one side with aluminum will be placed perpendicularly to the plasma flight path, where nitrogen ions (n-type SiC dopant) will bombard the wafer, simultaneously heating it while pushing accelerated dopants into the crystal lattice, a novel hybrid method which combines the best aspects of the two existing alternatives, conceivably doping the uncoated side to an n-type semiconductor while the coated to a p-type, creating a standard diode junction, which will be tested to determine the quality of this new processing method.

PS-ThP-34 Machine-Learning-Assisted Investigation of CF_3–X (X=H, F, I) Plasma Kinetics In Semiconductor Manufacturing for Etch Effectiveness and Environmental Sustainability, ***Chi-Yun Lin****, Jane Chang,* UCLA

Hydrofluorocarbons (HFCs) gases are commonly used in semiconductor manufacturing to etch silicon dioxide, an essential insulator in integrated circuits, either from chamber wall deposits or patterned features. CHF_3 plasma is utilized for its high etch rate (ER), comparable to CF_4, and favorable anisotropic etching characteristics, though its high global warming potential (GWP100) of 12400 and long atmospheric lifetime (LT) of 222 have prompted its phasedown by the EPA. CF_3I has a lower atmospheric lifetime (<0.005) and GWP100 (<1), which are 4-5 orders of magnitude smaller than those of HFCs, making it a promising alternative gas.

This work investigates CF_3X-based plasmas (where X = H, I) in etching SiO_2 with a focus on machine learning to extract meaningful kinetic parameters for modeling. CHF_3/O_2/Ar plasma was first used to evaluate the reduce and abate strategies. O_2 serves a dual role: process-gas additive to reduce the usage of CHF3 for improving SiO2 etching and abatement reactant for reducing high-GWP fluorocarbon emissions. The experimental and modeled SiO2 etch rate increased with measured emission of SiF_4 (kg-CO_2e) and the modeled ratio of fluorine flux to oxygen flux (Γ_F/Γ_O), reaching above 150 nm/min under selected conditions. The corresponding downstream composition was converted to $MMTCO_2e$ for CHF_3, CF_4, and C_2F_6. After introducing O2 to downstream abatement, the modeled $MMTCO_2e$ decreased by approximately a few orders of magnitude relative to the untreated emission.

CF_3I/O_2/Ar was evaluated as a lower-GWP alternative. A differentiable surface-kinetic model was developed to infer the unknown iodine

adsorption and abstraction probabilities, using experimental SiO2 etch rates as the ground truth, while modeled ion fluxes and etch rates served as known inputs. Descriptor information from CF_3X (X = F, Cl, Br, and I), including C–X bond dissociation energy, Si–X bond strength, and electronegativity, was used to define physically reasonable bounds for the unknown iodine-related surface kinetics. Automatic differentiation through the ODE solver reduced the average absolute percent error from 23% for the initial assumption to 12.5% after applying new surface kinetic by AI/ML inference. As the SiO_2 etch rate increases from 50–80 nm/min to above 100–130 nm/min, the corresponding measured and modeled emission for CF_3I and CF_4 decreases by an order of magnitude in $MMTCO_2e$.

Overall, selected $CF_3I/O_2/Ar$ operating conditions showed the SiO_2 etch rate increased by approximately 70% while the estimated emission impact reduce by an order of magnitude, indicating that higher etch performance can be achieved with lower greenhouse-gas-equivalent emissions.

PS-ThP-35 Advanced Waveform-Modulated Pulsed Biasing for Seam Suppression in Dielectric Gap-Fill Processes, ***Yejin Shin***, *Tae Cho,* WONIK IPS Co., Ltd., Republic of Korea*; Junghoon Kim,* WONIK IPS Co., Ltd.*; Hyun-Jong Woo, TaeIn Kim, YongBaek Jeon, TaeJoon Kim, Gyu-Tai Kim, DongIl Choi, Eun Sun Jung,* WONIK IPS Co., Ltd., Republic of Korea

Advanced waveform-modulated pulsed biasing techniques were investigated for surface treatment and profile modification during dielectric gap-fill processes. The primary advantage of this approach is the precise control of ion energy, enabling optimization of the biasing effect while minimizing plasma-induced surface damage. Dielectric films are commonly deposited using CVD or ALD processes; however, as next-generation memory devices adopt increasingly high-aspect-ratio structures, the risk of seam formation in gap-filled features has increased significantly.

Various approaches have been explored to suppress seam formation, including post-deposition densification treatments and profile-shaping processes designed to prevent premature pinch-off near the trench opening. These plasma-assisted surface modification processes require carefully controlled ion bombardment to regenerate the surface and reshape deposited materials.

To independently control ion energy and ion flux, dual-frequency plasma excitation using low- and high-frequency sources has been widely adopted. However, achieving independent controllability remains highly challenging, particularly in capacitively coupled plasma (CCP) reactors commonly used for dielectric deposition systems. To minimize coupling between the two frequencies, the lower-frequency source is typically selected in the range of several kilohertz to a few megahertz. Although this approach improves the controllability of ion energy and ion flux, the low-frequency bias often produces excessively energetic ion bombardment, resulting in undesirable sputtering or excessive surface treatment.

In this study, a waveform-modulated pulsed biasing technique was developed to maintain sufficiently high ion energy while minimizing perturbation of ion flux. By tailoring pulse-shape parameters, precise control of ion bombardment characteristics was achieved. To implement this technique in a PEALD system developed at Wonik IPS, several chamber components were newly designed, including a ground-layer-embedded high-temperature heater pedestal and a broadband RF notch filter.

Initial experimental studies demonstrated effective reshaping behavior of the filled dielectric layer, indicating the strong potential of advanced pulse waveform modulation for future seam-suppression and gap-fill optimization processes.

PS-ThP-36 Wafer Edge Yield Improvement through SOH Mask Tilt Optimization by Edge Insert Ring Height Adjustment, ***Junhyuk Choi,*** Samsung Electronics, Republic of Korea

All values except radius are normalized to arbitrary units (a.u.) for confidentiality.

As DRAM design rules shrink, the impact of wafer edge yield on overall profitability has significantly increased. However, in the Spin-On Hard mask (SOH) etch process, edge yield degradation was observed as the accumulated Radio Frequency (RF) time increased. Specifically, the extreme edge (E1) Bit-Line Bridge Disturb (BBD)—a defect associated with the outermost chips—deteriorated over time (Fig. 1). Notably, standard mass production monitoring metrics, such as Non-Pattern Wafer Etch Rate (NPW ER), top edge Critical Dimension (CD), and Virtual Metrology (VM), did not exhibit meaningful correlations with this yield loss.

