

Atomic Scale Processing Mini-Symposium

Room 116 - Session AP+EM+PS+TF-MoM

Area Selective Deposition (ASD) I

Moderators: Eric Joseph, IBM T.J. Watson Research Center, **Adrie Mackus**, Eindhoven University, Netherlands

8:15am AP+EM+PS+TF-MoM-1 Unlocking the Atomic Canvas: Applications and Challenges of Area Selective Deposition in Next-Generation Memory Devices, *Ebony Mays*, Micron Technology **INVITED**

The semiconductor industry is on the cusp of an AI-driven revolution, propelling scaling and density trends for integrated circuit devices. As we delve deeper into a 3D transformation in circuit architecture, we are driven to find solutions to memory and storage bottlenecks and capacity demands. This necessity is fueling a new wave of architectural, material, and process technology innovations that meet power, performance, and cost demands. The push to control material deposition and removal at the atomic scale over extremely high aspect ratios is more critical than ever. In this context, area selective deposition (ASD) emerges as a powerful tool to meet these evolving challenges. With the application of new materials at higher aspect ratios, we must continue to expand our toolbox with new precursor and deposition technologies for ASD. This talk will address some of the ensuing challenges and hurdles for the use of ASD in manufacturing applications for memory devices. It will also highlight opportunities for innovation and collaboration in these areas, emphasizing the need for future technology innovation. The future of the semiconductor industry hinges on our ability to innovate and collaborate in these critical areas.

8:45am AP+EM+PS+TF-MoM-3 Area-Selective Atomic Layer Deposition by Sputter Yield Amplification, *Arthur de Jong, M. Bär, M. Merckx, E. Kessels, A. Mackus*, Eindhoven University of Technology, Netherlands

Area-selective deposition (ASD) is an emerging technique in device fabrication that can bypass lithography-based fabrication of certain layers in a device stack that require perfect alignment. The distinction between growth and non-growth areas is commonly attained through chemical differences, such as selective precursor or inhibitor adsorption [1]. To expand the ASD toolbox, this study explores a physical approach that integrates (non-selective) atomic layer deposition (ALD) with area-selective sputter etching by ions of the undesired material deposited on the non-growth area. Sputter yield amplification occurs if a non-growth area contains an element with significantly larger mass than the incoming ion [2]. When an ion collides with such atom, the momentum is more effectively redirected upward compared to a collision with a lighter atom. This enhanced redirection augments the energy transfer to the deposited material on the non-growth area, thereby increasing the likelihood of etching. Conversely, the growth area should lack heavy elements, resulting in a considerably lower etch rate of the film that is deposited on top.

Selective sputter etching was investigated for SiO₂ and TiN films. On various substrates, a thin SiO₂ overlayer deposited by ALD was exposed to low-energy Ar ions (33-50 eV). The amount of SiO₂ removed depends significantly on the substrate (Al₂O₃, TiO₂, Nb₂O₅, MoO₃, HfO₂, Ta₂O₅, and WO₃ were investigated here). In general, the heavier the mass of the metal atoms in the substrate, the less SiO₂ is observed after the ion exposure. TiN was selectively deposited on Al₂O₃ with respect to a HfO₂ non-growth area by repeating supercycles of six TiN ALD cycles and Ar ion exposure from a plasma. Approximately 7.0 nm of selective growth is achieved on Al₂O₃ with only 0.15 nm on HfO₂ (giving 96% selectivity). The key benefit of (selective) sputter etching lies in its relative insensitivity to temperature and ALD chemistry. This proof-of-concept shows that exploiting sputter yield amplification can enable ASD processes that are complementary to the existing chemical approaches.

[1] A. J. M. Mackus et al., *Chemistry of Materials* 31, 2 (2019).

[2] S. Berg et al., *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* 10, 1592 (1992).

9:00am AP+EM+PS+TF-MoM-4 Effectiveness of SiO₂ Functionalization with Methyl versus Silyl Groups to Enable Area-Selective Atomic Layer Deposition of Al₂O₃, *Andrew Kaye*, Colorado School of Mines; *S. Agarwal*, Colorado School of Mines, USA; *H. Chandra, R. Pearlstein, X. Lei, A. Derecskei*, EMD Electronics, USA; *B. Zope*, Intermolecular, Inc.

Plasma-deposited SiO₂ films are extensively used in semiconductor manufacturing. Area-selective atomic layer deposition (AS-ALD) of a dielectric, such as Al₂O₃, on a target surface with SiO₂ as a non-growth surface, can simplify device processing. Gas-phase functionalization of SiO₂

using aminosilanes as small molecule inhibitors has been previously reported. Most studies show that growth nucleation during ALD occurs on the functionalized SiO₂ surface after just a few nanometers of deposition on the growth surface. It is speculated that nucleation on the SiO₂ surface occurs due to the availability of unreacted surface –SiOH groups. We tested this hypothesis by functionalizing the SiO₂ surfaces with different densities of surface –SiOH groups with two aminosilanes that offer a different degree of steric hindrance. Specifically, we functionalized of the plasma-deposited SiO₂ surface with N,N-dimethylaminotrimethylsilane (DMATMS) and di-sec-butylaminosilane (DSBAS). *In situ* infrared spectroscopy shows that DMATMS and DSBAS react with isolated surface –SiOH groups resulting in –Si(CH₃)₃ and –SiH₃ terminated surfaces, respectively. Due to steric hindrance from the bulky di-sec-butylamino ligand, ~50% of the surface –SiOH groups remained unreacted after functionalization of the as-deposited SiO₂ surface: these –SiOH groups became available for reaction with dimethylaluminum isopropoxide (DMAI) during Al₂O₃ ALD. In contrast, *in situ* 4-wavelength ellipsometry shows that functionalization of the as-deposited SiO₂ surface with DMATMS resulted in a nucleation delay of ~20 ALD cycles due to the much higher surface ligand coverage, which we attribute to a much smaller reactive leaving group. Next, we pre-annealed the as-deposited SiO₂ films at 500 °C, which lowered the surface –SiOH density by ~72%. After annealing, both inhibitors had nearly equal surface coverage, and reacted with most of the available surface –SiOH groups. However, surface functionalization with DMATMS still provided a nucleation delay of ~20 ALD cycles, while DSBAS did not provide any nucleation delay. On the pre-annealed surface, both DMAI and H₂O did not react with surface –SiH₃ or –Si(CH₃)₃ groups. Instead, we show that DMAI can strongly absorb onto surface Si–O–Si sites to initiate film growth. Since DMATMS provides a higher degree of steric blocking due to the bulkier –Si(CH₃)₃ ligand, there is still a nucleation delay on the pre-annealed SiO₂ surface even though the surface density of the ligands is much lower compared to the as-deposited surface.

9:15am AP+EM+PS+TF-MoM-5 Progress Towards a New Class of Area Selective Deposition Using Photoassisted Chemical Vapor Deposition on Thermally Sensitive Substrates, *B. Das, R. Rashmi*, University of Florida; *B. Salazar, C. Brewer*, University of Texas at Dallas; *L. McElwee-White*, University of Florida; *Amy Walker*, University of Texas at Dallas

Area selective deposition (ASD) has been successfully realized in microelectronics using high-temperature processes, but continued performance and scaling, new materials, and future device fabrication schemes require new low-temperature (<400 °C) ASD methods for metals, dielectrics and other films. In this talk we describe progress towards a new low (near room) temperature ASD method in which reactive functionalized self-assembled monolayers direct Ru film deposition using novel photoassisted chemical vapor deposition (PACVD) processes. The ideal precursor for photoassisted low temperature CVD is a volatile complex with a high quantum yield for ligand loss, which provides an empty coordination site for surface attachment. The surface-bound primary photoproduct then undergoes facile decomposition to the target material and for ASD selectively reacts with the functionalized SAM terminal groups. Our initial proof-of-concept studies employed (η³-allyl)Ru(CO)₃X (X = Cl, Br, I) precursors. Three SAMs were employed with –CH₃, –OH or –COOH terminal groups. Under UV light using (η³-allyl)Ru(CO)₃Br we showed that Ru(0) and RuO_x selectively deposits on –CH₃ and –OH terminated SAMs but not on –COOH terminated SAMs. We attribute this behavior to the formation of Ru-carboxylate complexes which block deposition. We further show that using (η³-allyl)Ru(CO)₃X (X = Cl, I) precursors only lead to molecular deposition and DFT calculations indicate that this is not due to the primary photoprocess but the energy required to lose a second carbonyl. Most recently we have studied a series of (η⁴-diene)Ru(CO)₃ (diene = butadiene, isoprene, 1,3-cyclohexadiene or cyclobutadiene) to further investigate the role of polyhaptic carbon ligands and the metal oxidation state. We have already demonstrated that these complexes undergo photochemical loss of CO and/or the diene and that exhaustive photolysis of the complexes in solution leads to the formation of colloidal Ru. In agreement with our observations using (η³-allyl)Ru(CO)₃Br we show that the primary photoprocess and the metal oxidation state are not the most important reaction variable for Ru metal deposition but rather the energy required to lose further ligands. Further we show that Ru selectively deposits on –COOH terminated SAMs and not on –CH₃ and –OH terminated SAMs.

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9:30am **AP+EM+PS+TF-MoM-6 A Stochastic Lattice Deposition Model for Visualization of ALD and Area-Selective Deposition of Metal Oxides, Nicholas Carroll, G. Parsons, North Carolina State University**

Area-selective deposition (ASD) is of interest to augment advanced lithographic patterning to achieve improved resolution and feature alignment. In addition to controlled substrate-dependent nucleation and growth, precise feature alignment will also require understanding and ability to adjust the lateral growth of ASD materials, for example, to control lateral “mushrooming”. Previous analytical models give insight into trends in thickness, selectivity, surface coverage, and areal nuclei density during ASD, but models capable of visualizing and analyzing lateral over-growth for various ASD processes are not as well known. In this work we describe a stochastic lattice deposition model capable of simulating atomic layer deposition (ALD) and ASD of metal oxide films with nucleation in a localized “growth” region and lateral over-growth of the film into an optional “non-growth” region. ALD cycles are simulated using a set of reactive sites (*i.e.* a hydroxyl group) that interact with an incoming precursor (*i.e.* trimethylaluminum) to produce randomly arranged metal and ligand sites on a 3D cubic grid lattice. The metal center binds to the oxygen site, and the remaining ligand groups are oriented adjacent to the metal center. The stoichiometry, density, and OH concentration in the resulting film can be tuned to experimentally reasonable values by implementing adjustments to the extent of packing and bridge-site reactivity during the ALD cycle. Using well-controlled ALD conditions, the model allows the extent of lateral growth over adjacent “non-growth” regions to be observed and quantified. To adjust the extent and shape of lateral growth, several parameters were considered, including enhanced attractive interactions between precursors and the non-growth substrate surface, localized substrate oxidation at the leading edge of the film, and others. We have also begun to use the model to consider the influence of non-planar substrate geometry in the extent of ASD. Results from model output will be compared to published experimental results, giving insights into possible physical and chemical mechanisms driving non-uniform ALD and ASD.

9:45am **AP+EM+PS+TF-MoM-7 Selective Deposition of Low k SiCOH and Surface Sialylation Repair of Low K Dielectrics for Nano Cu Interconnects, Son Nguyen, H. Shobha, A. Jog, H. Huang, B. Peethala, J. Li, J. Demarest, Y. Yao, IBM Research Division, Albany, NY**

In this paper, we demonstrate the integrated surface sialylation, low-k repair, and selective SiCOH deposition on 32 nm pitch Cu-SiCOH damascene structures to form a 5-6 nm raised SiCOH for the Fully Aligned Via (FAV) integration. Initially, the nominally damaged patterned SiCOH dielectric surface was repaired by UV sialylation process with carbonsiloxane to reduce the typical RIE patterning damage and cyclic selective deposition of Cobalt [4] by replenishing the surface carbon with UV/Thermal assisted carbonsilane precursor repair. The time-of-flight secondary ion mass spectrometry (ToF SIMS) analysis indicates nominal amount of carbon replenished on the SiCOH surface (see Figure 2). This surface sialylation repair reduces the capacitance and significantly improves the TDDB as shown in Figure 1. FTIR analysis also indicates an increased Si-CH₃ bonding in SiCOH surface after sialylation suggesting the replenishment of carbon on the SiCOH surface. After the initial one cycle SiCOH surface sialylation repair with Carbo-Siloxane precursor, additional selective SiC(O) films were deposited using multi step cyclic deposition and treatment processing steps as illustrated in Figure 3. The average selective deposition/H₂ plasma treatment steps per each cycle is about 6A. Electrical measurement on blanket MIS wafers yields a $k = 4.1 \pm 0.1$ for the selective SiCO layer which is 1.8 times lower compared to selectively deposited of AlO_x with $k \sim 7.5$ for FAV applications [2-3]. Figure 4 shows the various analyses for sialylation and SiC(O) selective deposition on SiCOH_Co capped Cu patterned surface. Clearly, sialylation repair penetrates to SiCOH and selective growth of 6 nm SiC(O) after cyclic processing steps. Figure 5 shows representative image of 32/36 nm pitch FAV structure fabricated after integrated sialylation and selective deposition of 4 nm SiC(O) with UV/Thermal Assisted Vapor Processing. Overall, the integrated Sialylation and selective provide a simpler the low k SiCOH dielectric repairs and selective dep of lower k SiC(O) dielectrics film for FAV and other planar surface applications in electronic device fabrication without the need of SAM that normally required in selective deposition.

REFERENCES

- [1] B. D. Briggs et al., "IEDM Tech. Dig., Dec. 2017 pp. 338-341
- [2] S. Van Nguyen et al., "Proc. IEEE Int. Interconnect Technol. Conf., paper S7-4, Jul. 2021 Kyoto, Japan.

[3] H.P. Chen, et al., International Electron Device Meeting 2021, paper 22.1, San Francisco, CA, USA

[4] C.C.Yang, B. Li, H. Shobha, S. Nguyen, A. Grill, J. Aubuchon, M. Shek and D. Edelstein. IEEE Electron Device Letter, Vol 33, No, 4, pp.588-560 (2012).

* Figures 1-5 are in supplement

10:00am **AP+EM+PS+TF-MoM-8 Atomic and Molecular Monolayers on Silicon as Resists for Area-Selective Deposition, Andrew Tepyakov, University of Delaware**

As the size of the components in electronic devices decreases, new approaches and chemical modification schemes are needed to produce nanometer-size features with bottom-up manufacturing. Atomic and molecular layers can be used as effective resists to block the growth of materials on non-growth substrates in area-selective deposition methods. However, in order for these monolayers to be useful, it is imperative to know the initial structure and reactivity of these modified surfaces and also to understand what happens when the selectivity is lost. This talk will summarize recent developments in our search for effective resists based on chlorination and bromination of silicon surfaces performed by solution and gas-phase modification methods and preparation of organic monolayers starting with these surfaces. The structure, stability, and reactivity of the modified surfaces will be evaluated with spectroscopic and microscopic techniques, and their performance as potential resists in ALD of titanium dioxide will be discussed. The TiO₂ deposition is performed using thermal ALD with tetrakisdimethylamidotitanium (TDMAT) or TiCl₄ as the source of titanium and water as the co-reactant. The selectivity of the process will be compared to that of unmodified (oxidized) silicon surfaces (prototypical growth surface) and of the H-covered silicon surfaces (prototypical non-growth surface).