To investigate the root cause, non-destructive Slope CD (SCD) metrology was employed to measure the mask left-right tilt at nine different radii (Fig. 2). The analysis confirmed a clear correlation between RF time, SCD values, and E1 BBD (Fig. 3). The identified mechanism is that as RF time accumulates, the edge ring is eroded, which alters the edge plasma sheath characteristics. This modification shifts the ion incident angle distribution, inducing a subtle tilt in the SOH mask profile at the wafer edge. When this non-uniform profile is transferred to the subsequent bit line, it results in E1 BBD defects. The analysis indicated that this degradation was most pronounced before the Actinium (a mechanical ring-lift technology for sheath control) compensation function initiated at RF time 4.

To address the mask tilt and resulting defects caused by plasma sheath distortion, the edge insert ring height was optimized. Reducing the ring height shifts the edge plasma sheath curvature area outward, thereby minimizing the sputtering variance caused by ion incident angles (Fig. 4). Based on a measured etch rate of 1.22 and considerations for measurement and process tolerances, the ring height was reduced from 2.1 to 1.6. Additionally, the Actinium application point was advanced from RF time 4 to 0 to proactively compensate for ring erosion from the start of the process.

The implementation of the 1.6 ring, combined with the adjusted Actinium timing, significantly reduced the correlation between SCD and RF time, demonstrating enhanced mask profile stability against RF time accumulation (Fig. 5). Consequently, the E1 BBD defect rate improved by approximately 3.66 over the RF time 0–4 range (Table 1). This study presents a practical, cost-effective, and data-driven edge ring optimization methodology applicable to high-volume manufacturing lines.

Atomic Scale Processing Mini-Symposium
Room 316 - Session AP1+EL+PS+TF-FrM

Thermal and Plasma-Enhanced ALD

Moderators: Dr. Sagar Udyavara, LAM Research, **Dr. Virginia Wheeler**, U.S. Naval Research Laboratory

8:15am **AP1+EL+PS+TF-FrM-1 Analyzing Plasma-Enhanced ALD of III-Nitrides via Experimental and Theoretical Studies**, *Steven Allaby, Heba Saleh, Fatih Bayansal,* ***Necmi Biyikli,*** University of Connecticut **INVITED**

Research efforts on low-temperature (T < 300 ℃) synthesis of crystalline III-nitride thin films using plasma-assisted ALD utilized various reactor configurations featuring different plasma sources. While our early III-nitride growth experiments using quartz-based ICP sources resulted in nanocrystalline/amorphous films with elevated oxygen impurities, shifting to stainless-steel based hollow-cathode plasma sources revealed highly (002) oriented polycrystalline III-nitride films on Si(100) and sapphire substrates. Upon further modification of the hollow-cathode plasma source and reactor chamber design, we have achieved monocrystalline AlN, quasi-epitaxial GaN and (002) oriented InN films on sapphire substrates at a common growth temperature of 200 ℃.

The films were deposited using conventional metal-alkyl precursors (trimethylaluminum, triethylgallium, trimethylindium) and various nitrogen plasmas (N_2/H_2/Ar, N_2/H_2, N_2/Ar, and N_2-only) as metal precursor and nitrogen co-reactant, respectively. *In-situ* ellipsometry and optical emission spectroscopy (OES) were employed to monitor the surface ligand-exchange reactions, plasma surface interactions, and formed reaction byproducts in real-time. *Ex-situ* spectroscopic ellipsometry measurements revealed the film thickness variation, growth-per-cycle (GPC) and optical properties of the III-nitride films. When compared to reference films grown on Si(100) substrates, growth-per-cycle (GPC) values obtained for III-nitride films on c-plane sapphire substrates showed a notable increase. Moreover, a significant improvement of crystalline order has been observed for all binary nitride films grown on sapphire substrates, achieving or approaching epitaxial quality films. We attribute this significant improvement in crystal quality to the synergistic impact of customized HCP-ALD reactor, large-diameter third-generation hollow-cathode plasma source, and optimized growth conditions (plasma gas mixture, rf-power, pressure).

To gain further insight into how different plasma mixtures and radical species affect III-nitride film quality, we have carried out density functional theory (DFT) based simulations of both metal-organic and plasma half cycles. The computational studies revealed how different adsorbed metal-organic precursor surface groups interact with hydrogen and nitrogen radicals by depicting energetically favorable reaction routes. These results are compared and correlated with the experimental observations, deciphering the critical role of hydrogen radicals.

8:45am **AP1+EL+PS+TF-FrM-3 Optical Bandgap and Thermal Stability Driven High–κ Engineering of HfAlO Dielectrics on a 200 mm ALD Platform**, ***Partha Mukhopadhyay,*** *Zuriel Caribe, Ivan Fletcher, Jim Fulford,* Tokyo Electron America, USA

This work demonstrates the tunable high–κ, optical, and thermal stability characteristics of hafnium aluminate ($Hf_xAl_{1-x}O$) thin films synthesized using a 200 mm high–volume batch atomic layer deposition (ALD) platform. Precise monolayer–level engineering of HfO_2/Al_2O_3 superlattice structures enables controlled Al incorporation, which systematically modulates the optical bandgap, dielectric constant, and electrical structure of the alloy. A key outcome is that increasing Al content systematically increases the optical bandgap of the alloy from 5.5 – 6.5 eV, accompanied by improved film density and structural uniformity, which directly influences the dielectric response and reliability of the material.

At lower Al content (~0.31), the alloy exhibits superior dielectric properties with κ > 22 and a capacitance density of 12.46 fF/μm^2, representing ~29% enhancement over HfO_2, attributed to suppressed oxygen vacancies and reduced trap density. With increasing Al composition, the widened bandgap increases barrier height, resulting in reduced leakage current and improved dielectric robustness. A higher Al fraction (~0.56) demonstrates a breakdown electric field of ~8 MV/cm, exceeding HfO_2 by over 3 MV/cm, while maintaining low leakage (~10^{-6} A/cm^2) even after 650 ℃ annealing. Notably, increasing Al content significantly enhances the thermal budget of the dielectric stack, stabilizing the amorphous phase and preventing dielectric degradation at elevated temperatures, while preserving relatively high κ values compared to pure Al_2O_3.

XPS analysis reveals systematic shifts of Hf4f and Al2p peaks toward higher binding energies with increasing Al concentration, indicating modified bonding characteristics and enhanced ionic contributions, consistent with bandgap widening and improved film stability. These electronic structure changes correlate with reduced surface charge transfer effects and improved dielectric integrity. Additionally, the films exhibit excellent capacitance linearity over applied voltage and stable frequency response, making them highly suitable for RF applications.