10:30am **AP+EM+PS+TF-MoM-10 Selectivity Loss During Area-Selective Deposition Processes: The Role of Chemical Passivation and Steric Shielding, M. Merkk, P. Yu, I. Tezsevin, A. Mackus, Eindhoven University of Technology, Dept. Applied Physics, Netherlands; Tania E. Sandoval, Universidad Técnica Federico Santa María, Dept. Chemical and Environmental Engineering, Chile**

INVITED

Area-selective deposition (ASD) processes have been an extensive area of research for the past few decades. Strategies to achieve selectivity include the use of self-assembled monolayers, inherent selectivity of precursor molecules, and most recently, the use of small molecule inhibitors (SMIs). All these different approaches require a fundamental understanding of the mechanism at every step of the process, and more importantly, what determines selectivity loss. In the case of SMIs, there are several challenges related to their vapor phase dosing to be overcome to improve selectivity, such as, reaching high packing, chemical passivation, and steric shielding.[1-2]

This study explores the connection between chemical passivation and steric shielding with selectivity loss using SMIs. Specifically, how the adsorption of the SMI acetylacetone influences the nucleation of trimethylaluminum (TMA), dimethylaluminum isopropoxide (DMAI), and tris(dimethylamino)aluminum (TDMAA) on the non-growth area through displacement reactions.

Through a combination of experimental and theoretical characterization, we found that the observed changes to the non-growth area during ASD are related to the reactivity of the precursor towards the inhibition layer. Infrared spectroscopy reveals that 23% of TMA adsorbs on the non-growth area after SMI adsorption, exceeding DMAI and TDMAA by more than an order of magnitude. Density functional theory calculations are used to explore the role of chemical passivation by calculating adsorption energies of SMI and precursor, as well as displacement energies. We found that differences in reactivity across precursors and SMI are an important metric to determine displacement.

In addition, we carried out molecular dynamics to characterize the role of steric shielding by looking at the inertness of the non-growth area after SMI adsorption, and the different pathways of the precursor to reach the surface. These results show that the adsorption configurations of acetylacetone provide different degrees of steric shielding, where the most weakly adduct promotes precursor adsorption.[3] Moreover, they also show how the small size of TMA is detrimental to blocking as it can easily reach the surface, while TDMAA is more hindered from adsorption. Overall, this study provides important insights into the mechanism for selectivity loss, and highlights the different contributions to precursor blocking, providing a thorough understanding of inhibition in ASD processes.

- [1] J. Li, et al. J. Vac. Sci. Technol. A 40, 062409, 2022

[2] P. Yu, et al. *Appl. Surf. Sci. J.apsusc.2024.160141*, 2024

[3] M.J.M. Merckx, et al. *Chem. Matter.* **32**, 3335–3345, 2020

11:00am **AP+EM+PS+TF-MoM-12 Computational Screening of Small Molecule Inhibitor Candidates for Area-Selective Atomic Layer Deposition**, *Joost Maas, I. Tezsevin, P. Yu, M. Merckx*, TU / Eindhoven, Netherlands; *T. Sandoval*, Universidad Tecnica Federico Santa Maria, Chile; *A. Mackus*, TU / Eindhoven, Netherlands

Area-selective atomic layer deposition using small molecule inhibitors (SMIs) represents a promising avenue to facilitate the downscaling of nanoelectronics. SMIs eliminate challenges such as alignment errors by enabling bottom-up selective growth using vapor-phase processing. Two main factors play a role in the viability of SMI candidates: (i) the inhibitor molecules must adsorb strongly and selectively on the non-growth area and (ii) these molecules must pack densely once adsorbed. In this contribution, these two factors are investigated using density functional theory (DFT) and random sequential adsorption (RSA) simulations respectively.¹ RSA simulations mimic the adsorption of molecules as they arrive one-by-one in gas-phase and are used to determine the chemical passivation (by means of coverage and surface density) and steric shielding (by means of the fraction of covered area) performance of the SMIs.² RSA is computationally lightweight and easily scalable.

A four tier simulation approach is followed to screen SMI candidates: (1) DFT on small clusters to determine whether adsorption is energetically favorable and to determine the adsorption configuration. The adsorption configuration is then used to create a 2D footprint of the molecule, such that it can be used in (2) initial RSA simulations of the candidate SMIs, yielding the coverage and fraction of covered area. (3) Based on this initial screening, the most promising candidates are further tested using periodic DFT to improve the accuracy of our approximation, and (4) RSA is re-run using the updated geometry. By narrowing down the list of candidates within each step, time is spent more efficiently on more complex simulations. A list of 30+ candidates is screened for Al₂O₃, SiO₂, AlN, and Si₃N₄ using this method; surfaces chosen for their applications in semiconductor industry (AlN was included for a comparison between oxides and nitrides). The list of candidates is comprised of carboxylic acids and diketones, a selection inspired on the experimental performance of (among others) Hacac and acetic acid. Further divisions are made to investigate the effect of the carbon chain length (up to 5 for valeric acid), halides in the SMI, and reactive atoms (O/N/S). In line with simulation results, experimental results indicate that acetic acid performs well as an SMI, lending credence to the screening approach. Our analysis suggests that formic acid, acetamide, valeric acid, acetadiimidine, and imidodicarbonic diamide are promising candidates to be used as SMIs for ASD processes.

1. J. Li; et al. *JVST A* **2022**, 40 (6), 062409

2. Mameli, A.; et al. *ACS Nano* **2017**, 11 (9), 9303–9311.

11:15am **AP+EM+PS+TF-MoM-13 Ordering of Small Molecule Inhibitors to Block Precursor Adsorption on Cu During Area-Selective Atomic Layer Deposition: A Computational Study**, *Ilker Tezsevin, J. Maas, M. Merckx*, Eindhoven University of Technology, Netherlands; *S. Semproni, J. Chen*, Intel Corporation; *T. Sandoval*, Universidad Técnica Federico Santa María, Chile; *A. Mackus*, Eindhoven University of Technology, Netherlands

Thanks to their industrial compatibility, small molecule inhibitors (SMIs) offer a promising route for achieving area-selective atomic layer deposition (ASALD) in semiconductor fabrication. Cu is widely used in integrated circuits as an interconnect material and is a target non-growth area for many ASD applications. This study explores the adsorption and packing of SMIs on the Cu surface to achieve ASALD considering Cu as the non-growth area.

SMIs are dosed in the vapor phase and arrive one-by-one on random surface sites. Therefore, SMIs typically cannot form a dense ordered layer, leaving some surface sites uncovered and available for precursor adsorption.^{1,2} To promote the packing on the surface, an SMI favoring lateral interactions and surface mobility on the non-growth area is required such that a self-assembled monolayer (SAM)-like packing can be achieved. Our screening for effective SMIs using density functional theory (DFT) calculations led to the discovery of the great potential of pyridazine (C₄H₄N₂), which exhibits strong adsorption on Cu via its nitrogen atoms. Random sequential adsorption simulations³ of pyridazine on Cu show that it can densely pack on the surface with a surface density of more than 2.4 molecules per nm² such that precursors with a radius larger than 0.3 nm

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cannot reach the surface. Furthermore, detailed DFT and molecular dynamics studies suggest that pyridazine molecules show ordering on the Cu surface. Due to its unique adsorption configuration, pyridazine molecules favor lateral interactions resulting in a SAM-like ordering. Additionally, the pyridazine adsorption configuration allows for diffusion or rotation of the inhibitor on Cu with an activation barrier of less than 0.22 eV, enabling denser packing on the surface. In summary, the pyridazine molecule exhibits exceptional adsorption energetics on the Cu surface promoting a densified inhibitor layer on the non-growth area. Hence the unique properties of pyridazine may bridge the gap between the industrial applicability of SMIs and the efficiency of SAMs, making it a promising candidate for ASALD applications targeting Cu non-growth areas.

(1) Merckx, M. J. M.; et al. *Chem. Mater.* **2020**, 32 (18), 7788–7795.

(2) Tezsevin, I.; et al. *Langmuir* **2023**, 39 (12), 4265–4273.

(3) Li, J.; et al. *J. Vac. Sci. Technol. A* **2022**, 40 (6), 062409.

11:30am **AP+EM+PS+TF-MoM-14 Revealing the Mechanisms for Loss of Selectivity in Area-Selective ALD Using in-Situ Infrared Spectroscopy**, *Eric H. K. Wong, M. Merckx, J. Maas, I. Tezsevin, W. Kessels*, Eindhoven University of Technology, The Netherlands; *T. Sandoval*, Universidad Tecnica Federico Santa Maria, Chile; *A. Mackus*, Eindhoven University of Technology, The Netherlands

To fulfil the needs for self-aligned fabrication in sub-5 nm technology nodes in nanoelectronics, much research efforts have been devoted to the development of area-selective atomic layer deposition (AS-ALD). The use of small-molecule inhibitors (SMIs) is considered to be an industrially-compatible option due to its vapor-phase dosing. Our previous works have provided mechanistic insights into the first cycle of AS-ALD of SiO₂ as a model system for understanding blocking by SMIs [1, 2]. However, the mechanisms for loss of selectivity in AS-ALD remain unexplored which is critical to improving the selectivity. In this work, we performed in-situ reflection-absorption infrared spectroscopy (RAIRS) measurements as a function of the number of cycles to reveal the mechanisms of the selectivity loss.

Twenty cycles of an ABDC-type process [3] comprising an acetylacetone (Hacac) inhibitor dose (step A), a bis(diethylamino)silane (BDEAS) precursor dose (step B), and subsequently two plasma (H₂ and O₂) exposure (steps D and C) were carried out on the non-growth area Al₂O₃. RAIRS spectra were taken after the steps A, B, and DC. We learned in previous work that the adsorption of Hacac on Al₂O₃ results in a mixture of chelate and monodentate adsorption configurations, with the chelate configuration being the effective form for precursor blocking [2]. Our results from the current study indicate that the precursor-blocking by the inhibitor layer decreases as a function of cycles. In addition, the mixture of inhibitor adsorption configuration changes to a higher chelate-to-monodentate ratio. DFT calculations indicate that the SiO₂ defects formed due to the partial loss of selectivity prevent the successful re-application of the inhibitor molecules in the subsequent cycles. In summary, our results suggest that the change of chemical character of the non-growth area due to the formation of defects escalates the loss of selectivity. Furthermore, this work demonstrates a general approach for inspecting the mechanisms for loss of selectivity that can be extended to other AS-ALD systems.

[1] A. Mameli et al., *ACS Nano*. **11**, 9303–9311 (2017).

[2] M. J. M. Merckx et al., *Chem. Mater.* **32**, 3335–3345 (2020).

[3] M. J. M. Merckx et al., *Journal of Vacuum Science & Technology A*. **39**, 012402 (2020).

11:45am **AP+EM+PS+TF-MoM-15 Use of Sulfide Inhibitors for Multi-Surface Passivation and Area Selective Deposition**, *Summal Zoha, B. Gu*, Incheon National University, Republic of Korea; *F. Pieck, R. Tonner Zeck*, Leipzig University, Germany; *H. Lee*, Incheon National University, Republic of Korea

In recent years, the area-selective atomic layer deposition (AS-ALD) process has excelled over conventional methods for precise and area-selective thin film deposition. This area selective deposition (ASD) method has displayed promising capability for 2D and 3D nanoscale patterning. With the help of inhibitor molecules capable of tailoring the surface properties, thin films can be deposited only on desired growth surfaces using AS-ALD without any unwanted growth on non-growth surfaces. In this regard, small molecule inhibitors (SMIs) have recently gained a lot of attention for their inhibiting capabilities despite having small sizes. The choice of surface inhibitor is crucial in determining the growth, non-growth surface, and the degree of surface passivation. In this study, three organosulfide inhibitors have been utilized for AS-ALD on metal, oxide, and nitride surfaces, Cu, SiO₂, and TiN,

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respectively. These inhibitors display selective adsorption on the Cu surface and in some cases on the SiO₂ surface, while the TiN surface remains unaffected by the inhibitors. The density functional theory (DFT) study revealed that the inhibitors are capable of decomposing to assist the adsorption of their constituents on the Cu and SiO₂ substrates, thereby simultaneously inhibiting two surfaces through a single inhibitor. A comparison between the organosulfide inhibitors was performed to comprehend blocking behavior. Blocking results of HfO₂ ALD revealed that the longer straight-chained organosulfide inhibitor was able to uphold better blocking properties than compared to the shorter and branched organosulfide inhibitor. This concept of multi-surface inhibition by a single inhibitor can be an essential approach for Si device fabrication where several surfaces are exposed under AS-ALD processes.

Plasma Science and Technology

Room 124 - Session PS1-MoM

Plasma Processes for Advanced Logic

Moderators: John Arnold, IBM Research Division, Albany, NY, Angélique Raley, TEL Technology Center America

8:15am **PS1-MoM-1 Mechanism of Formation of Roughness During Ru Direct Etching**, *Miyako Matsui*, Hitachi Ltd., Japan; *M. Miura, K. Kuwahara*, Hitachi High-Tech Corp., Japan

Scaling of logic devices is still mainly driven by fabricating three-dimensional structures. As device scaling continues, alternative metal interconnects are required to replace Cu that enable reduction of metal pitch at the back end of the line. Ru is a candidate for an alternative interconnect material with metal pitch of 20 nm and beyond because a Ru interconnect is expected to have lower effective resistance than that of a Cu interconnect at such small pitches. Ru is expected to be etched directly, which leads to new scaling boosters such as semi-damascene patterning. In addition, to reduce interconnect resistance, roughness or other damage should be suppressed. In our previous study, we investigated the mechanism of Ru etching and the effects of protection layers formed on the sidewall of a line-and-space Ru pattern etched using Cl₂/O₂-based plasma. In this study, we investigated the mechanism of formation of line-width-roughness (LWR) of a Ru pattern with 32-nm pitch by using Cl₂/O₂-based plasma. We also investigated the influence of mask-pattern roughness and Ru line grain-boundaries on LWR.

We investigated the influence of the roughness of the Si₃N₄ mask pattern on that of the Ru pattern. Before and after Ru etching, LWR was measured by a high voltage CD-SEM, namely, critical-dimension-scanning electron microscope using an incident electron beam at energy of 45 keV. The high voltage CD-SEM was used to simultaneously measure both LWR of the mask-pattern and that of the Ru line. LWR of the mask pattern was measured from the image formed by the secondary electrons and that of the Ru line was measured from the image formed by the backscattering electrons (BSE). These measurements showed that after the Ru etching, LWR of the Si₃N₄ mask pattern and that of the Ru line depend on ion flux, which was adjusted by changing the duty cycle of wafer bias power. When wafer bias power was applied continuously, width of the Si₃N₄ mask became larger and LWR became smaller because the Si₃N₄ mask was widened by the re-deposition of the Si containing by-product. On the contrary, LWR of the Ru line remained mostly constant even when the ion flux was reduced. According to these results, it is necessary to measure LWR of the Ru line from BSE images because LWR of the mask after etching and that of the Ru line are not necessarily correlated.

We also investigated the effect of the grain boundary of Ru on LWR formed at the edge of the Ru line pattern. It was found that sidewall etching tends to proceed from the grain boundary. Accordingly, it is important to prevent the grain boundary from being etched by forming uniform passivation layers on the sidewall.

8:30am **PS1-MoM-2 Enabling Advanced Beol Interconnect Scaling Through Ruthenium Subtractive Etch Patterning**, *Shravana kumar Katakam*, IBM Research Division, Albany, NY; *N. Joy, D. Yan*, TEL Technology Center, America, LLC, Albany, NY; *C. Penny, C. Park, K. Motoyama, H. Shobha, Y. Mignot, J. Lee*, IBM Research Division, Albany, NY

With the ever-increasing demand to shrink the critical dimensions (CDs) for advanced technology complementary metal-oxide-semiconductor (CMOS) nodes, the demand to shrink the backend-of-the-line (BEOL) metal line pitch is also increasing. Traditionally the copper (Cu) damascene process has been the main candidate, but modeling results indicate that it may be

difficult to scale Cu damascene processes beyond 20nm pitch due to increase in-line resistance. In this regard, ruthenium (Ru) metal is a potential candidate for replacing copper for tighter pitch nodes beyond 20nm pitch. This is attributed to its superior electrical performance compared to traditional copper resistance at these line widths. Ru patterning is through subtractive etch as opposed to damascene process for Cu metals and it has been established that Ru can be patterned easily using chlorine (Cl₂) and oxygen gas (O₂) chemistries due to formation of volatile by products for relaxed pitches, but we run into difficulties as the pitch becomes tighter than 20nm pitch (P20).

The unique challenges during patterning at P20 or less are attributed to significant hardmask swelling from HM re-deposition during the etching process resulting in incomplete Ru etch at the regions affected by HM swelling. Additionally, the oxide re-deposition also results in severe RIE lag demanding a significant amount of over etch compromising pattern fidelity at min pitch structures.

In this work, we have systematically analyzed the changes to the plasma as the etch progresses and identified a possible mechanism for the HM swelling. With the understanding of these mechanisms, we were able to tune the plasma parameters to successfully reduce the HM swelling significantly to the levels that can be tolerated at the tighter pitches of P18 and beyond. We will also enlist some possible approaches to reduce swelling in the context of scaling the Ru etch for even tighter pitches of P16 and beyond.

8:45am **PS1-MoM-3 Atomic Level Control of Plasma Etching Using Various Pulsing and Cyclic Technologies for Leading-edge LSI**, *Masaru Izawa*, Hitachi High-Tech Corp., Japan

INVITED

The cell size of logic LSI has been reduced by adopting Design-Technology Co-Optimization (DTCO) and pitch scaling using double patterning or EUV lithography. Recently, Gate-All-Around (GAA) FETs are being developed for the production of advanced nodes. For the fabrication of leading-edge devices, not only high selective vertical etching but also lateral etching is required. In terms of vertical etching, various pulsing technologies have been investigated, including gas switching using microwave ECR (M-ECR) plasma. For lateral etching, DCR (dry chemical removal) with IR lamp has been applied. This paper discusses some etching challenges in leading-edge devices, particularly related to EUV, DTCO, and GAA.

In EUV tri-layer etching, a mask reconstruction process (MRP) has been developed [1], where area-selective deposition is applied to reduce line-width roughness (LWR) and protect the EUV resist. In Si/SiGe fin etching, an atomic layer etching (ALE) function that includes source, wafer RF bias, and gas pulsing is adopted to achieve a vertical profile with high selectivity. Additionally, hydrogen gas is added to suppress etch depth and CD differences between Si and SiGe fin profiles [2]. In WFM (work function metal) patterning, DC pulse technology is applied to minimize fin damage [3]. The erosion of the fin top is reduced by 57% using this technique, and charging effects are also mitigated by using DC pulses. Furthermore, lateral etching processes using the DCR tool have been studied [4]. For example, etching a 2.5 nm space in Si₃N₄ film using a thermal cyclic ALE scheme was achieved without microloading. Lateral etching of SiO₂ and W has also been investigated.

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[4] K. Shinoda *et al.*, J. Phys. D **50**, 194001 (2017).

9:15am **PS1-MoM-5 Investigating Plasma Interaction with Ultrathin Polymethylmethacrylate Films for EUV Lithography**, *Shikhar Arvind, E. Witting Larsen, P. Bezaud, J. Petersen, S. De Gendt*, IMEC, Belgium

State-of-the-art extreme ultraviolet (EUV) lithographic scanners can now pattern with 12 nm half pitch resolution. To enable this high-resolution patterning requires the use of ultrathin (sub-50 nm) photoresists (or resists). This is due to pattern stability concerns of high aspect ratio structures, as well as the exceptionally short depth of focus of high numerical aperture (NA) scanners¹. But the use of ultrathin resists further complicates pattern transfer as unintended plasma-induced effects during dry etching are more pronounced. The vacuum ultraviolet (VUV) photons generated in plasma are of particular interest for us as they can cause considerable resist modification. A better understanding of the interaction of plasma species, particularly of VUV photons with ultrathin resists is critical for enabling pattern transfer of sub-10 nm features.

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Here, we study the impact of VUV photons, argon ions, and argon plasma on a 40 nm thick polymethylmethacrylate (PMMA) film². Using a deuterium lamp, an industrial ion beam etch tool, and an industrial inductively coupled plasma etch tool, we exposed the polymer to VUV photons, ions, and plasma, respectively. The exposed samples were then analyzed for chemical and physical changes using multiple characterization techniques. We observe that the thin resist thickness caused the vacuum ultraviolet photons interact with the entire bulk of the PMMA film, while the ions only affect the surface and near surface region. The photon exposed samples formed smaller polymer fragments at low exposure doses and further started to crosslink at high doses. In contrast, the ion modification led to carbonization of only the top few nanometers of the polymer film, leaving the bottom bulk intact. The plasma exposed sample showed changes characteristic to both vacuum ultraviolet photons and ions, and their synergism. It was stratified with a 1.34 ± 0.03 nm thick ion-caused carbonized layer on top of 13.25 ± 0.12 nm photon-induced crosslinked layer. By studying the impact of the individual plasma constituents on ultrathin PMMA, we thus establish a baseline testing methodology for plasma-resist interactions on a simple model system, which we will further deploy on novel resists for EUV lithography.

References:

1. A. Burov, A. Vaglio Pret, and R. Gronheid, "Depth of focus in high-NA EUV lithography: a simulation study," in *SPIE Photomask Technology 2022*.
2. Shikhar Arvind, Esben W. Larsen, Philippe Bezaud, John Petersen, Stefan De Gendt; Impact of vacuum ultraviolet photons on ultrathin polymethylmethacrylate during plasma etching. *J. Vac. Sci. Technol. A* 1 May 2024; 42 (3): 033009. <https://doi.org/10.1116/6.0003541>

9:30am **PS1-MoM-6 In situ Hard Mask Growth for Break Healing in Ultra-Thin Layers Patterning**, Rémi Vallat, P. Bézaud, B. Chowrira, IMEC, Belgium; A. Fathzadeh, KU Leuven and Imec, Belgium; K. Filippidou, L. Souriau, K. Ronse, IMEC, Belgium

One of the challenges introduced by High NA EUV lithography include defectivity management, particularly when working with (ultra-)thin resists and low EUV exposure doses¹. Reducing the bridges and breaks issues is thus a major point of focus when patterning Line/Space². Traditionally, a descum step is used to remove bridges, resulting in a reduced resist budget for underlayer patterning and leading to the creation of breaks. Therefore, recovering breaks is a strategic capability for defect reduction.

The method consists of patterning an underlayer of suitable thickness for thin resists and run an in situ PECVD process onto this underlayer, selectively to the material below in order to prevent and recover breaks³. This way, the hard-mask budget is increased in-situ during the etch process to prevent the formation of breaks while patterning from a thin underlayer (~10nm). This approach is presented in Fig1. Moreover, this method offers a reduced environmental footprint compared to conventional one as thinner ULs need fewer Global Warming Potential gases (GWP)⁴. Patterning of such ultra-thin layers (≤ 5 nm) may come with high bridge/ break density which can be addressed by using this break healing strategy, thanks to in-situ selective HM growth.

In this work, the selectivity of deposition has been achieved, along with a notable decrease in break density and these results are shown in Fig2 and Fig3. However, the presence of additional deposited material brings new challenges. The focus of this work is to investigate the etch mechanisms which occur at the amorphous Carbon layer level, as well as to ensure the pattern transfer uniformity. Preliminary defectivity measurements will also be explored. Applications for both resist types, CAR and MoR, will be discussed. MoR is expected to induce more breaks, particularly problematic for low dose strategies. In addressing this issue, our break healing strategy emerges as a potential candidate for further exploration.

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[2] P. De Bisschop, *J. Micro/Nanolithogr. MEMS MOEMS*16, 041013 (2017)

[3] R. Vallat et al, *AVS69*, (PS+NS+FrM-3) (2023)

[4] P. Bézaud et al. *Advanced Etch Technology and Process Integration for Nanopatterning XIII*. SPIE (2024)

9:45am **PS1-MoM-7 Plasma Etching of Low K Materials from Room Temperature to -40°C in Different Fluorine-Based Chemistries**, Daniel Santos, C. Vallee, University at Albany-SUNY

Plasma etching of ultra-low-k materials at aggressive back end of line (BEOL) nodes has become increasingly challenging as plasma induced

damage becomes a significant challenge to overcome. Conventional reactive ion etching (RIE) processes usually occur at a temperature near room temperature or higher in which diffusion of radicals will damage low-k materials surface. Alternatively, to limit diffusion mechanisms and prevent damage, cryogenic cooling of a substrate sub < -100 C can be used. However, cooling substrates and controlling surface exposed to plasma to temperature down to -110 C in 300 mm etching chamber is a technical challenge. This is why alternative solutions can be found using a low temperature process (down to -60 °C) that behaves like a cryogenic process. For this work we propose to study the plasma etching of low k materials exposed to different fluorine precursors with a substrate temperature going from room temperature to -40 °C. For this purpose, we use a 300 mm dual frequency CCP chamber equipped with a low-temperature electrostatic chuck to conduct our experiments. A shadowing methodology is used to study the plasma/surface reactions with surfaces exposed to radicals only and surfaces exposed simultaneously to radicals and ions. By way of comparison, we chose to use two precursors with very different properties:

1. a fluorocarbon precursor with a high triple point temperature favoring condensation mechanisms, for which we observed a switch from an etching regime to a deposition regime in RIE mode at $T = -20$ °C. However, the shadowing mask study shows that when the surface is only exposed to radicals, the regime is always the same, deposition.
2. NF_3 gas which has a very low triple point temperature that should not do any deposition. When lowering the temperature, not only is the etching regime not suppressed, but its speed is also increased. This result is explained by the increases of surface coverage by F etching radicals. Using the shadowing methodology, we observed that the etching is highly suppressed at -40 °C compared to room temperature in the absence of ions

Patterned damascene structure are also tested to observe the benefits of low temperature etching. Furthermore, we propose to add hydrogen to NF_3 plasma to promote HF formation and study its impact on low k etching when going from room temperature to -40 °C.

10:00am **PS1-MoM-8 Mitigating Plasma-Induced Damage in Low-K SiCOH Thin Films by Cryogenic Etching Process**, R. Chowdhury, T. Poché, Seonhee Jang, Y. Tesfamariam, University of Louisiana at Lafayette

The integration of semiconductor chips to enhance their performance has led to the widespread use of low-dielectric-constant materials with a relative dielectric constant of $k \leq 3.5$, particularly as intermetal dielectric (IMD) materials within multilevel interconnects. This choice aims to minimize resistance-capacitance delays associated with microchip operation. Plasma etching of low-k materials presents a significant challenge due to plasma-induced damage (PID), which can increase the k-value and degrade its quality. This degradation is attributed to factors such as the formation of polar bonds, losing surface hydrophobicity, and carbon depletion.

To mitigate PID damage, this research focuses on reducing the degradation of low-k films during etching by employing a cryogenic process. Cryogenic conditions offer a promising strategy to alleviate PID damage, as etching by-products condense within the pores of the materials, protecting them from plasma-active radicals. By incorporating cryogenic etching process, significant reductions in dielectric degradation can be achieved.

Low-k SiCOH thin films were fabricated using plasma-enhanced chemical vapor deposition (PECVD) of the tetrakis(trimethylsilyloxy)silane precursor at room temperature. Dry etching process was conducted using CF_4 , SF_6 , CHF_3 , and C_4F_8 gases at both room temperature and cryogenic temperatures (up to -120 °C) in an inductively coupled plasma-reactive ion etching (ICP-RIE) system. Tetraethyl orthosilicate (TEOS) oxide was used as a reference material for calculating etch rates and etch selectivity. The etch selectivity of the SiCOH film over the TEOS was compared between regular and cryogenic etching processes.

Fourier transform infrared (FTIR) spectroscopy identified four prominent bonds in the films which were C-H_x stretching, Si-CH_3 bending, Si-O-Si stretching, and $\text{Si-(CH}_3)_x$ bending vibration modes. The equivalent damage layer (EDL) was calculated based on the variation in the peak area of Si-CH_3 bending and Si-O-Si stretching peaks, with SF_6 gas causing the highest amount of EDL compared to other gases. However, all gases showed a decreasing trend in EDL value when etching was performed at cryogenic temperatures, indicating reduced PID damage.

Electrical properties such as the k-value, leakage current density, breakdown field, and time-dependent dielectric breakdown (TDDB) were also measured to evaluate an improvement in their electrical performance under cryogenic etching confirming reduced PID damage. These findings highlight the potential of cryogenic etching as a promising approach to mitigate PID damage and improve the quality of low-k films.

10:30am PS1-MoM-10 Investigation of Cryogenic Fluorine-Based Etching of TaN with Selectivity to SiOCH Low-k, Ivo Otto IV, C. Vallée, University at Albany College of Nanotechnology, Science, and Engineering (CNSE)

The industry shift from silicon dioxide and aluminum as the respective dielectric and conductor within the back-end-of-the-line (BEOL) interconnect superstructure to SiOCH low-k dielectric (ULK) and copper improved key metrics such as RC delay, but had inherent integration challenges, one of which was copper diffusion into the ULK film. The solution was the use of diffusion barriers, which are required in current integration schemes to prevent copper diffusion. TaN is a key diffusion barrier candidate because of strong dielectric adhesion and low in-plane resistivity properties at 2-3 nm thicknesses. Creation of the BEOL interconnect superstructure is completed in cycles to create each metal level, requiring the repeated selective removal of not only copper, but the TaN diffusion barrier, selective to the ULK.