The 200 mm batch ALD platform ensures excellent uniformity, repeatability, and scalability for compositionally engineered dielectrics. Overall, this study highlights that Al–content–driven optical bandgap tuning, coupled with improved thermal stability and enhanced breakdown strength, provides a powerful route to customize high–κ behavior in HfAlO. This enables optimized performance trade–offs between capacitance density, leakage, and reliability, making HfAlO a compelling material system for advanced MIM capacitors in BEOL, RF, and memory technologies.

9:00am **AP1+EL+PS+TF-FrM-4 Atomic Layer Deposition Metal and Barrier Layers Enabling Next Generation Interconnects**, *Matthew Weimer, Sara Harris,* Forge Nano*; Thomas Moffat,* NIST-Gaithersburg*; Dane Lindblad,* Forge Nano*; Daniel Josell,* NIST-Gaithersburg*;* ***Arrelaine Dameron,*** Forge Nano

Device miniaturization continues to push the technological boundaries of manufacturing processes and integrated circuit (IC) manufacturing must keep pace to meet the design requirements for next-gen transistors. Back end of line (BOEL) fabrication poses several challenges to chip scaling: most notoriously the copper bottleneck in which thick barrier layers and resistance capacitance (RC) delays limit functional interconnect pitch to 21 nanometers [1]. To overcome this critical barrier, low resistivity, conformal metal films have been studied for hybrid metallization; decreasing interconnect resistance and reducing barrier layer thicknesses. As interconnect pitch decreases line-of-sight PVD copper barrier/seed layers experience pinch off and void formation [2]. This work explores the use of ruthenium (Ru) and lower resistivity thermal ALD iridium (Ir) thin films for copper seed layers to enable next generation interconnects. Thermal ALD Ir and Ru deposited at 250 ℃ both demonstrate conformal deposition on 10:1 aspect ratio through glass vias (TGVs) and show void free copper fill using a cyclic pulsed electrochemical deposition process. Deposited in partnership with ALD SiO2 and TiN layers, this completes a metal barrier seed solution for TSVs. As expected, the primary difference between the Ir and Ru is electrical resistivity. Seed film resistivity as deposited on TGVs was measured using four-point probe; a 10 nm Ru film measured 41 μΩ·cm and a 10 nm Ir film measured 16 μΩ·cm. Successful copper electrochemical deposition (ECD) at various ECD potentials, was completed with 10 nm of Ir with (resistivity 16 μΩ·cm) and 20 nm of Ru (resistivity 22 μΩ·cm) with the full layer stack for these film shown in Figure 1. Reduction in required layer thickness combined with improved electrical properties and demonstrated conformality can serve as crucial steps forward for advanced interconnects and BEOL architecture. Additionally, this work compares Ir film quality as deposited at 250 ℃ and 300 ℃. Ir deposited at 300 ℃ exhibits improved environmental stability when compared to 250 ℃ Ir as measured with 4-point probe after aging in atmosphere over several months. 300 ℃ Ir also shows a shortened nucleation delay, and optical constants (n and k) more closely aligned to bulk Ir values, as measured with spectroscopic ellipsometry. Ir film characterization for both temperatures including XPS, XRR, XRD and AFM is ongoing, and will be presented

9:15am **AP1+EL+PS+TF-FrM-5 Tuning the Mechanical Properties of Silica Aerogels Using Atomic Layer Deposition**, ***Victor Vogt,*** *Ali Madanchi, Katherine Rybkin, Andrés Miranda Mañón, Andrej Lenert, M.D. Thouless, Neil Dasgupta,* University of Michigan

Silica aerogels are a key material used in aerospace, catalysis, and energy applications due to their ultralow density and thermal conductivity as well as high solar transparency. Specifically, they show promise as an emerging transparent insulating material in concentrating solar thermal energy generation.[1] In our recent work we have shown that atomic layer deposition (ALD) can be used to improve the thermal stability of silica aerogels at high temperatures of up to 800 ℃.[2,3] This was attributed to the ability of ALD to conformally modify the pore structure of the aerogels and form a more thermally stable phase at the surface. However, silica aerogels also suffer from low strength and fracture toughness, restricting their potential applications and making practical implementation difficult due to the risk of brittle fracture in assembly or operation.

In this study, we utilize sub-nanometer ALD treatments to conformally modify silica aerogels with aspect ratios > 100,000:1. We demonstrate a monotonic increase in stiffness with increasing number of ALD cycles, resulting in a ~30-fold increase in elastic modulus after 3 cycles of Al_2O_3 (nominal ~4 Å thickness). This result is investigated using finite element modeling (FEM) of the aerogel nanostructure, which reveals the key factors which drive the large increase in elastic modulus. Furthermore, we show that ALD increases the fracture toughness of the aerogels, resulting in a ~7-fold increase in fracture toughness after 3 ALD cycles. Due to the ultra-thin and conformal nature of the ALD layer, the porous nanostructure is maintained, allowing the aerogels to maintain high solar transparency and low thermal conductivity. This method enables a pathway to broader applications for silica aerogels through improving their mechanical durability while maintaining the favorable properties of low thermal conductivity and high optical transparency over a range of operating temperatures.

References:

[1] McEnaney, K., Weinstein, L., Kraemer, D., Ghasemi, H. & Chen, G. Aerogel-based solar thermal receivers. *Nano Energy* **40**, 180–186 (2017).

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[3] Z.J. Berquist, A.J. Gayle, N.P. Dasgupta, and A. Lenert, Transparent Refractory Aerogels for Efficient Spectral Control in High-Temperature Solar Power Generation. *Adv. Funct. Mater.* **32**, 2108774 (2022).

9:30am **AP1+EL+PS+TF-FrM-6 Multilayer FUV Coatings Using ALD-Grown LaF_3 and ZrF_4, *John Hennessy,*** Jet Propulsion Laboratory

We report on the targeted development of atomic layer deposition processes for high-refractive-index metal fluorides, specifically focusing on lanthanum fluoride and zirconium fluoride. The primary objective is to integrate these ALD-deposited materials into multilayer optical coatings designed for demanding far-ultraviolet (FUV) applications. By successfully combining ALD processes for lanthanum and zirconium fluorides with established processes for lower-index materials, we enable the fabrication of specialized optical components that are critical to various NASA applications. As a demonstration of this ALD capability, a 16-layer AlF_3/LaF_3 mirror was fabricated and shown to achieve an average reflectance exceeding 90% within a band centered around 140 nm. Finally, we discuss the prospects for increasing coating complexity and further optimizing FUV performance.

9:45am **AP1+EL+PS+TF-FrM-7 Controlling the Crystallinity of V_2O_5 Deposited by Plasma-Enhanced Atomic Layer Deposition*, Scott Walton,*** *Peter Litwin, Neeraj Nepal, Maria Sales, David Boris, Michael Johnson, Mackenzie Meyer, Virginia Wheeler,* Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) is a low temperature, conformal, layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach to ALD generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas-phase chemistry to produce amorphous, crystalline, and epitaxial films of varying types and characteristics. Importantly, by carefully controlling the plasma properties, it has been shown that the degree of crystallinity and phase selection is possible.