ULK films attain dielectric constant values of between 2-3 by incorporating non-polar bonds (Si-CH₃) and pores into their structure, making ULK sensitive to abrasive processes like CMP and physical, ion-assisted etching. Radical-dominated, fluorine etching of TaN with respect to ULK also comes with challenges because of the high volatility of SiF₂, SiF₄, and CF_x ULK etch byproducts. We have previously explored methods to accomplish radical fluorine etching of TaN with selectivity to ULK as an alternative landing process on the ULK, for BEOL integration. Selective deposition of an SiOF film on the ULK film compared to the TaN, while etching the TaN, allowed the selective etching of TaN with respect to ULK. In this work, we explore the use of radical NF₃/SiF₄ discharges, without O₂ addition (1), at sub-zero sample temperatures ranging from -45 °C to 0 °C (2). In this investigation, we seek to reduce the possibility of ULK damage by (1) removal of radical and atomic O interaction with the ULK film and (2) reduce the diffusion path for F to limit F diffusion through any SiF_x deposition on the ULK, and to limit F diffusion within the SiOCH structure itself. *Ex-situ* spectroscopic ellipsometry is utilized to characterize film thickness changes after processing in addition to characterization of changes in film refractive index. *Ex-situ* X-ray photoelectron spectroscopy is used to probe the sample surface to characterize surface film properties, while *ex-situ* Fourier-transform infrared spectroscopy is used to analyze bulk changes in the SiOCH ULK bonding structure. Though this multi-modal investigation, we gain insight in the mitigation of SiOCH ULK damage using an O₂-free, sub-zero process to selectively remove TaN.

10:45am PS1-MoM-11 Overview of Mutually Compatible Approaches for Sustainable Patterning Process Development, Philippe BEZARD, IMEC Belgium; A. Fathzadeh, KU Leuven and Imec, Belgium; R. Vallat, K. Filippidou, E. Gallagher, IMEC Belgium; S. De Gendt, KU Leuven and Imec, Belgium; F. Holsteyns, IMEC Belgium

Various approaches can be employed to ensure the sustainability of a process. One option is to utilize new molecules as reactants, aiming to reduce the quantities and/or the impact of emitted fragments in the atmosphere. If suitable candidate molecules are not available, materials that require environmentally harmful gases could be replaced with others that do not rely on such chemistries, for example, replacing a sacrificial SiO₂ hard-mask with amorphous carbon. Alternatively, the process flow can be adjusted to avoid the need for these materials altogether.

When changing materials is not feasible, there are several ways to further minimize gas consumption. One approach is to increase throughput without increasing gas flows, often achieved by using higher RF powers or pressures. Thinning down the layer is another option, but this increases the selectivity requirements of patterning steps. In such cases, in-situ reconstruction of the hard-mask, as demonstrated by Vallat et al., can provide thicker, usable hard-masks at the expense of patterning a much thinner problematic layer [1].

To regulate the selectivity of hard-mask deposition and subsequent patterning steps, Transient Assisted Plasma Processing (TAPP) [2] can be employed to significantly reduce gas consumption while maintaining excellent patterning performance and compatibility with High-Volume Manufacturing throughput. Combining these hard-masks with etch processes based on TAPP is particularly appealing because it offers better

control over the precursor's fragmentation, resulting in improved deposition selectivity at low substrate temperatures.

In a transient-assisted plasma etching process, these hard-masks can serve as a passivation source by carefully managing their sputtering while allowing the etch to proceed, eliminating the need for often problematic passivating gases. Furthermore, to further eliminate the requirement for environmentally harmful passivation gases, low-density plasmas can be utilized in conjunction with low partial pressure of reactants and overall gas flows. The scarcity of neutral species in such plasmas reduces the risks of bowing and undercutting, requiring minimal passivation to achieve the necessary patterning performance.

This paper will present an overview of the characteristics of these various approaches and illustrate how they can be combined to significantly reduce the consumption of environmentally harmful gases.

[1] Rémi Vallat, "Break healing and LER mitigation for low dose EUV exposure," in *AVS 69th*, November 5-10, (AVS 69th, Portland, OR, 2023).

[2] A. Fathzadeh, *J. Vac. Sci. Technol. A* 42, 033006 (2024), <https://doi.org/10.1116/6.0003380>

Plasma Science and Technology Room 124 - Session PS2-MoM

Atmospheric Plasma Processing

Moderator: François Reniers, Université Libre de Bruxelles, Belgium

11:00am PS2-MoM-12 Adapting Atmospheric Pressure Plasma Sources to Fit Diverse Applications, Michael Johnson, Naval Research Laboratory, USA
INVITED

Atmospheric pressure plasma technology offers the potential to utilize plasmas in applications occurring outside the confines of a vacuum chamber, opening many new, exciting opportunities. However, generating a plasma at atmospheric pressure comes with challenges that limit its viability. In particular, large electric fields are needed to break down air (~30 kV/cm) while the generated plasma volumes are comparatively small, and energy can be quickly lost to gas heating. This presentation describes novel approaches to nonthermal plasma generation at atmospheric pressure that address these key hurdles to their wider adoption. Piezoelectric transformers are solid-state transformers that create large voltages via electromechanical conversion, providing a small form factor, high gain alternative for generating atmospheric-pressure plasma jets. These transformers enable the production of plasma jets with characteristics similar to those driven by standard high voltage power supplies while only requiring tens of volts. Given the low input voltages, multiple jets can be operated in parallel to facilitate a synergistic increase in plasma volume and enhanced control over species production. Alternatively, gas management can be used to expand the functional volume of jets without an increase in applied power. Additionally, nanosecond pulsed power approaches improve the energy efficiency of plasma production, which can be advantageously used to improve water remediation in a plasma-liquid reactor. Example systems will be discussed and described through a variety of plasma diagnostics to illustrate how the approaches to applied power and plasma generation impact the plasma properties and applications, with an eye on developing more sustainable and versatile plasma sources.

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

11:30am PS2-MoM-14 Atmospheric Plasma Deposition of Bio-Based Composite Coatings for Enhanced Functional Properties of Paper, Kamal Baba, F. Loyer, N. Boscher, P. Choquet, Luxembourg Institute of Science and Technology (LIST), Luxembourg; I. Husic, A. Mahendran, J. Sinic, C. Jocham, H. Lammer, Wood K plus - Kompetenzzentrum Holz GmbH, Austria

Functional coatings on paper surfaces often rely on low-recyclable synthetic feedstock and wet chemistry techniques, leading to extended processing times and increased material usage. In this work, we address these challenges by the development of functional bio-based composite coatings reinforced with sustainable fillers using atmospheric pressure plasma as sustainability-oriented coating technology.

Various low viscosity acrylated biobased monomer, including Vanillyl Alcohol Methacrylate (VAM), Eugenyl Methacrylate (EM) and Isosorbide Methacrylate (IM), were used as resin to form the polymeric coating. While seashell particles (SS) or cellulose nanocrystals (CNC) were used as

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sustainable additives. The targeted applications of these formulations are the enhancement of release function, water vapor barrier and antimicrobial properties of paper substrates.

The polymerization of these different monomers was possible thanks to a liquid assisted dielectric barrier discharge approach with either Argon or Nitrogen as plasma gases, and ultrasonic nebulization as monomer injection method. The plasma polymerization of coatings with a thickness ranging from 0.5 to 2 μm on Si wafers, Glassine and Barrier 60g paper was evidenced by FTIR, showing a successful conversion of vinyl double bonds. . The degree of conversion was calculated from the FTIR spectra to assess the effect of the plasma parameters on the polymerization and coating properties. Notably, the polymerization degree increases with the applied plasma power yielding longer polymer chains, as evidenced by high resolution mass spectrometry analyses. This technique revealed the possibility of favoring the formation of polymer compositions rich in organic mono- or di-methacrylate chains in a plasma-polymer matrix by adjusting the plasma power. SEM imaging confirmed the homogeneity of the coatings and a uniform distribution of the particles. The addition of SS and CNC particles to the VAM or EM coating affects both hydrophobicity and surface energy, likely impacting the release properties of the coated surface. The VAM composite coating exhibited the best release function for coated Glassine paper (<250cN/25mm according to Finat10/TESA 7475 test), whereas the lowest water vapor transmission rate for barrier paper was achieved with the EM composite coating (<50g/m²day/bar).

On the other hand, antibacterial properties were achieved through plasma coating with isosorbide methacrylate alone, effectively targeting the E. Coli bacterial strain without the incorporation of any additional additives.

11:45am **PS2-MoM-15 Atmospheric Air Plasma Pre-treatment of Plastics**, **Aunic Goodin**, North Carolina State University; *R. Walker, J. Alcalá*, University of Michigan, Ann Arbor; *T. Das*, California Institute of Technology; *S. Chakraborty, S. Bepari, D. Kuila*, North Carolina A&T State University; *W. Goddard*, California Institute of Technology; *J. Foster*, University of Michigan, Ann Arbor; *S. Shannon*, North Carolina State University

In 2018 almost 36 million tons of plastic waste was produced in the US with only 9% recycled that year. One of the limiting factors for reusing or recycling plastic waste is the difficulty of conversion into usable products. One potential solution for this is a plasma pretreatment followed by a catalytic deconstruction into C2-C4 olefins. Catalytic deconstruction of plastics is a viable method for using plastic waste. Atmospheric plasma is investigated primarily for cost-effective pretreatment of the plastics. The oxidation of the plastics through the plasma treatment provides a potential avenue for the catalyst to more easily break down the material. The initial concept is shown with a pin-to-plate discharge within vials for analysis of the gas by-products as well as material analysis. The combination of VUV, UV, electron, and ion bombardment modifies the surface of the polymer for oxygen absorption both during and after treatment from the oxygen in normal air. This oxidation will be measured and quantified through XPS, contact angle measurements, FTIR spectroscopy, and RAMAN spectroscopy. The analysis of the gas products through mass spectroscopy is compared to molecular dynamics and reactive force-field simulations to understand the mechanism of the process. The plastics polypropylene and polyethylene are treated as powders, beads, and sheets of varying particle size/thickness, molecular weight, and density. The variation of the samples gives an indication of the material shape and characteristics for future processing and also allows for different analyses depending on the material's shape and thickness. These plastics are also treated in liquid plasma for comparison of the surface modifications. Analysis of the products of the catalytic deconstruction is done by GC/MS to characterize potential value-adding C2-C4 olefins and compare the process with and without plasma treatment.

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Atomic Scale Processing Mini-Symposium

Room 116 - Session AP1+EM+PS+TF-MoA

Area Selective Deposition (ASD) II

Moderators: Satoshi Hamaguchi, Osaka University, Japan, Greg Parsons, North Carolina State University

2:30pm **AP1+EM+PS+TF-MoA-5 Area Selective Deposition: Advances, Challenges and Future Technology Enablement, Kandabara Tapily, J. Smith, A. deVilliers, G. Leusink**, TEL Technology Center, America, LLC INVITED K. Tapily, J. Smith, A. deVilliers, G. Leusink

TEL Technology Center, America, LLC, 255 Fuller Road, suite 214, Albany, NY 12203

To achieve higher performance, higher density, and lower cost, for decades the semiconductor industry has relied on aggressive scaling of the device feature size using top-down lithography. Additionally, scaling is driving the need for new materials introduction, new processes and new device architectures increasing the integration complexity. As a result, the industry has introduced several scaling boosters such as high k / metal gate, stress engineering, air gaps and recently area selective deposition to meet the power performance area cost or PPAC requirement.

Advanced device architectures such as gate-all-around (GAA) and complimentary field-effective transistors (CFET) require additional design / technology co-optimized (DTCO) solutions to continue the device scaling roadmap. Selective deposition of materials is fundamental not only for the reduced cost and complexity of manufacturing these advanced devices, but also as fundamental solutions to promote power / performance / CPP scaling of these advanced device architectures.

Surface engineering is key in successfully realizing defect free area selective deposition. Surface sensitive and reaction driven processes such as atomic layer processes (deposition and etch) will be key enabler in some of the required selective deposition processes (1).

This talk will discuss the status and approaches of area selective deposition technology and challenges the industry is facing in implementing future technology nodes. We will go over multiple examples of how novel selective deposition processes can accelerate the industry roadmap in terms of PPAC scaling.

References:

1. G. N Parsons, R. D Clark, *Chem. Mater.*, 32(12), 4920 (2020).

3:00pm **AP1+EM+PS+TF-MoA-7 Examining UV-Induced Functional Group Formation on 2D Nanomaterials for Patterned ALD, Azeez O. Musa, A. Werbrouck, N. Paranamana, M. Maschmann, M. Young**, University of Missouri-Columbia

In our previous work, we employed a focused electron beam (e-beam) within an environmental scanning electron microscope (eSEM) to break down water vapor, allowing for the precise creation of hydroxylated patterns on highly oriented pyrolytic graphite (HOPG) surfaces. These patterns facilitated subsequent atomic layer deposition (ALD) in patterned areas, offering exceptional control over spatial resolution (exceeding 42 nm), and surface selectivity (ranging from 69.9% to 99.7%). However, despite its precision, the use of an e-beam is time-consuming and lacks industrial scalability due to the limited functionalization area on the substrate. In this study, we aim to explore the feasibility of patterning large areas of 2D material using UV irradiation in the presence of water vapor. Specifically, we seek to understand the impact of the direct UV ionization of water vs. ionization of water from secondary emitted electrons. Our experimental setup utilizes a custom-built hot-walled viscous-flow ALD reactor equipped with a vacuum ultraviolet (VUV) source unit with a peak emitted wavelength of 160 nm. This UV source incorporates a compact deuterium lamp with a MgF₂ window and UV photons are focused onto the sample using a convex MgF₂ lens to enhance photon flux density. We posit that the UV irradiation induces the formation of hydroxyl defects on the HOPG surface. To verify this, we employ spectroscopy including X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and Raman spectroscopy (RS), assessing the formation of functional groups on 2D material surfaces. We also examine the impact of UV-functionalization on ALD nucleation and growth onto 2D materials. Our studies inform the applicability of this method for patterned thin-film deposition for semiconductor manufacturing.

3:15pm **AP1+EM+PS+TF-MoA-8 ASD of Low Temperature Cu Capping Layers for Polymers-Based 3D Technologies, Silvia Armini**, IMEC Belgium; A. Brady Boyd, Aberystwyth University, UK; E. Chery, IMEC Belgium

With the constant increase of complexity in integrated systems, more and more connections are required between adjacent chips. Advanced packaging technologies using heterogeneous integration rely heavily on the interconnects redistribution layer (RDL) for this routing.

The most promising option to further reduce the interconnect dimensions relies on a dual-damascene process using photo-sensitive polymers as dielectric.

Unfortunately, using a polymer as a dielectric presents serious reliability challenges as polymers are generally unable to block the diffusion of oxygen, resulting in copper oxidation even at temperatures below 200 °C. Additionally, copper oxidation is not self-limiting.

As the critical dimensions of the lines are scaled down, high rates of oxidation are therefore a major reliability concern.

Recently the possibility of protecting the copper lines from oxidation through very thin ALD layers was demonstrated. For example, HfO₂ films as thin as 9 nm have been shown to effectively prevent copper oxidation during aggressive corrosion stress tests. Nevertheless, despite their minimal thickness, these dense films, deposited on the full surface of the wafer, are known to lead to mechanical stress. Ultimately, this stress can result in delamination and fracture during the next process steps.

To overcome this issue, area-selective deposition of TiO₂ and Al₂O₃ capping layers on Cu with respect to polymers are studied and their reliability performance investigated

3:30pm **AP1+EM+PS+TF-MoA-9 SiO₂ Fluorination/Passivation for Area-Selective Deposition of TiO₂, ZnO, and Polymer on Metal and SiN_x vs. SiO₂, Jeremy Thelven, H. Oh, H. Margavio, G. Parsons**, North Carolina State University

Challenges related to nanoscale pattern alignment are motivating research in chemically-directed patterning by Area-Selective Deposition (ASD) for future 3D devices. Recently, we have begun to explore the growth and inhibition mechanisms of metal oxide ALD materials (Al₂O₃, ZnO, and TiO₂) on hydroxylated and fluorinated SiO₂, and hydroxylated and fluorinated silicon nitride, SiN_x. The ability to selectively react and deposit on an oxide vs nitride surface is recognized as a key problem due to the wide use of SiO₂ and SiN_x in electronic device processing, and because of the chemical similarity of these surfaces. To explore ASD on SiN_x and SiO₂, we exposed blanket SiN_x and SiO₂ wafers to multiple doses of molybdenum hexafluoride, MoF₆, at low temperature (~200°C). Based on XPS analysis, the MoF₆ exposure leads to fluorination of both surfaces. Then, we performed polypyrrole (PPy) oxidative-CVD using pyrrole monomer and SbCl₅ as a surface oxidant. For the oxidative CVD process, 15 seconds of CVD produced ~50 nm of deposition on receptive surfaces. We found that PPy deposited readily on SiN_x surface after some nucleation delay, but on SiO₂, only isolated nuclei were formed. Control experiments using SiN_x and SiO₂ substrates without the MoF₆ exposure step showed uniform deposition on both substrates. To extend this demonstration of ASD of SiN_x vs SiO₂ to other materials and substrates, we tested ALD of TiO₂, ZnO, and Al₂O₃ SiO₂, SiN_x and Mo metal after exposure to MoF₆. We find that this selective fluorination passivation of the SiO₂ surface allows for selective growth of TiO₂ and ZnO on Mo vs SiO₂, whereas ALD Al₂O₃ using TMA/H₂O showed uniform, non-selective deposition. Moreover, after exposing SiO₂ and SiN_x to MoF₆, TiO₂ ALD using TiCl₄/H₂O deposited on SiN_x after some delay, whereas a much longer delay was observed on SiO₂. The mechanisms behind selectivity, and the extent of metal-fluoride exposure needed to achieve passivation is currently under investigation. Direct comparisons between metal oxide ALD nucleation on SiO₂, SiN_x and metal after exposure to MoF₆ will give insight into mechanisms necessary to achieve high selectivity, as well as provide options for advanced multi-material ASD schemes.

Atomic Scale Processing Mini-Symposium

Room 116 - Session AP2+EM+PS+TF-MoA

Modeling and Simulations of Atomic Layer Processing

Moderators: Satoshi Hamaguchi, Osaka University, Japan, Greg Parsons, North Carolina State University

4:00pm **AP2+EM+PS+TF-MoA-11 Atomistic Simulations on the Fundamental Aspects of Atomic Layer Processing (ALP)**, *Bonggeun Shong*, Hongik University, Republic of Korea **INVITED**

As size of electronic devices are miniaturized to nanoscale, the precision of their fabrication processes is becoming extremely demanding. Atomic layer deposition (ALD) is a vapor phase thin film deposition technique based on sequential, self-limiting surface reactions. Through ALD, high conformality on high-aspect ratio substrates, thickness control at the Angstrom level, and tunable film composition are achievable. Furthermore, area-selective ALD (AS-ALD) has recently emerged as a possible alternative bottom-up approach for nanoscale patterning. With these advantages, ALD is gaining interest as a powerful tool for many industrial and research applications, especially in microelectronic fabrication. Furthermore, atomic layer etching (ALE) is emerging as a novel technique that can provide atomically controlled etching of materials. These technologies with atomic layer precision are often altogether referred to as atomic layer processing (ALP). Ideally, the entire ALP processes are based only on the surface chemistry of the substrates. Thus, it is important to understand their surface reaction mechanisms in order to improve the process conditions and material quality, and even to design novel materials and processes. With development of modern simulation tools, utilization of atomistic calculations is becoming increasingly useful toward deeper understanding and design of such chemical reactions. However, ALD processes often face limitations toward fabrication of next-generation semiconductor devices due to their size scale and structural complexity; furthermore, such problems are often convoluted with challenges toward realistic simulations of surface chemical processes. In this talk, analysis of fundamental surface chemistry of various ALP based on computational chemistry methods, as well as development of new processes and materials based on chemical simulations will be presented.

4:30pm **AP2+EM+PS+TF-MoA-13 Understanding Process Parameters in High-Aspect-Ratio ALD via Transport Modeling**, *Victor Vogt*, University of Michigan; *A. Gayle*, National Institute of Standards and Technology (NIST); *A. Miranda Manon*, *A. Lenert*, *N. Dasgupta*, University of Michigan

Atomic layer deposition (ALD) is a powerful tool to modify ultra-high-aspect-ratio structures with unparalleled conformality. We have recently demonstrated the ability of ALD to modify silica aerogels with aspect ratios greater than 60,000:1 and improve their thermal stability from ~600°C to ~800°C, for applications in concentrating solar thermal energy generation.¹ To facilitate conformal ALD modifications on these extreme aspect ratios, a reaction-diffusion model was developed to precisely predict infiltration into the aerogel as a function of exposure time and number of doses, enabling tunable control of the infiltration depth.²

In this study, we have built upon our previous reaction-diffusion model to explore the effects of exposure time, precursor temperature, and number of aerogels coated on process time and precursor utilization. We analyze process parameter trends in terms of the governing reaction-diffusion mechanism and relevant equations. These trends are then validated experimentally via energy dispersive x-ray spectroscopy (EDS) mapping of the infiltration depth. Additionally, we explore the relationship between number of aerogels coated and reactor volume, and we analyze the impacts of this on ALD reactor design for high-aspect-ratio substrates. Finally, we demonstrate that ALD can be used to tune the mechanical strength and stiffness of silica aerogels, a key limitation of these materials in practical applications. This work will enable a greater understanding of high-aspect-ratio ALD processing as well as its potential applications in the modification of porous materials.

References:

¹ 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.* **2022** *32*, 2108774.

² A.J. Gayle, Z.J. Berquist, Y. Chen, A.J. Hill, J.Y. Hoffman, A.R. Bielinski, A. Lenert, and N.P. Dasgupta, Tunable Atomic Layer Deposition into Ultra-High-Aspect-Ratio (>60000:1) Aerogel Monoliths Enabled by Transport Modeling, *Chem. Mater.* **2021** *33* (14), 5572-5583.

4:45pm **AP2+EM+PS+TF-MoA-14 Modeling Remote Inductively Coupled Plasmas for Plasma-Enhanced Atomic Layer Deposition**, *Mackenzie Meyer*, *D. Boris*, *M. Johnson*, *J. Woodward*, *V. Wheeler*, US Naval Research Laboratory; *M. Kushner*, University of Michigan, Ann Arbor; *S. Walton*, US Naval Research Laboratory

Plasma-enhanced atomic layer deposition (PEALD) uses a plasma step to generate the necessary reactive species, allowing atomic layer deposition (ALD) processes to occur at lower temperatures and with additional reaction chemistries compared to thermal ALD. Remote inductively coupled plasma (ICP) sources are often used in PEALD as they limit electrons and ions at the growth substrate while providing radicals from the plasma. However, remote ICP systems, particularly downstream of the source, are not fully understood. Modeling of remote ICPs can contribute to an understanding of these systems. In this work, modeling of remote ICPs is performed using the 2D Hybrid Plasma Equipment Model (HPEM). The remote ICPs are based on the Veeco Fiji G1 and G2 sources operating in an N₂/Ar mixture. Both inductively and capacitively coupled power contribute to the power deposited into the plasma. The results of the model are compared to experimental measurements reported, including atomic N density in the plasma source and electron density and plasma potential downstream in the spatial afterglow of the ICP. The model is also used to examine the production of species that are not measured, including metastable N₂, as well as the absolute and relative fluxes of reactive species to the substrate, for a range of operating conditions. The results are then linked to the growth of nitride films in an effort to quantify the relative importance of different operating modes and reactive species. This work is partially supported by the Naval Research Laboratory base program.

5:00pm **AP2+EM+PS+TF-MoA-15 Prediction of Plasma-induced Changes in Surface Morphology and Composition during Atomic Layer Deposition: A Combined Ab-Initio and Monte Carlo Approach**, *G. Hwang*, *Ting-Ya Wang*, University of Texas at Austin

Atomic layer deposition (ALD) has emerged as a method offering enhanced precision and control in comparison to traditional chemical vapor deposition. It operates through alternating cycles of two half-cycle reactions, ensuring sequential and self-limiting deposition. However, thermal ALD necessitates high deposition temperatures (> 400 °C), particularly for nitridation. Although employing plasma can reduce these surface temperatures, plasma can have detrimental effects on materials too, including modification of the chemical composition and densification, which profoundly impact crucial material properties such as dielectric constant.

Therefore, understanding the plasma-induced changes in surface morphology and composition is crucial. However, existing experimental techniques encounter limitations in surface analysis. Non-polar bonds, such as N₂ dimer, are inactive under infrared (IR) spectroscopy. X-ray photoelectron spectroscopy causes surface damage to a certain extent. Moreover, overlapping signals may render the analysis uncertain and challenging. Theoretical methods have their own set of limitations. Molecular dynamics (MD) simulations allow the study of dynamic processes but are constrained by limitations in both length and time scales, which make it unsuitable for ALD systems, where primary reactions fall into the category of rare events.

The integration of kinetic Monte Carlo (kMC) with density functional theory (DFT) presents a promising simulation approach for ALD. However, a notable challenge lies within kMC, specifically the requirement for a predefined list of permissible events. Traditionally, researchers identify a set of reactions considered most significant. Yet, given the numerous potential events occurring on a surface and the criticality of rare events in ALD, outcomes derived from a manually compiled list may sometimes lack authenticity.

We developed an atomistic, off-lattice, and three-dimensional simulator that integrates kMC and DFT, and employed a strategic approach to formulate a comprehensive event list, with the goal of encompassing a wide range of potential surface reactions. Our investigation centered on assessing the effects of N₂, H₂, and NH₃ plasmas on SiCN material, including examination of the roles played by radicals and ion bombardment. Furthermore, we also studied the influence of process conditions, including temperature and pressure, while also analyzing the influence of oxygen exposure.

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5:15pm **AP2+EM+PS+TF-MoA-16 Modelling and Simulation of Plasma-Enhanced Atomic Layer Deposition of Silicon Nitride Over Sidewall Surfaces of a Closing Narrow-Gap Trench**, *Jomar Tercero, K. Ikuse, S. Hamaguchi*, Osaka University, Japan

Molecular dynamics (MD) simulations were performed to study the transport mechanisms of chlorine (Cl) atoms during the plasma-enhanced atomic layer deposition (PE-ALD) of silicon nitride (SiN). PE-ALD is a technique to deposit highly precise and uniform thin films required for nanoscale semiconductor devices. The typical PE-ALD process involves sequential and self-limiting surface reactions, facilitating the formation of monolayers in a layer-by-layer manner.[1] In the case of SiN PE-ALD, chlorosilanes such as SiH₂Cl₂ are commonly used as Si-containing gas precursors. During the first half-cycle, Si atoms of the precursors adsorb on the surface, whose surface atoms are then terminated by Cl atoms. Subsequently, the surface is exposed to nitrogen (N) and hydrogen (H)-containing plasmas. During this second half-cycle, H atoms react and capture Cl atoms on the surface, forming volatile hydrogen chloride (HCl) molecules.[2] In this study, our focus is PE-ALD of SiN over a trench structure when the gap is closing and the two facing sidewalls are approaching each other. In the desorption/nitridation half-cycle, Cl atoms must be removed from the extremely narrow gap by Cl or HCl diffusion if the gap is closing. The diffusion coefficients of Cl atoms in such narrow gaps were evaluated from molecular dynamics (MD) simulations, under different conditions for the surface temperature (700, 800, and 900 K), gap distance (0.6, 1, and 2 nm), and H density. The MD simulations revealed that, without H atoms, Cl diffusion was highly restricted. H atoms were observed to capture Cl atoms, assisting their transport in the narrow gap. Additionally, we observed the formation of H₂ molecules, some of which penetrated the SiN bulk and diffused. The results indicate that, as the two facing SiN sidewalls approach each other and the gap diminishes, the transport of atoms and molecules in the gap becomes restricted and therefore the ALE process slows down, eventually forming a seam between the two facing sidewalls.

References

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- [2] R. A. Ovanessian, E. A. Filatova, S. D. Elliott, D. M. Hausmann, D. C. Smith, and S. Agarwal, "Atomic layer deposition of silicon-based dielectrics for semiconductor manufacturing: Current status and future outlook", *Journal of Vacuum Science and Technology A*, 37, 060904 (2019).

Plasma Science and Technology

Room 124 - Session PS1-MoA

Plasma Surface Interactions

Moderators: **Sumit Agarwal**, Colorado School of Mines, **Tetsuya Tatsumi**, Sony Semiconductor Solutions Corporation, Japan

1:30pm **PS1-MoA-1 Advanced Semiconductor Plasma Processes Pioneered by Understanding and Controlling Plasma-Surface Interactions**, *Masaru Hori, M. Sekine, T. Tsutsumi, K. Ishikawa*, Nagoya University, Japan **INVITED**

Plasma processes were introduced into semiconductor manufacturing more than 50 years ago, leading to today's nanoscale, three-dimensional integrated circuit manufacturing and explosive scientific and industrial advances. One of the core technologies is reactive ion etching (RIE). Initially, the focus of basic science was on why RIE occurs, with many reports and discussions on fast etching, material-to-material selectivity and fine shape control reactions resulting from the interaction of ions and radicals from the plasma with diverse materials, forming a unified understanding of RIE principles. However, the current demand for microfabrication technologies aimed at fabricating devices of 2 nm or smaller requires further understanding of nanometer reaction regions called surface modified layers, mixed layers, condensed layers, and damaged layers resulting from ion, radical and solid interactions. Here, we would like to name this reaction region the meta-layer due to the need for a unified understanding and definition as a science. In addition to pioneering atomic layer etching and self-organized growth processes of three-dimensional nanomaterials by measuring and controlling the meta-layer, wet-like etching techniques have recently been produced by utilizing the interaction between plasma and liquid phase. The identification and control of this meta-layer is the key to

the core science and applications for future advances in advanced plasma processing. In this talk, the importance of identifying and controlling the plasma-induced meta-layer in plasma processes used to fabricate logic and memory devices will be explained. The relationship between the reaction dynamics occurring in the meta-layer and the etching mechanism will then be discussed based on *in-situ* FT-IR, *in-situ* XPS and *in-situ* ellipsometry observations of chemical reactions occurring in the meta-layer induced by the plasma process. Furthermore, based on the analysis of meta-layer structures formed in various plasma processes using TOF-SIMS and *in-situ* TEM-EELS, the evolution of state-of-the-art semiconductor manufacturing processes produced by meta-layer science and the precise control of non-equilibrium reaction fields in which active species and solids and liquids work together will be mentioned.