In this work, we demonstrate the ability to manage the crystallinity of V_2O_5 through careful control of the plasma characteristics during growth in a Kurt J. Lesker 150 LX PEALD system. We employ both plasma diagnostics and material characterization techniques to understand the process-to-structure-property relationship while varying the input power, operating pressure, and gas flow ratio. Optical emission spectroscopy (OES) and Langmuir probe measurements are used to characterize the production and delivery of energetic and reactive species to the growing film surface, while x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy are used to characterize the physico-chemical properties of the V_2O_5 films. We find that by varying the operating pressure in the system during the plasma process, the films can be selectively deposited in an amorphous or crystalline state. We link the transition from amorphous to crystalline material to the energy flux density delivered to the material surface during deposition and derive an estimate of the critical energy flux density necessary for crystallization. Lastly, we discuss these results more broadly and the applicability of these findings to other material systems. This work is supported by the Naval Research Laboratory base program.

10:00am **AP1+EL+PS+TF-FrM-8 Epitaxial Growth of VN on Si_3N_4(0001)/Si(111) Using Molecular Beam Epitaxy*, Nuri Oncel,*** *Mehmet Ozdogan, Carlos Munoz, Deniz Cakir,* University of North Dakota*; Randy Duma,* Quantum Design*; Rajendra Dulal,* University of North Dakota

We report on the epitaxial growth of VN thin films on β-Si_3N_4 (0001)/Si(111) substrates using molecular beam epitaxy. The growth process and resulting film properties were systematically investigated using in-situ reflection high-energy electron diffraction (RHEED) and ex-situ scanning/transmission electron microscopy (S/TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), energy-dispersive spectroscopy (EDS), and electrical transport measurements. RHEED and cross-sectional TEM analyses confirm the formation of epitaxial VN(111) films, with growth proceeding via a Volmer–Weber Island mechanism followed by coalescence. Increasing nitrogen flux during deposition significantly improves film continuity, stoichiometry, and crystalline quality. Structural characterization reveals an azimuthally aligned epitaxial relationship without the expected in-plane rotational reconstruction, indicating that interfacial bonding and strain relaxation dominate over simple lattice-mismatch considerations. XPS and EDS measurements confirm near-stoichiometric VN composition with reduced oxygen incorporation at higher nitrogen flux. Electrical measurements demonstrate ohmic transport across the VN/Si_3N_4/Si heterostructure, suggesting efficient carrier transport through the ultrathin dielectric layer via tunneling or defect-assisted conduction. Low-temperature transport measurements reveal a suppressed superconducting transition temperature relative to bulk and oxide-supported VN films, attributed to compressive strain and structural disorder. These results establish Si3N4(0001)/Si(111) as a viable platform for integrating epitaxial VN with semiconductor technology and provide insight into nitride–nitride heteroepitaxy and interface-driven property modulation.

Atomic Scale Processing Mini-Symposium
Room 316 - Session AP2+EL+PS+TF-FrM

Enabling Atomic Scale Processing (ALD/ALE) by leveraging new Precursors and Surface Reactions

Moderators: Prof. Austin Minnich, California Institute of Technology, **Dr. Angel Yanguas-Gil**, Argonne National Laboratory

10:30am **AP2+EL+PS+TF-FrM-10 Plasma-Enhanced ALD of SiO_2 with an Alternative Precursor: From Mechanistic Insight to Area-Selective Deposition*, James Jensen,*** *Jay Swarup, James Engstrom,* Cornell University

Silicon dioxide (SiO_2) is and has been an extremely important thin film material in microelectronics and related fields.The great majority of approaches to atomic layer deposition (ALD) of SiO_2 involve the use of plasma since, for example, the Si-H bond is resistant to reaction with molecules such as H_2O and O_2.We have examined the use of an alternative Si precursor, which we refer to as di-isopropylamido trisilylamine [DiPA(TSA)], employing an O_2 plasma as the co-reactant. The precursor contains only Si-N and Si-H bonds.We have investigated the process using *in situ* real time quartz crystal microbalance (QCM) techniques in a custom-built hot-wall reactor, which provides detailed insight into the half-reactions, and the presence of nucleation delay.We find that ALD with DiPA(TSA) occurs over a large temperature window, spanning a range of T = 120 – 285°C.The thickness deposited per cycle decreases with increasing temperature, from 4.7 Å-cycle^{-1} at T = 120°C to 2.9 Å-cycle^{-1} at T = 285°C.These rather large rates of growth from ALD reflect the silicon content in the precursor (three atoms per molecule).From QCM a nearly complete loss of the di-isopropylamido ligand is implicated in the precursor half reaction.The deposited thin films have been characterized using *ex situ* X-ray photoelectron spectroscopy (XPS), X-ray reflectivity (XRR), spectroscopic ellipsometry (SE) and atomic force microscopy (AFM).From XPS we find that the thin films are near stoichiometric (O:Si ~ 1.9) over the entire range of temperatures, while the expected impurities (e.g., C, N) are < 1%.From XRR we find that the thin film density increases from 2.24 g-cm^{-3} at T = 120 °C, to 2.38 g-cm^{-3} at T = 285 °C, which can be compared to the values for amorphous silica (2.20), and quartz (2.65).From AFM we find that the thin films are continuous and smooth exhibiting an average roughness of 0.54 nm at T = 120 °C (19 nm thick film), and 0.30 nm at T = 285 °C (13 nm thick film).Finally, we have conducted a preliminary set of studies concerning blocking PE-ALD growth of SiO_2 on Al_2O_3 using acetylacetone

(Hacac) and we find the deposition can be blocked for at least 10 cycles, over the temperature range *T* = 120-285 °C.