2:00pm **PS1-MoA-3 Concurrent Thin Film Deposition in Fluorocarbon Plasmas as a Function of Gas Phase and Surface Reactions**, *Austin Krauss*, University at Albany; *Q. Wang, N. Smieszek, S. Voronin, A. Ko*, Tokyo Electron America; *S. Tahara*, Tokyo Electron Ltd., Japan; *C. Vallee*, University at Albany

High aspect ratio (HAR) etching in fluorocarbon plasmas has presented challenges in the pursuit of continuous shrinking of the integrated circuit technological node. With increasing aspect ratios of etched features, maintaining a constant channel critical dimension (CD) requires precise control of the plasma species involved. As such, the advancement of existing plasma processing techniques depends on a complete understanding of transport and surface interactions of electrically charged and neutral species (i.e. radicals) within HAR channels.

For better understanding of such mechanisms and better control over neutral species delivery and distribution inside etch channels, we characterized the transport of radical species in the process chamber as a function of the distance from the plasma source, as well as their transport through capillary plates with different aspect ratios. The experiments were performed in an inductively coupled C₄F₈/O₂/Ar discharge at 20 mTorr to minimize collisions between the molecules inside of the micrometer-scale capillary via holes. The plasma phase chemistry composition and the nature of the radicals transported to the substrate were controlled by adjusting of the O₂ flow rate; the experimental films were grown on SiO₂ substrates, attached to the rear side of the capillary plates. In addition, the composition of the radicals diffusing toward the substrate was controlled through variation in sample distance from the plasma source and was monitored *in-situ* by spatially-resolved optical emission spectroscopy (OES) and spatially-resolved mass spectrometry. The composition and deposition rates of the films were determined as a function of AR via X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), respectively.

Surface analysis indicated significant reduction in the film deposition rate and a lower carbon content with increase of the channel length, which could be addressed to higher consumption of CF and CF₂ species (compared to CF₃) on the via wall. Addition of O₂ to the plasma has shown a decrease of the CF_x species with higher carbon content in the plasma phase and carbon concentration in the film, which can be used as a knob for deposition uniformity control inside of a via. Additional characterization of the radical flux, its composition at different distances from the plasma source, and its impact on the film properties will be discussed.

2:15pm **PS1-MoA-4 Investigation of Highly Diffusive Point Defects During Si Plasma Etching**, *Nobuyuki Kuboi, K. Saga, M. Miyoshi, T. Hamano, S. Kobayashi, T. Tatsumi*, Sony Semiconductor Solutions Corporation, Japan; *K. Eriguchi*, Kyoto University, Japan; *Y. Hagimoto, H. Iwamoto*, Sony Semiconductor Solutions Corporation, Japan

The quantitative prediction and precise control of plasma-induced damage during Si etching for detailing the regions of amorphous, dangling bonds, and point defects are essential for optimizing the performance of CMOS devices. Particularly, regions of two formers with concentrations of 10¹⁸-10¹⁹ atoms/cm³ have been studied and modeled extensively [1][2][3]. Insights obtained from these studies are used for suppressing damage to these layers to realize plasma processes with low damage. To enhance the performance of advanced CMOS devices with complex structures, understanding the mechanisms of formation and distributions of point defects with less than 10¹⁷ /cm³ is crucial. However, limited studies have focused on the effects of point defects generated during Si etching.

Therefore, we focused on point defects as Si etching damage and proposed simulation modeling for Si interstitials (I). These interstitials are highly diffused and interact with nearby interstitials and incident hydrogens from plasma to form clusters (I_m). Considering the energy balance between an

incident ion and sum of forming energy of each cluster during Si trench etching, I_3 or I_4 cluster can be formed at most. In the proposed model, this transient phenomenon was included depending on the substrate temperature.

To confirm the validity of the damage model, we analyzed photoluminescence (PL) data after Si trench etching with or without hydrogen irradiation and revealed that the model assumptions are reasonable for the variations of the observed PL intensities originating from point defects. Furthermore, we performed in-situ XPS on the B1s spectrum in the highly Boron-doped Si substrate after Ar^+ ion irradiation as damage with a temperature variation of 25, -50, and -120 °C. At 1.5-nm depth from the surface corresponding to the a-Si region, the B1s intensity did not vary, but the intensity at the 6-nm region increased with the decrease in the temperature (i.e., -50 and -120 °C) and decreased when the substrate temperature of -120 °C was back to 25 °C. This experimental result revealed various phenomena with the depth on the nanometer scale and supports the proposed formulation as the diffusion phenomena of Si interstitials.

Consequently, we revealed that the diffusion of Si interstitials induced by plasma irradiation can be suppressed by extremely low temperature. Furthermore, cryo etching exhibits considerable potential for not only improving etched profile with high selectivity but also suppressing plasma-induced Si damage.

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2:30pm PS1-MoA-5 Effect of Bias Voltage and H₂ Addition on the Formation of Ammonium Salt Layer during RIE of SiN_x in a CH₂F₂/Ar Plasma, Xue Wang, Colorado School of Mines; P. Kumar, T. Lill, H. Singh, M. Wang, T. Ozel, Lam Research Corporation; S. Agarwal, Colorado School of Mines

During the etch of SiO₂ and SiN_x in a fluorocarbon plasma, the selective etch is believed to be realized by the accumulation of a fluorine-deficient graphitic carbon layer on the SiN_x surface. While the hydrofluorocarbon gases are also widely used in the selective etch of SiO₂ to SiN_x, the mechanism of SiN_x retardation is still unclear. It has been hypothesized that in addition to the graphitic carbon layer, another blocking layer—ammonium fluoride or ammonium fluorosilicate—may form on the SiN_x surface. These layers can retard or even fully stop the etching of SiN_x. The formation of an ammonium salt layer has been reported in some atomic layer etching and reactive ion etching (RIE) processes. However, the mechanism of formation of these ammonium salts, their thermal stability, and stability under directional ion bombardment are not fully understood.

In this work, we investigate the effect of temperature, bias voltage, and H₂ addition on the formation of an ammonium salt layer during RIE of plasma-deposited SiN_x in a CH₂F₂/Ar plasma. Using *in situ* attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) spectroscopy, we monitored the surface bonding changes of SiN_x film during RIE over a temperature range of 25–150 °C at bias voltages over the range of 100–300 V. As expected, the etch rate was lower at a lower bias voltage (see Figure 1), and the etch stopped with rapid accumulation of ammonium salt layer (NH₄ bending mode at ~1430 cm⁻¹ and NH₄ stretching mode at ~3000–3300 cm⁻¹ in Figure 2) and graphitic hydrofluorocarbon layer (C=C stretching mode at ~1600 cm⁻¹ in Figure 2). Interestingly, no salt or graphitic carbon layers formed when we decoupled the RIE process into a CH₂F₂/Ar plasma deposition step and an Ar plasma activation step with a bias voltage of -240 V. This implies that the formation of ammonium salt and graphitic carbon layers requires the participation of etch byproducts and plasma species. We also observed that, after adding H₂ into feed gas, the SiN_x etch at room temperature and under bias voltage of -240 V proceeded linearly with no accumulation of ammonium salt and graphitic carbon layers. We speculate that the graphitic carbon layer was efficiently removed with H₂ addition, making the ammonium salt layer unstable when it was exposed to high-energy ion bombardment. We anticipate that SiN_x etching with HF plasma may provide further insights into the formation mechanism of ammonium salt layer by eliminating the graphitic carbon layer that forms on the SiN_x surface prior to an etch stop.

2:45pm PS1-MoA-6 Plasma-Induced Oxidation in Micron-Sized Droplets: Evaluating Transport Limitations, Dongxuan Xu, P. Bruggeman, University of Minnesota

Cold plasmas interacting with liquids at ambient conditions provides a unique chemical reactive environment and so have been studied extensively for a broad range of applications - material synthesis, wastewater treatment, and disinfection. The plasma-liquid interface, a thin liquid region bridging plasma gas phase and bulk liquid phase, is crucial for reactive chemistry in the liquid phase. Typically, highly reactive plasma gas phase species (i.e., e⁻ and OH) are injected into the liquid phase and readily react with solutes at this interface. As the redox processes in this interface occur on timescales of ns to μs while the transport of reactive gas phase species and liquid solutes occurs on timescales of tens of μs to seconds, the rate of conversion is in many cases not limited by the speed of the reaction but by transport. Specifically, conversion yields for a plasma-liquid system can be limited by both the gas phase reactive species flux into the liquid and the diffusion/convection of solutes from the bulk liquid to the interface where reactions occur.

In this study, we evaluate the effect of these transport limitations on OH-driven oxidation processes in an RF-driven diffuse glow discharge at atmospheric pressure. A droplet generator enables the generation of a train of droplets (40 μm diameter) passing through the homogeneous plasma allowing us to study the interaction of a micron-sized droplet with a plasma at a well-defined droplet residence time (10 ms). Here, the dominant liquid phase transport within the droplet is diffusion of the bulk liquid solute towards the plasma-liquid interface.

Firstly, we treated the redox couple ferri/ferrocyanide in the plasma-droplet system to confirm oxidation is the dominant reaction. Next, various solutes were treated at different initial concentrations, and we observed two trends: 1) an initial linear increase in solvent conversion with increasing solvent concentration consistent with solute diffusion limited conversion, 2) and a saturation of the solvent conversion independent of the solvent concentration consistent with a conversion that is limited by the gas phase reactive species flux into the liquid. We show that these results can be described by a 1D reaction-diffusion model which also allows us to determine the gas phase OH flux into the droplet. Finally, we compared these derived OH fluxes with calculated estimates of OH fluxes in the gas phase independently determined with measured bulk gas phase OH densities as boundary condition. The results are in excellent agreement and show that for molecules that readily react with OH radicals, conversion can be described by OH-driven plasma-induced chemistry.

3:00pm PS1-MoA-7 Effects of Si/N Ratio on Plasma-induced Damage Creation in Silicon Nitride Films, Takahiro Goya, K. Urabe, K. Eriguchi, Kyoto University, Japan

Various properties of SiN films have been designed by optimizing the stoichiometry (Si/N ratio). For example, Si-rich SiN films with their superior mechanical property such as high hardness [1] are one of the promising candidates for an anti-plasma erosion layer called a “hard” mask. It is widely known that plasma exposure results in the creation of defects in SiN films, leading to the change of the designed properties by Si—N network modification. Thus, the property degradation during plasma process (plasma-induced damage: PID) [2] is considered to be a critical issue for SiN film design and/or plasma process optimization. In this study, we investigated the effects of PID on the mechanical property change in SiN films with various Si/N ratios, in combination with optical analysis. The SiN films were prepared using PECVD on Si substrates. The thicknesses were approximately 200 nm and the refractive index n showed 1.9 ~ 2.2 depending on the Si/N ratio. All samples were exposed to inductively coupled Ar plasma. DC self-bias voltage was -200 V and the exposure time was 60 s. For mechanical property analysis, a nanoindentation technique was employed. We adopted the contact stiffness S (obtained from the slope of an unloading curve) as a measure of the mechanical property [3]. Since it turned out that a single loading/unloading process could not reveal a clear change in S by plasma exposure due to stochastic variation etc., we performed cyclic (time-dependent) loading/unloading measurements with an iteration time $N = 75$. An increase in S with an increase in Si/N ratio was found for Si-rich SiN films ($n > 2.05$), while no apparent increase was seen for N-rich SiN films ($n < 2.05$). To clarify the Si/N ratio effects, the change in the extinction coefficient k estimated by spectroscopic ellipsometry was investigated. A decrease in k was observed for the Si-rich SiN films after plasma exposure. Since the optical bandgap is narrower and the S value is larger in SiN films, compared to SiO₂ films, we anticipate that the change is attributed to the surface oxidation [4] of the damaged layer. The present findings imply that Si-rich SiN films are more significantly subject to PID,

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leading to the degradation of the anti-plasma feature (hard mask property) during plasma processing steps.

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3:15pm **PS1-MoA-8 Highly Selective SiN Etching by HF Plasma, Megan Manos**, Hitachi High-Tech America, Inc.; *Y. Kurosaki*, Hitachi High-Tech America, Inc., Japan; *J. Ditto*, Hitachi High-Tech America, Inc.; *T. Maeda*, *T. Hattori*, Hitachi High-Tech, Corp., Japan; *M. Yamada*, Hitachi, Ltd., Japan; *Y. Ishii*, Hitachi High-Tech America, Inc.; *H. Ohtake*, Hitachi High-Tech, Corp., Japan; *K. Maeda*, Hitachi High-Tech Corp., Japan

Recently, it has been found that combination of H and F is critical for highly selective SiN etching over SiO in dry etching. HF is suggested to work for SiN etching as a catalyst by lowering the activation energy of F migration, while NO is well known to promote SiN etching as well [1]. In addition, HF is a promising etching gas with low GWP (Global Warming Potentials) and has capability of SiN etching by reactive ion etching or evaporating ammonium salts by ion bombardment [2,3].

In this study, we investigated isotropic etching of SiN by HF remote plasma and found high selectivity to SiO of over 100. HF plasma was generated by an inductively coupled plasma source and radicals were supplied to the wafer through an ion shield plate. LPCVD-SiN and thermally oxidized SiO were used for checking the etching capability.

Highly diluted Ar/HF plasma (Ar/HF = 20) showed continuous SiN etching while SiO and poly-Si with native oxide layer were hardly etched. Once HF flow was increased, poly-Si started to be etched and SiO showed slight etching. Selective SiN etching over SiO was still observed due to increasing SiN etching rate. Note that SiN etching was observed with small amounts of F radicals as suggested by using dilute HF gas and optical emission spectroscopy (OES). OES showed small signals of fluorine in HF plasma when compared a conventional gas such as SF₆. In fact, small addition of H₂ suppressed SiN etching due to scavenger effects. When tuning process pressure, the etching rate had a maximum at around 100 Pa while the OES signals of fluorine monotonically decreased. These results indicate that HF assists to enable SiN etching even with small number of etchants while achieving the extremely high selectivity over SiO. Addition of SF₆ slightly reduced SiN etching rate while poly-Si etching rate rapidly increased, supporting the mechanism that the reduction of HF partial pressure suppressed SiN etching. No clear XPS signal of ammonium salt was observed after etching on SiN samples and the etching rate has a maximum at around 0°C. These results suggest that SiN etching occurs not through the formation of ammonium fluorosilicate (AFS), which is well known to promote SiN etching, since the boiling point of AFS is over 100°C. In the structure of SiN/SiO multilayers, Ar/HF plasma showed lateral etching of SiN tiers without specific loss of SiO tiers.

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3:30pm **PS1-MoA-9 Dense-Amorphous-Carbon (DAC) Formation from Ion bombardment of Plasma Deposited FCH Films: Temperature and Precursor Dependence, Sang-Jin Chung**, University of Maryland, College Park; *P. Luan*, *M. Park*, TEL Technology Center America; *G. Oehrlein*, University of Maryland, College Park

The passivation layer deposited during high-aspect-ratio-contact (HARC) etching is important for protecting the sidewall from forming various etch defects. The etch resistance of these often-carbon-based films plays a crucial role in effective profile control. Ion bombardment of polymeric films creates bond scissioning in the surface layer, which often results in the formation of a thin and dense amorphous carbon (DAC) layer above the bulk.¹

In this work, we evaluate the mechanisms of DAC layer formation on plasma-deposited (hydro)fluorocarbon (FCH, FC) films and their etch resistance at various ion energies. Various HARC etching precursors (Ar/C₄F₆, Ar/C₄F₈, Ar/CHF₃, Ar/CH₂F₂, or Ar/CH₃F) were used to deposit FCH/FC on Si, oxide, or nitride materials, on both blanket as well as in trench-like HAR structures^{2, 3}. After film deposition, the chamber was cleaned, and DAC film was formed using ion bombardment from noble gas (Ar) plasma under self-bias. With various ion energies (25, 50, 75, 100, and 125 eV) and substrate temperatures, the thickness and composition of films were monitored in real-time using *in-situ* ellipsometry. Initial results show

that the DAC film formation from FCH deposited by higher -H containing precursors show greater changes, indicated by higher refractive index of the DAC layer compared to the deposited bulk layer, which is due to ion driven depletion of F from the FCH films. During the initial phase of Ar ion bombardment, the etch rate (ER) is very high as there is no DAC layer. The ER gradually reaches a steady state as the DAC layer forms. At higher ion energies the DAC layer thickness is greater, and after a certain thickness the DAC layer greatly inhibits the bulk etch rate. When treating the film with sequentially higher ion energies, we found that the DAC thickness increases, and the ER reaches a peak at ~75 eV after which the ER decreases. When reversing the ion energy, we found that both the DAC thickness and ER decreases. Depending on the film chemistry, higher overall ER could be achieved with optimized ion energy up-ramp (F rich FC films) or down-ramp (F poor FCH films), which highlights the importance of the DAC layer thickness and chemistry to the ER. When comparing DAC layers formed at -20 °C or 10 °C, we found that the refractive index is smaller at -20 °C and the DAC layer is less dense, which allowed for a higher etch rate. The formation and properties of DAC films will also be studied at -60 °C substrate temperature. Chemical composition of the films before and after Ar plasma treatment will be reported.

Plasma Science and Technology

Room 124 - Session PS2-MoA

Plasma Chemistry and Catalysis I

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

4:00pm **PS2-MoA-11 Stress Reduction of Hydrogenated Amorphous Carbon Films by Controlling Incorporation of Carbon Nanoparticles, Kazunori Koga**, *S. Ono*, *T. Okumura*, *K. Kamataki*, *M. Shiratani*, Kyushu University, Japan

INVITED

Stress reduction of hydrogenated amorphous carbon (a-C:H) films has been an important topic in improving the performance of the protective coating, which has been employed for the masking of dry etching, automotive parts, and electrodes of batteries [1,2]. Metal nanoparticle incorporation into the films has been one conventional method to reduce stress [3,4]. However, it led to metal contamination of the films, resulting in the deterioration of the semiconductor device performance. In this study, inspired by the insertion of the metal nanoparticles, we aimed to relieve the stress by incorporating the carbon nanoparticles (CNPs) into the a-C:H films. As the first step, we have successfully controlled the size of nanoparticles by plasma chemical vapor deposition (CVD) [5,6]. Then, we succeeded in controlling the coverage of carbon nanoparticles (CNPs) deposited on substrates using capacitively coupled plasma chemical vapor deposition (CVD), which has been widely employed in large-area deposition. From TEM images, deposited CNPs were classified into two size groups. The mean size of the smaller CNP group is around 5 nm, and that of the larger CNP group is around 25 nm. We succeeded in controlling the coverage Cp of CNPs with discharge duration without unexpected agglomeration. Based on the results, we fabricated a-C:H/CNP/a-C:H sandwich-like films using the parallel plate plasma CVD reactor. Ar and CH₄ mixture gas was introduced from the top of chamber at 19 sccm and 2.6 sccm, respectively. The total pressure was kept at 0.3 Torr. The gas flow rate and the pressure were same as those for the CNP deposition. The mass density of deposited a-C:H films is 1.88 g/cm³. The dependence of the film stress on the Cp. With increasing the Cp, the stress decreases from 1.59 GPa at Cp= 0 % to 1.02 GPa at Cp= 8.9 %. It shows same value for Cp= 15.9 %. The reduction rate is 35.8 %. On the other hand, the films' thickness and refractive index were kept at approximately 320 nm and 2 regardless of the Cp. The results indicate that a small amount of CNP incorporation can reduce the film stress.

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- [4] R. Paul, et al., *Appl. Surf. Sci.* **257**(24), pp.10451-10458 (2011).
- [5] S. H. Hwang, et al., *Diam. Relat. Mater.* **109**, 108050 (2020).
- [6] S. H. Hwang, et al., *Plasma and Fusion Research: Regular Articles* **14**, 4406115 (2019).

4:30pm **PS2-MoA-13 Is Plasma Electrochemistry Just Electrochemistry at Plasma-Liquid Interfaces? Learnings from Organic Reactions, Casey Bloomquist**, *E. Aydil*, *M. Modestino*, New York University

In plasma electrochemical synthesis, one of the electrodes of a traditional electrochemical cell is replaced by plasma. Recent work has focused on using plasma-generated solvated electrons to perform reductive chemistry

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in aqueous solutions. In this study, we explored the use of plasma electrochemistry for the largest industrial organic electrosynthesis process, the electrohydrodimerization of acrylonitrile (AN) to adiponitrile (ADN), a precursor to Nylon 6,6. We used a DC pin-to-liquid Ar plasma to study both negative polarity and positive polarity plasma interactions with aqueous AN. Interestingly, we did not produce ADN, which was expected to be created through radical coupling in a negative polarity plasma. However, we did produce H_2 , H_2O_2 , propionitrile (PN), O_2 , CO_2 , C_2 , and C_3 hydrocarbons and AN-derived polymers with amounts depending on the AN concentration, current, and polarity. H_2 was produced in amounts 10 – 20 times that expected from Faradaic currents, highlighting the importance of non-electrochemical reactions. PN, a competing reaction in traditional ADN electrosynthesis, was produced at rates commensurate with Faradaic currents under negative potentials. However, under positive potentials, PN production was much higher than predicted by Faradaic currents, suggesting that PN production under either polarity may be produced via non-electrochemical pathways. Clearly, there is more to plasma electrochemistry than just electrochemistry.

4:45pm PS2-MoA-14 Nonequilibrium Plasma Aerotaxy of $In_xGa_{1-x}N$ Nanocrystals, *Dillon Moher, E. Thimsen*, Washington University in St. Louis
Semiconductors with good stability in harsh chemical environments, tunable band gap, and non-toxicity are sought after for solar energy conversion and solid-state light sources. The solid solution of InN and GaN ($In_xGa_{1-x}N$) is a good candidate material whose band gap depends on the mole fraction of InN in the GaN (x). Full control over the composition can provide photon absorption and emission from the ultraviolet to the infrared. However, homogeneous thin film $In_xGa_{1-x}N$ with intermediate x is plagued by strain-induced threading dislocations and phase segregation due to the miscibility gap. High material quality and tunability may be achieved in freestanding $In_xGa_{1-x}N$ nanocrystals, absent of epitaxial growth and having distinct mixing behavior due to nanoscale effects. Moreover, nanocrystals may have 3D quantum confinement effects, high specific surface area, and compatibility with solution processing. Yet, their synthesis is underdeveloped. In this work, the synthesis of $In_xGa_{1-x}N$ nanocrystals by nonequilibrium plasma aerotaxy was demonstrated. STEM-EDS observation showed that individual nanocrystals consisted of a mixture of InN and GaN. The nanocrystals, deposited into thin films, had a composition-dependent band gap demonstrated by UV-Vis extinction spectroscopy. Annealing procedures were pursued to improve the crystallinity and photoluminescence of the nanocrystal films. Decomposition of the nanocrystals, which occurred at temperatures of 600 °C and above, was suppressed when the nanocrystals were first coated with Al_2O_3 deposited by atomic layer deposition. Furthermore, the photoluminescence of the nanocrystals increased by an order of magnitude. This new synthesis strategy for $In_xGa_{1-x}N$ nanocrystals is a step towards advanced optoelectronic applications, paving the way for further research into material property optimization and integration into devices.

5:00pm PS2-MoA-15 Plasma-Based Reforming of LNG?, *N. Lim, Michael Gordon*, UC Santa Barbara

Developing novel reacting systems for more sustainable use of our natural resources is central to both reducing the risks associated with CO_2 emissions and making the long-term transition to a more circular, sustainable, and electrified economy. Moreover, developing technologies to leverage and reform the energy density of global commodities such as liquified natural gas (LNG), to produce clean H_2 , olefins, and solid carbon without producing CO_2 , could be game changing. Toward this end, we have been exploring how plasmas might be directly excited in liquid methane at cryogenic conditions to create value-added products.

This talk will highlight our preliminary work on striking and sustaining low (60 Hz) and high (~20 kHz) frequency, as well as pulsed, plasma discharges directly in liquid methane at ~100K (**Figure 1**), with emphasis on (i) the reactor configuration (i.e., with rotating electrodes to prevent carbon buildup), (ii) yield of H_2 and other (solid) hydrocarbon products, (iii) energy efficiency, and (iv) management and characterization (SEM/TEM) of the solid carbon product (**Figure 2**). Although the four-phase reaction environment encountered at cryogenic conditions – namely, plasma, gaseous H_2 , slurry of frozen C_2+ hydrocarbons, and solid carbon – presents many challenges, it is still possible to generate H_2 , some C_2 olefins, and a graphite-like carbon product.

Various aspects of this unorthodox cryogenic reaction environment will be discussed including: what might be going on in the discharge?, is the

plasma thermal or nonthermal?, does the input energy vaporize the methane?, how can the carbon be managed?, what products are formed under different plasma conditions?, what is the H_2 production rate and SER?, and might this process be a better or more useful way to re-gasify and reform LNG?

Quantum Science and Technology Mini-Symposium Room 123 - Session QS1+EM+MN+PS-MoA

Materials + Devices for Quantum Systems

Moderators: Parag Banerjee, University of Central Florida, Jaesung Lee, University of Central Florida

1:30pm QS1+EM+MN+PS-MoA-1 Elastic Layered Quantum Materials, *Jiun-Haw Chu*, University of Washington

INVITED

Recently elastic strain has emerged as a powerful tool for probing and controlling quantum materials. By changing chemical bond lengths, elastic strain can modulate electronic structure up to very high energy scale. Additionally, as a second rank tensor, strain enables access to various instabilities associated with different symmetry channels. In this talk, I will discuss several examples of the application of strain to unconventional electronic orderings in van der Waals layered materials, including zigzag antiferromagnetism, charge density waves and excitonic insulators.

2:00pm QS1+EM+MN+PS-MoA-3 Controllable Extended Defect States in Topological Insulators and Weyl Semimetals, *Eklavya Thareja, J. Gayles*, University of South Florida; *I. Vekhter*, Louisiana State University

Over the past decade study of topological materials has emerged as one of the most active areas in condensed matter physics, owing to a wide range of their proposed applications ranging from quantum computing to build information technology is their robustness to disorder. However, in addition to the immunity of their electronic states against disorder, one needs ways to control the properties of these electronic states in these materials. We show that extended defects such as line defects and planar defects host localized states in Topological Insulators and Weyl Semimetals, which are two common topological materials. These localized states can be manipulated by controlling the scattering at the defects, for example, by using an external magnetic field. This leads to controllable spin accumulation and non-dissipative currents near the defects, due to spin-momentum locking. These results bring us closer to functional applications.

2:15pm QS1+EM+MN+PS-MoA-4 Topological Interfacial State in One-Dimensional h-BN Phononic Waveguide, *Y. Wang, Sanchaya Pandit*, University of Nebraska - Lincoln

Artificial topological structures have gained considerable research attention in the fields of photonics, electronics, mechanics, acoustics, and many others, as they promise robust propagation without loss along the edges and interfaces. In this work, we explored the topological states in one-dimensional (1D) phononic waveguides empowered by hexagonal boron nitride (h-BN), a hallmark two-dimensional (2D) material with robust mechanical properties that can support phonon propagation in high frequency regime. First, degenerate trivial and nontrivial topological structures were designed based on the Su-Schrieffer-Heeger (SSH) model. The dispersion engineering was then performed to match the passbands and bandgaps for these two topological structures through optimizing the geometric parameters of the unit cells. An interfacial state emerged when connecting these two sets of unit cells together and forming the 1D waveguide. The topological nature of this interfacial state, immune to structural and material parameter perturbation, was verified with the variation of strain and thickness in the waveguide. The phononic topological state studied here can be further coupled with defect-related quantum emitters in h-BN, opening the door for next-generation hybrid optomechanical circuits.

2:30pm QS1+EM+MN+PS-MoA-5 Scanning Nano-Optical Imaging of Quantum Materials, *Guangxin Ni*, Florida State University

Scanning near-field Nano-Optical imaging is an invaluable resource for exploring new physics of novel quantum materials. Surface plasmon polaritons and other forms of hybrid light-matter polaritons provide new opportunities for advancing this line of inquiry. In particular, nanopolaritonic images obtained with modern scanning nano-infrared tools grant us access into regions of the dispersion relations of various excitations beyond what is attainable with conventional optics. I will discuss this emerging direction of research with two examples from 2D layered

quantum

materials.

2:45pm **QS1+EM+MN+PS-MoA-6 Engineering of Erbium-Implanted Lithium Niobate Films for Integrated Quantum Applications**, *Souryaya Dutta*, College of Nanotechnology, Science, and Engineering (CNSE), University at Albany; *A. Kaloyeros, S. Gallis*, College of Nanotechnology, Science, and Engineering (CNSE), University at Albany (UAlbany)

Rare-earth-doped materials have garnered significant attention as material platforms in emerging quantum information and integrated photonic technologies. Concurrently, advances in its nanofabrication processes have unleashed thin film lithium niobate (LN), LiNbO_3 , as a leading force of research in these technologies, encompassing many outstanding properties in a single material. Leveraging the scalability of ion implantation to integrate rare-earth erbium (Er^{3+}), which emits at 1532 nm, into thin film lithium niobate can enable a plethora of exciting photonic and quantum technologies operating in the telecom C-band. Many of these technologies also rely on coupling via polarization-sensitive photonic structures such as waveguides and optical nanocavities, necessitating fundamental material studies.