10:45am **AP2+EL+PS+TF-FrM-11 Temperature-Dependent Growth Behavior of Aluminum Oxide Using Dimethylaluminum Isopropoxide and Water**, ***Azeez O. Musa,*** University of Missouri-Columbia*; Hemant Kumar, Campbell Sweet,* University of Missouri, Columbia*; Justin R. Walensky,* University of Missouri-Columbia*; Matthias J. Young,* University of Missouri, Columbia

Area-selective atomic layer deposition (AS-ALD) requires precursors with controlled surface reactivity to enable selective film growth on targeted regions while minimizing unwanted nucleation on non-growth surfaces. Dimethylaluminum isopropoxide (DMAI) has emerged as a promising alternative to trimethylaluminum (TMA) for AS-ALD applications due to its reduced reactivity and non-pyrophoric nature. However, experimental mechanistic studies of DMAI/H_2O ALD and the influence of deposition temperature on growth behavior remain limited. In this work, the temperature-dependent growth characteristics of Al_2O_3 ALD using DMAI and H_2O were investigated using in situ quartz crystal microbalance (QCM) measurements together with ex situ X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), and spectroscopic ellipsometry. DMAI was synthesized from aluminum isopropoxide and trimethylaluminum in 79% yield and >95% purity, with product formation confirmed by ^{1}H NMR spectroscopy. Real-time QCM measurements were used to examine precursor adsorption, ligand removal behavior, saturation conditions, and mass gain per cycle (MGPC) between 100 and 200 °C. Al_2O_3 growth at 100 °C exhibited a lower MGPC (~19 ng cm^{-2} cycle^{-1}) and less stable saturation behavior compared to films deposited between 150 and 200 °C, where the average MGPC remained approximately constant at ~29 ng cm^{-2} cycle^{-1}. Single-cycle QCM analysis further revealed distinct differences in surface reaction behavior between low- and intermediate-temperature growth regimes. These findings provide experimental insight into DMAI/H_2O ALD surface chemistry and establish growth conditions relevant to the development of DMAI-based AS-ALD processes.

11:00am **AP2+EL+PS+TF-FrM-12 Void-free Thermal ALD BaTiO3 Thin Films Prepared by Removing Water Dose after Ba Precursor**, ***Jiayi Chen,*** Georgia Institute of Technology, China*; Mark Losego,* Georgia Institute of Technology, USA*; Asif Khan,* Georgia Institute of Technology

This talk will discuss our efforts to develop a robust atomic layer deposition process (ALD) to create ferroelectric $BaTiO_3$ (BTO) thin films using Bis-(1,2,4 triisopropylcyclopentadienyl)-Barium and Titanium Isopropoxide precursors.Ferroelectric materials are potential candidates for future low voltage RAM and NAND memory because of their reversible two polarization states under low external electric field. While the CMOS compatible gate dielectric materials HfO_2 and $Hf_{0.5}Zr_{0.5}O_2$ are ferroelectric, they have high coercive fields that make it difficult to lower switching voltages below 1 V. Therefore, perovskite ferroelectric materials, like $BaTiO_3$ are desirable to use for these applications because their coercive voltages can be an order of magnitude lower, approaching 0.1 V.However, these ferroelectric films must be deposited by ALD to match the conformality and small thickness requirements desired for RAM and NAND memory. While reports exist for ALD processes of these materials, most if not all those reports use ALD recipe of “A metal precursor – oxidant – B metal precursor – oxidant”. This talk will present our finding that high quality BTO films can still be deposited with recipe in the form of “H_2O – Ba – Ti” or “H_2O – Ba – Ba – Ti”. A hypothetical ALD chemistry mechanism is proposed. These reactions can happen at 280 °C, but not 220 °C. Inverting the precursor sequence, such that H_2O – Ti – Ba, does not work. XRD confirms the formation of BTO crystal lattices through these novel recipes. One benefit of these recipes is getting void-free BTO films after annealing, whereas our previous studies show that conventional ALD recipes produce BTO films with voids because of the evaporation of H_2O during annealing. 40 nm BTO film deposited with this dehydration recipe shows high dielectric constant of 72 with low dielectric loss at the magnitude of 10^{-3}.

11:15am **AP2+EL+PS+TF-FrM-13 Optimizing Molybdenum Pentachloride Delivery for Vapor Deposition Processes**, ***James Maslar,*** *Vladimir Khromchenko, Berc Kalanyan,* NIST-Gaithersburg

Molybdenum metal has favorable properties for ultrathin layers compared to metals such as copper and tungsten and, therefore, has attracted much recent interest as a potential material for interconnects and gate metallization. A common method for forming ultrathin metal layers in high volume manufacturing is vapor deposition. For vapor deposition of molybdenum metal layers, molybdenum pentachloride is a common precursor. However, molybdenum pentachloride is a solid and can be difficult to reproducibly deliver from the precursor canister to the deposition surface in a tool, depending on delivery conditions and canister design. Also of concern is the presence of molybdenum oxychloride impurity species in the canister, and whether the oxychlorides are being generated during delivery or are present in the supplied material. The primary goal of this study was to characterize the process space for pulsed delivery of molybdenum pentachloride with respect to overall mass carryover, pulse-to-pulse stability, and impurity evolution. The approach used in this study was to quantify the amount of molybdenum pentachloride and molybdenum oxychlorides in an argon carrier gas as a function of carrier gas flow rate, system pressure, canister temperature, and canister design. Quantification was based on direct absorption measurements in the ultraviolet-visible and infrared spectral regions. The results of this study should facilitate the identification of process conditions that optimize molybdenum pentachloride for different applications.

11:30am **AP2+EL+PS+TF-FrM-14 Atomic Layer Modulation of Ru-Ir Alloy Thin Films for Low-Resistivity Interconnect Applications**, ***Yoonseo Choi,*** *Wonjoong Kim, Byungchan Lee, Minhyeok Lee, Han-Bo-Ram Lee,* Incheon National University, Republic of Korea

As semiconductor devices continue to scale down, Ru and Ir have attracted attention as promising candidates to replace Cu interconnects because their short mean free path and low bulk resistivity lead to a low figure-of-merit (FOM). However, ALD-grown single Ru and Ir thin films suffer from increased resistivity at thicknesses comparable to their mean free path due to enhanced electron scattering, particularly surface scattering, and film discontinuity. In this study, a Ru-Ir system was designed and fabricated by atomic layer modulation (ALM) to mitigate the thickness-dependent resistivity. ALM sequentially exposes different precursors to the surface with purge steps between each precursor exposure, followed by co-counter reactant exposure, enabling multicomponent thin films growth within a single atomic-layer cycle. In particular, the ratio of each element is controlled by the surface reactivity, adsorption behavior, and steric hindrance effects of the precursors, making ALM advantageous for forming compositionally uniform Ru-Ir alloy thin films even at reduced thicknesses. In this work, Ru-Ir alloy thin films were deposited at 250 °C by sequentially pulsing tricarbonyl(trimethylenemethane)ruthenium ($Ru(TMM)(CO)_3$) and tricarbonyl (1,2,3-η)-1,2,3-tri(tert-butyl)-cyclopropenyl iridium ($C_{18}H_{27}IrO_3$) as Ru and Ir precursors, respectively, with O_2 as the counter reactant. To design the process and understand the composition-control mechanism, density functional theory (DFT) and Monte Carlo (MC) simulations were used to analyze precursor surface reactions and their effects on film composition. In addition, a deep-learning-based framework (IDEAL) was used to explore candidate compositions and crystal structures for Ru-Ir alloy films. X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses confirmed that ALM-grown Ru-Ir films formed a solid solution without distinct phase separation. The electrical properties varied depending on the alloy composition; while single Ru and Ir films showed resistivity above 40 μΩ·cm at 7 nm, Ir-rich Ru-Ir films exhibited a relatively low resistivity of 37.6 μΩ·cm at 5 nm. The high crystallinity of the Ir-rich Ru-Ir films was also consistent with the IDEAL framework prediction. These results demonstrate that ALM-based Ru-Ir alloy thin films can overcome the thickness-scaling limitations of single-component Ru and Ir thin films and have potential as next-generation interconnect materials for replacing Cu.

11:45am **AP2+EL+PS+TF-FrM-15 Pulsed Thermal Etching of Amorphous TiO_2 Thin Films Using $MoCl_5$**, ***Hyuenwoo Yang,*** National Institute for Science and Technology (NIST)*; James Maslar, Berc Kalanyan,* NIST-Gaithersburg

Gas-phase pulsed etching has emerged as a promising approach for advanced thin-film processing, enabling controlled and potentially low-damage material removal with advantages in process integration over conventional continuous etching methods. Despite growing interest in pulsed etching, including atomic layer etching (ALE), the thermal etching chemistry of metal halides—particularly $MoCl_5$—remains largely unexplored for oxide materials. In this work, we investigate the pulsed thermal etching of amorphous TiO_2 thin films by $MoCl_5$ in a warm-walled viscous-flow reactor. Thickness changes were monitored in real time by in-situ spectroscopic ellipsometry during repeated $MoCl_5$/Ar cycles, while delivered precursor dose and impurity content were monitored upstream using a non-dispersive UV–vis gas analyzer.

Amorphous TiO_2 films on Si/native SiO_2 exhibited clear thickness loss under repeated $MoCl_5$ exposure, with etching behavior that depended strongly on substrate temperature, $MoCl_5$ source temperature, and Ar purge duration. Increasing the $MoCl_5$ source temperature increased the measured UV–vis

absorbance signal and produced a corresponding increase in TiO_2 etch rate, indicating that precursor delivery is a key parameter controlling the etching behavior. A substrate-temperature-dependent process window was also observed: etching was strongly suppressed at 150 °C and 350 °C, while the highest etch rate was observed near 250 °C. Temperature-switching experiments further showed that the low-temperature suppression was reversible upon heating to 250 °C, whereas exposure at 350 °C led to an etch-inactive state that did not recover after returning to 250 °C.

To our knowledge, this is the first report of TiO_2 etching using pulsed $MoCl_5$ chemistry. This work establishes an initial process window for $MoCl_5$-based thermal oxide etching and identifies precursor dose, substrate temperature, delivery history, and purge duration as important variables governing pulsed TiO_2 etching.

Plasma Science and Technology
Room 315 - Session PS-FrM

Novel Chemistries and Materials in Plasma Processing

Moderators: Prof. Kenji Ishikawa, Nagoya University, Japan, **Dr. Thorsten Lill**, Lam Research Corporation

8:15am **PS-FrM-1 Low Energy Remote Plasma and Non-Plasma Methods for Highly Selective Etching of Advanced Nanodevices***, **Mark Kawaguchi**,* LAM Research **INVITED**

In the pursuit of higher performance semiconductors, device length scales continue to shrink down to nanometer dimensions with emerging chip designs increasingly dependent on 3D structures to maintain scaling. Memory manufacturers have already deployed 3D NAND devices with ongoing development for 3D DRAM devices. Advanced logic manufacturers have already deployed 3D FinFET devices and are beginning to deploy more complex GAA (Gate-All-Around) 3D devices as well. Building 3D structures has increased the need for more sophisticated selective etching. As these selective etches have become critical to the formation of the device, atomic precision material loss is required with low contrast materials. We review exemplary materials systems where insufficient selectivity control necessitates innovative approaches such as remote-plasma radicals with atomic layer passivation & ultra-low residual ions as well as plasma-less low energy thermal chemical etching.

Dummy polysilicon removal requires full removal of the polysilicon with minimal film loss to dielectric films such as silicon oxide and silicon nitride. Remote-plasma radical etch removes the polysilicon, but it is desirable to improve film damage control due to higher energy reactants reaching the surface. The first approach applies atomic layer passivation to modify the top monolayer of an oxide encapsulation layer. Epitaxial film damage is improved by hindering diffusion of halogen radicals through the encapsulating film. The second approach reduces the higher energy reactant flux to the surface. We characterize the intensity of higher energy reactants by measuring the residual ion flux to the wafer surface.By modifying flow geometry above the wafer, the residual ion flux is reduced over 2 orders of magnitude, in the range of nA/cm^2, and results in improved material loss.

GAA device integration relies on depositing and subsequently removing SiGe layers to form Si-nanowires or nanosheets. Besides the bulk SiGe etch, we highlight strict film loss requirements that require highly selective native oxide removal prior to removing SiGe layers. We describe a thermal chemical etching approach that applies wet etch mechanisms in a vacuum environment. Etch rates are tunable over a wide range from 2-200 A/min as well as high selectivity to both silicon and silicon nitride materials. In addition, we have applied a Langmuir-Hinshelwood surface kinetics model to extract steady state reactant surface coverage.We find that the surface coverage is sub-monolayer, and over a broad surface coverage range, localized etching characteristics are well-behaved as measured by AFM roughness.

8:45am **PS-FrM-3 A Novel Si Etch Chemistry for CFET Fin Definition***, **Yifeng Zhou**, Hiroto Ohtake,* Applied Materials, Inc.

CFET channel design requires upper ~75% fin etch profile to be straight and smooth, in addition to the traditional requirements for profile loading, etch depth loading, line edge roughness, and mask selectivity. New etch chemistry and process structure are necessary to meet those challenges as the conventional Cl2- and SF6-based fin etch chemistries ran out of steam.

This study introduces a cyclical process featuring a BCl3/NF3 based etching step and a CH4/SO2 based passivation step that provides straight and smooth upper 85% profile, with minimal profile and depth loading among various pattern pitches.

Profile control: NF3 is the main etchant and BCl3 provides effective passivation for Si and SiGe sidewalls. HBr can provide more passivation, via re-deposition of less volatile SiBrx etch products. NF3:BCl3 and NF3:HBr gas flow ratios are the main knobs for profile control.

Si/SiGe scalloping: Scalloping results from relatively higher lateral etch rate of SiGe compared to that of Si. While SO2/CH4 passivation step helps reduce scalloping by forming Ge-S bonds, standalone H2 trim steps eliminates scalloping by trimming Si faster than SiGe.

Profile loading: iso/dense profile loading roots from sidewall passivation delta between spaces with difference widths. Directional breakthrough step removes more passivation from more sloped sidewalls to allow for more taper correction in subsequent etch steps.

Depth loading: SO2/CH4 passivation step deposits thicker carbon polymer on wider trenches, negating the higher etch rate from higher neutral fluxes.

9:00am **PS-FrM-4 Creation and Recovery of Defects in Lead Zirconate Titanate Thin-Films introduced by Inductively Coupled Plasma Reactive Ion Etching***, **Madeleine Petschnigg**, Marco Deluca,* Silicon Austria Labs GmbH, Austria*; Susan Trolier-McKinstry,* The Pennsylvania State University

Due to their excellent actuation performance, with an $|e_{31,f}|$ coefficient of about 15 Cm^{-2}, lead zirconate titanate (PZT) based thin-films are widely adopted for actuator type piezoelectric micro electromechanical systems (piezoMEMS), including inkjet printer heads[1–4], micro speakers[5,6], micro coolers[7,8] and auto focus devices[9,10].In the fabrication of piezoMEMS devices, accurate patterning of the active layer plays a key role. By combining physical and chemical mechanisms, inductively coupled plasma reactive ion etching (ICP-RIE) allows the fabrication of highly anisotropic profiles at high etch rates while maintaining a high selectivity against masking and stop-layer materials.

Plasma assisted dry etching techniques, like ICP-RIE, however, can degrade the patterned PZT and alter its dielectric and piezoelectric properties, which manifests itself in a decreased permittivity, and/or a decreased remanent polarization [11–14]. Degradation is a concern not only when the PZT surface is directly exposed to etching conditions, but alsothrough the introduction and migration of defects at etched side walls [14,15].Potential sources for degradation include changes in surface chemistry due to selective etching or contamination, crystallographic damage due to bombardment, and potential liberation of hydrogen from organic resist masks.Althoughthe electromechanical properties may be recovered by annealing treatments [11,16,17]at 500°C and above, a comprehensive study of the required temperature and time for recovery has yet to be done.

This work aims to uncover the primary mechanism responsible for the degradation of PZT during ICP-RIE patterning, including the effect of pre- and post-etch electrode deposition as well as the presence of hydrogen-containing gases during the plasma etch. Based on this, a targeted recovery treatment procedure will be defined, and the patterning process flow optimized.

Nb-doped PZT films will be deposited by sputtering on Pt-coated Si wafers and patterned by ICP-RIE. The electric properties as well as the aging behavior of pristine samples will be compared to samples right after the etch and after recovery. The potential incorporation of hydrogen will be assessed by Raman spectroscopy. Thermally stimulated depolarization current (TSDC) measurements and charge-based deep level transient spectroscopy (Q–DLTS) will provide insight on the difference in the films defect chemistry.

9:15am **PS-FrM-5 Plasma-Surface Interactions of Polyurea Deposited on SiO2 and SiNx with HF Plasmas***, **Wallis Scholl**,* Colorado School of Mines*; Mingmei Wang, Thorsten Lill, Wenyu Zhang, Louis Kim, Harmeet Singh,* Lam Research Corp*; Sumit Agarwal,* Colorado School of Mines

Fluorocarbon plasmas have been traditionally used to etch SiO_2 and SiN_x during semiconductor processing. Because fluorocarbon radicals inherently lower the etch rate by depositing a polymer on the SiO_2 or SiN_x surface, the industry is transitioning to C-free reactive plasmas, such as HF. As a result, new techniques are needed to enhance surface passivation and etch selectivity during HF plasma etching. During etching of high aspect-ratio (HAR) features, sidewall passivation is needed to preserve the profile. Molecular layer deposition (MLD) is a technique for depositing organic and hybrid organic-inorganic films. We studied the HF plasma interactions after a polyurea film deposited by MLD on top of SiO_2 or SiN_x. We have shown in previous work that MLD polyurea film deposited on top of SiO_2 or SiN_x can protect the underlying material from etching. During HF plasma etching of

blanket films on a planar substrate, the polyurea film acted as a sacrificial layer and prevented SiO_2 or SiN_x etch while the polyurea was present. When the polyurea was completely consumed by reaction, the SiO_2 or SiN_x film was etched at its baseline etch rate (see Figure 1). The presence of polyurea also delayed the formation of ammonium fluorosilicate on the SiN_x surface, which is known to form on the surface in the presence of HF, and SiF_4 and NH_3 generated as etch products.

In this work, we also deposited polyurea onto 65:1 aspect ratio holes in SiO_2-SiN_x stacks, which were then exposed to an etching plasma to evaluate sidewall passivation. Scanning electron microscopy images show that the polyurea film reduced the diameter throughout the entire depth, showing both the conformality of the MLD film as well as successful passivation of the sidewalls. Subsequent etching of these features preserved the critical dimension compared to etching without the polyurea film (see Figure 2). Further, *in situ* infrared spectroscopy was used to monitor polyurea interactions with plasma species to better understand the etch mechanism. We exposed the films to a remote HF plasma and HF gas to mimic the conditions in HAR structures. While the radical species in the remote HF plasma gradually removed the polyurea film, it remained largely intact during exposure to HF gas. Fluorination of the polymer film was observed prior to its removal, suggesting that polyurea is removed as volatile hydrofluorocarbon fragments during HF plasma etching. Additionally, we show that during etching at a higher substrate temperature of 150 C, the presence of polyurea enhanced the SiO_2 etch rate: we attribute this to activation of HF through hydrogen-bonding interactions with the amines in the polyurea film.

9:30am **PS-FrM-6 Long-Term Influence of Fluorine Containing Plasmas and Gases on Sapphire (Single-Crystal Al2O3) and Ni-Based Alloy Surfaces**, ***Takuya Ishihara***, *Nozomi Kida, Hidenobu Tochigi, Keigo Iwamoto,* Azbil Corporation, Japan*; Kazuo Karahashi,* Nagoya University, Japan*; Satoshi Hamaguchi,* The University of Osaka, Japan

In semiconductor manufacturing processes such as dry etching or chemical vapor deposition, capacitance manometers are widely used as essential vacuum pressure sensors to monitor and control the pressures of process gases. These gauges must be corrosion-resistant against process gases such as halides and their radicals generated by the plasmas. The diaphragm material of the manometer is especially important because, if its surface is altered by such corrosive gases, the sensor would send imprecise output signals possibly with the zero-point drift or pressure sensitivity shift. The errors are caused by the changes in mechanical properties of the diaphragm arising from the formation of the modified surface layer. For this reason, Ni-based alloys or polycrystalline ceramics of aluminum oxide (Al_2O_3) are typically used as the diaphragm material of capacitance manometers. More recent capacitance manometers employ sapphire (single-crystal α-Al_2O_3) as their diaphragm material, which is of specific interest in this study [1]. Recent studies on the interactions of polycrystalline Al_2O_3 with fluorine-containing plasmas indicated the formation of aluminum fluoride layers on Al_2O_3 exposed to such plasmas [2,3,4,5,6]. We have reported the results of ion beam experiments to understand the surface modification mechanisms of Ni-based alloys and polycrystalline Al_2O_3 film by fluorine-containing plasmas [7,8]. In addition, Ni-based alloy samples were exposed to xenon difluoride (XeF_2) gases for 3 and 6 months and their fluorinated surfaces were analyzed [9]. In this study, we obtained 12 months XeF_2 exposure data of Ni-based alloys, in which fluorine continued to diffuse even after one year, unlike in sapphire.Furthermore, the differences in surface states between sapphire and nickel-based alloys upon exposure to XeF_2 or NF_2 remote plasma will also be reported.

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[2] Chen Chien-Wei, *et al*, J. Vac. Sci. Technol. A Vol.41 No.1 Page.012602(pp9) (2023)

[3]Kim Yewon, *et al*,Appl. Surf. Sci. Vol.641 Page. Null (2023)

[4]Vos Martijn F. J., *et al*,J. Phys. Chem. C Vol.125 No.7 Page.3913-3923 (2021)

[5]Chittock Nicholas J., *et al*,Appl. Phys. Lett. Vol.117 No.16 Page.162107(pp5) (2020)

[6]Fischer Andreas,et al, J. Vac. Sci. Technol. A. Vol.38 No.2 Page.022603(pp7) (2020)

[7] T. Ishihara, *et al*, the AVS 70th International Symposium & Exhibition (2024)

[8]H. Kang, *et al* Jpn. J. Appl. Phys. Vol. 64 Page: 046001(pp8) (2025)

[9] T. Ishihara, *et al*, the AVS 71st International Symposium & Exhibition (2025)

9:45am **PS-FrM-7 Investigations of Oxygen-Containing Plasma Etching of Diamond**, ***Justin Boles***, University of Houston*; Louis E. S. Hoffenberg, Jack S. Draney, David. B. Graves,* Princeton University*; Vincent M. Donnelly,* University of Houston

Plasma etching of single-crystal diamond is vital for the development of next-generation power electronics and quantum platforms based on nitrogen-vacancy complexes (NV-centers). Despite this, little has been reported on the fundamental etching mechanisms, including the roles of ions and neutrals. Here we report a detailed study of the etching of single-crystal diamond (100) in O_2/Ar magnetically-confined, inductively-coupled plasmas, using a combination of optical emission spectroscopy, ion flux measurements, etching rate measurements, and simulations. Fluxes of positive ions (O^+, O_2^+, Ar^+) to the (100) diamond surface were determined from ion saturation current measurements and Langmuir probe measurements, while O and O_2 number densities were determined using optical emission actinometry. Optical emission spectroscopy was further employed to measure gas temperature (via N_2 rotational spectroscopy) and identify CO and CO_2 reaction products. Etch rates were measured via masking and optical profilometry as functions of ion energy and $\%O_2$ in Ar. In "pure" (98% or 100%) O_2 plasmas, with an O-to-O_2^+ flux ratio of about 25:1, the etch rate and product optical emission intensities obeyed a square root of ion energy dependence, with a threshold near 11 eV. The etching yield (C atoms-per-ion) was 7.5 at a mean ion energy (DC self-bias voltage plus plasma potential) of 215 eV. If CO were the only product, and since physical sputtering yields are much lower, O atoms must be playing a dominate role in etching at this energy. As the feed gas ratio was changed from pure O_2 to 20%O_2/Ar at constant pressure (10 mTorr), ICP power (300 W), and ion energy (215 eV), the total positive ion flux remained nearly constant (1-2 $X10^{16}cm^2s^{-1}$) and the O-to-ion flux ratio actually increased to between 40:1 and 50:1, while the yield decreased monotonically to about 3.5 C-per-ion, still much larger than the sputtering yield of 0.16 C-per-Ar^+. The yields as a function of O-to-ion flux ratio and $\%O_2$ in Ar compare favorably with molecular dynamics simulations.

This work supported by the U.S. Department of Energy, Office of Science, Office of Fusion Energy Sciences under Award No. DE-SC0024537.

10:00am **PS-FrM-8 The Effect of Remote Ar Plasma Exposure on the Crystalline Structure of VO_2**, ***Peter Litwin***, *Neeraj Nepal,* U.S. Naval Research Laboratory*; Marc Currie,* US Naval Research Laboratory*; Andrew Lang, Luis Carrillo, David Boris, Michael Johnson, Scott Walton, Virginia Wheeler,* U.S. Naval Research Laboratory

The effect of chemically inert plasmas on the surface of thin film materials is of interest because it allows for an additional means to deliver energy to a material beyond increasing the material's temperature. This could be of use in cases where energy needs to be delivered to specific layers or interfaces in a heterostructure without subjecting the entire material stack to higher temperatures or to overcome energetic barriers, such as those associated with material crystallization (or amorphization) or the formation of metastable phases. However, plasmas make for a complex environment due to the various energy contributions from ions, electrons, excited species, and photons. Despite this complexity, an increased understanding of energy transfer by controlling the fluence and energy of ions at the plasma-surface interface opens additional avenues in material engineering. This may be particularly true for plasma-enhanced atomic layer deposition (PEALD) processes where thin films are cyclically exposed to plasmas during deposition and thus could benefit from an increased understanding of the interaction between plasmas and material surfaces.

In this work, we look at the impact of remote Ar plasmas on crystalline VO_2 thin films deposited by ALD as a function of plasma power and substrate bias. Thermal ALD of VO_2 was carried out at 150 °C using TEMAV and O_3 and subsequently crystallized in a dedicated thermal annealing vacuum system following a previously established process[1]. We find that the Raman signature of the equilibrium monoclinic phase of VO_2 (m-VO_2) decreases after exposing the sample to a remote Ar plasma beyond a minimum power or substrate bias threshold. Interestingly, this process is reversible, i.e., the signature of m-VO_2 can be recovered by exposing the sample to a subsequent Ar plasma of decreasing power or bias starting below the initial threshold required to reduce the m-VO_2 signature. These results suggest one of two possibilities: either amorphization of the film and subsequent recrystallization or selective stabilization of different VO_2 phases based on the plasma condition used. TEM analysis indicates the plasma-treated material is in fact highly crystalline despite the decreased signature of m-

VO_2, which suggests the latter of the two explanations. This presentation will discuss the details of these experiments and, with the aid of in situ plasma diagnostics, attempt to elucidate the plasma parameters responsible for the behavior observed.

[1] J. Phys. Chem. C 2017, 121, 19341−19347

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