Toward this goal, we have conducted an extensive study on the role of implantation and post-implantation processing in minimizing implantation-induced defectivity in x-cut thin film LN. By leveraging this, we have demonstrated an ensemble optical linewidth of ~ 140 GHz of the Er emission at 77 K. Our demonstration showcases the effectiveness of our ion implantation engineering in producing cutting-edge Er emission linewidth in thin film LN at higher temperatures compared to values reported for diffusion-doped bulk materials at liquid helium temperatures (~ 3 K). Furthermore, we show that the Er photoluminescence (PL) is highly polarized perpendicular to the x-cut LN c-axis through a systematic and combinational PL and high-resolution transmission electron microscopy (HRTEM) study. These results indicate that using Er rare-earth emitters in thin film LN, along with their polarization characteristics and related ion implantation engineering, presents a promising opportunity to produce highly luminescent Er-doped LN integrated photonic devices for nanophotonic and quantum applications at telecom wavelengths.

Quantum Science and Technology Mini-Symposium

Room 123 - Session QS2+PS-MoA

Advanced Fabrication and Plasma Techniques for Quantum Applications

Moderators: *Angelique Raley*, TEL Technology Center America, *Sebastian Engelmann*, IBM T.J. Watson Research Center, *David Pappas*, Rigetti Computing

4:00pm **QS2+PS-MoA-11 High-Rate (>50 nm/hour) Plasma-Enhanced ALD of Superconducting $\text{Nb}_x\text{Ti}_{1-x}\text{N}$ with Substrate Biasing for Quantum Technologies**, *Silke Peeters, L. Nelissen*, Eindhoven University of Technology, Netherlands; *D. Besprozvanny*, Oxford Instruments Plasma Technology, UK; *N. Choudhary*, University of Glasgow, UK; *C. Lennon*, Oxford Instruments Plasma Technology, UK; *M. Verheijen*, Eindhoven University of Technology, Netherlands; *M. Powell, L. Bailey*, Oxford Instruments Plasma Technology, UK; *R. Hadfield*, University of Glasgow, UK; *E. Kessels*, Eindhoven University of Technology, Netherlands; *H. Knoops*, Oxford Instruments Plasma Technology, UK

The advancement of a wide range of quantum technologies hinges on improvements in materials and their interfaces. Plasma-enhanced atomic layer deposition (PEALD) enables the growth of high-quality superconducting thin films with atomic-scale control. Scalable integration of PEALD in the diverse field of superconducting quantum device fabrication requires the development of versatile, high-throughput processes.

We demonstrate PEALD of superconducting $\text{Nb}_x\text{Ti}_{1-x}\text{N}$ films at a high rate of > 50 nm/hour on the Oxford Instruments PlasmaPro ASP system. The RF-driven remote capacitively coupled plasma (CCP) ALD system with small chamber volume allows for low-damage conditions and short cycle times. The CCP source is combined with RF substrate bias functionality allowing for ion-energy control. The depositions consist of NbN and TiN supercycles using the TBTDEN and TDMAT precursors and an $\text{Ar}/\text{H}_2/\text{N}_2$ plasma at a table temperature of 320°C .

$\text{Nb}_x\text{Ti}_{1-x}\text{N}$ films are prepared with film thicknesses ranging from 5 to 100 nm with $< 5\%$ non-uniformity on a 150 mm diameter wafer. Four-point probe measurements yield low room-temperature resistivities increasing with Nb
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content from $160\ \mu\Omega\ \text{cm}$ (41 nm TiN) to $284\ \mu\Omega\ \text{cm}$ (25 nm NbN). The films are stoichiometric with a low ~ 2 at.% O impurity content. Accurate $\text{Nb}_x\text{Ti}_{1-x}\text{N}$ composition control through supercycling is demonstrated from $x=0$ to $x=1$, with the C content increasing from 10 at.% to 19 at.% and the N content correspondingly decreasing from 40 at.% to 26 at.%. EDX mapping confirms homogeneous mixing of Ti and Nb and XRD reveals all prepared films are fcc polycrystalline. The crystallinity and conductivity of the films can be tuned by RF substrate biasing. TEM imaging of the most conductive 50 nm $\text{Nb}_{0.5}\text{Ti}_{0.5}\text{N}$ film prepared with 90 V bias reveals a disordered polycrystalline film in agreement with XRD, which shows peak broadening beyond 50 V bias.

$\text{Nb}_{0.5}\text{Ti}_{0.5}\text{N}$ films of 5 nm to 100 nm thickness display superconducting transitions at critical temperatures of 3.5 K to 10 K. A high sheet kinetic inductance of $470\ \text{pH}/\text{sq}$ is found for the 5 nm film prepared with 90 V bias. Superconductivity is also confirmed for all explored compositions and substrate bias voltages. As a result, the film properties can be tailored whilst maintaining the high quality required for quantum applications. The novel ALD configuration negates the need for long plasma exposures to achieve this quality. This tunability and high rate of the $\text{Nb}_x\text{Ti}_{1-x}\text{N}$ deposition process puts forward PEALD as a promising technique to tackle material challenges in a wide range of quantum technologies.

4:15pm **QS2+PS-MoA-12 Plasma etch study of NbTiN/aSi/NbTiN Josephson Junctions for Superconducting Digital Logic**, *Yann Canvel, S. Kundu, V. Renaud, A. Pokhrel, D. Lozano, D. Vangoidsenhoven, B. Kennens, A. Walke*, IMEC Belgium; *A. Herr*, IMEC

In the development of next-generation logic devices, an attractive complement to CMOS technology would be to leverage the superconducting technology which operate at a low temperature. Superconducting Digital Logic (SDL) devices are attractive as they are inherently faster and have much less power dissipation than their CMOS counterpart. Although SDL devices have existed for decades now, there have been fundamental challenges to scale down its main components and related interconnects. To provide groundwork for exploring SDL device integration, and a possible hybrid integration of SDL/CMOS circuits, one of the key patterning challenges is the Josephson Junction (JJ) device fabrication. JJ devices are the active devices of SDL technology that can potentially provide computational density, energy efficiency and interconnect bandwidth beyond conventional electronics.

In this communication, an in-depth plasma etch investigation is reported to demonstrate the patterning of high-density junctions with diameters between 210-500nm and CD control of $< 2\%$ across the 300mm wafer. Using the Reactive Ion etching (RIE) technique, the study has firstly consisted of developing a non-standard NbTiN etch process which enables to pattern the JJ pillars through the Top Electrode (TE) and the aSi barrier, down to the Bottom Electrode (BE) with a precise etch landing control. Subsequent etch processes have then required successive engineering optimization to build up the final device. Some of the main challenges to tackle were the etch residues mitigation, the reduction of oxidized NbTiN interfaces and the final electrical contact with the Top metal. The successful fabrication of high density NbTiN/aSi/NbTiN junctions has offered the first demonstration of a Josephson Junction compatible with CMOS BEOL. Some electrical measurements at room and cryogenic temperatures will complete the investigation by showing high critical current, high speed and device stability up to 420°C .

Pokhrel, A *et al.*, First Demonstration of High Density NbTiN/aSi/NbTiN Josephson Junctions. *IEEE Symposium on VLSI Technology & Circuits (VLSI)*, (2024).

Pokhrel, A. *et al.* Towards Enabling Two Metal Level Semi-Damascene Interconnects for Superconducting Digital Logic: Fabrication, Characterization and Electrical Measurements of Superconducting $\text{Nb}_x\text{Ti}_{1-x}\text{N}$. *IEEE International Interconnect Technology Conference (IITC)*, (2023).

Holmes, D. S. *et al.* Energy-Efficient Superconducting Computing - Power Budgets and Requirements. *IEEE Transactions on Applied Superconductivity* **23**, 1701610–1701610 (2013).

Herr, Q. P. *et al.* Ultra-low-power superconductor logic. *Journal of Applied Physics* **109**, 103903 (2011).

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4:30pm **QS2+PS-MoA-13 Patterning Improvements and Oxidation Mitigation of Nb_xTi_(1-x)N Metal Lines Processes for Superconducting Digital Logic**, *Vincent Renaud, Y. Canvel, A. Pokhrel, S. Iraci, M. Kim, B. Huet, J. Soulie, S. Sarkar, Q. Herr, A. Herr, Z. Tokei*, IMEC, Belgium

One promising alternative to standard CMOS technology is Superconducting Digital Logic (SDL) which enables computing at cryogenic temperature and, thus, performs faster at a reduced cost and power. Recently, it was demonstrated that a two-metal level BEOL unit process using Nb_xTi_(1-x)N for the metal lines with a critical dimension of 50nm could be achieved on 300mm wafers. Cryogenic temperature electrical measurement showed that the lines and via of the device have a critical temperature of 12-13.4 K and a critical current density of 80-113 mA/μm². It was also highlighted that one of the crucial challenge in the making of this technology was the oxidation of the Nb_xTi_(1-x)N metal lines during the direct metal etch process of the material itself and/or during the conception of the full device. This oxidation negatively impacts the electrical performance of the wire and could become a serious showstopper for the scalability of the device.

The goal of this study is to discuss different approaches for constructing and patterning the Nb_xTi_(1-x)N metal lines while mitigating the oxidation of the device during the process. Different Hard-Mask (HM) materials have been investigated, as well as alternative HM removal processes. Finally, an in-situ encapsulation of the Nb_xTi_(1-x)N metal lines post-etch process has been experimented to mitigate the oxidation the device when exposed to the air or during the sub-sequent dielectric gap-fill. These experiments were coupled with electrical measurements at room and cryogenic temperature with the aim of validating the best fabrication process for the Nb_xTi_(1-x)N metal lines for SDL devices.

Pokhrel, A. *et al.* Towards Enabling Two Metal Level Semi-Damascene Interconnects for Superconducting Digital Logic: Fabrication, Characterization and Electrical Measurements of Superconducting Nb_xTi_(1-x)N. *IEEE International Interconnect Technology Conference (IITC)*, (2023).

Holmes, D. S. *et al.* Energy-Efficient Superconducting Computing - Power Budgets and Requirements. *IEEE Transactions on Applied Superconductivity* **23**, 1701610–1701610 (2013).

Herr, Q. P. *et al.* Ultra-low-power superconductor logic. *Journal of Applied Physics* **109**, 103903 (2011).

4:45pm **QS2+PS-MoA-14 Patterning of TiN and TaN for advanced superconducting BEOL**, *Thibaut Chêne*, CEA-LETI, France; *R. Segaud, F. Nemouchi, S. Minoret*, CEA-Leti, France; *F. Gustavo*, CEA INP Grenoble, IRIG, France; *J. Garrione, T. Chevolleau*, CEA-Leti, France

The development of new quantum technologies based on superconducting Qubits or spin Qubits becomes a major subject of interest for applications in communication and data computing. Such technology operating at low temperature requires a superconducting routing development.

The superconducting materials have been selected based on their superconducting properties and their integration capabilities in an industrial process flow. The integration is based on a top down approach by patterning successively both metals with a selective etch process to define lines and vias.

To develop the patterning process, a 40 nm thick film of TiN or TaN is deposited by PVD on a SiO₂ layer over 300 mm silicon wafers. Then the lithography is performed on a 193nm stepper to achieve 150 nm line and via critical dimension (CD). Etching developments are carried out on a 300 mm industrial ICP chamber using Cl₂ chemistry with or without HBr or CH₄ addition. A parametric study of Cl₂ based chemistries is performed to achieve a straight profile with low CDbias and also to determine the selectivity of TaN over TiN. Optical Emission Spectroscopy (OES) and quasi in-situ X-ray Photo-electron Spectroscopy (XPS) are conducted to better understand the etching mechanisms.

Regarding the TiN, straight profiles and good CD control are achieved with Cl₂/HBr chemistries but micromasking is observed. The micromasking phenomenon will be further discussed in terms of plasma/surface interaction based on the quasi in-situ XPS analyses. The addition of CH₄ instead of HBr prevents the micromasking while keeping a rather straight profile with an etch rate of 70 nm/min. For the TaN, whatever the etching chemistries, lower etch rates are observed in comparison with TiN. This trend is attributed to a higher Ta-N binding energy and lower etch by-product volatility. The Cl₂/HBr and Cl₂/Ar plasma chemistries lead both to CD loss and tapered profile mainly due to a lack of selectivity with the PR. Oppositely, the Cl₂/CH₄ chemistry allows achieving straight TaN profile by adjusting the amount of CH₄. The patterning of 80 nm vias for both TiN and

TaN are obtained by combining resist trimming and the etching processes previously optimized for the narrow lines. After this patterning process optimization, the T_c of 150 nm CD structures is measured using a specific test vehicle for both TiN and TaN thin films. We will then leverage the TiN:TaN etching selectivity of 4.6 achieved by tuning the Cl₂/CH₄ amount to integrate TiN vias on TaN lines.

5:00pm **QS2+PS-MoA-15 Optimization of Superconducting Transition Metal Nitride Films Deposited by Reactive High-Power Impulse Magnetron Sputtering**, *Hudson Horne, C. Hugo, B. Reid, D. Santavicca*, University of North Florida

Ultra-thin films of transition metal nitrides are used to create superconducting devices such as superconducting nanowire single-photon detectors, kinetic inductance detectors, and parametric amplifiers. Nanowires made from such materials also have applications in quantum computing, for example as high-impedance, low-dissipation shunts to suppress charge noise in superconducting qubits. In this work, we explore the use of high-power impulse magnetron sputtering (HiPIMS) to optimize the superconducting properties of transition metal nitride thin films for such device applications.

Initial work has focused on niobium nitride deposited using a reactive process in which a niobium target is sputtered in the presence of nitrogen gas. We compare films deposited on silicon substrates via HiPIMS and conventional DC sputtering, and we find that HiPIMS can produce films of the same thickness with a higher critical temperature and a lower normal-state resistivity. Film composition and structure are characterized with scanning electron microscopy, wavelength-dispersive x-ray spectroscopy, and x-ray diffraction, and these results are correlated with the electrical properties of both unpatterned films and nanowires. These characterizations suggest that the improved superconducting properties of the HiPIMS films is the result of optimizing the stoichiometry in the desired δ crystal phase. We show that further improvement in the critical temperature is possible through the use of an aluminum nitride buffer layer and through substrate heating.

We have begun extending these studies to other materials such as titanium nitride and hafnium nitride. This work seeks to systematically explore the HiPIMS process for optimizing transition metal nitride films with an emphasis on ultra-thin films for quantum device applications.

This work was supported by the National Science Foundation through grants ECCS-2000778 and ECCS-2117007.

Atomic Scale Processing Mini-Symposium Room 116 - Session AP1+EM+PS+TF-TuM

Atomic Layer Etching I: Thermal Processes

Moderators: Steven M. George, University of Colorado at Boulder, Austin Minnich, California Institute of Technology

8:00am **AP1+EM+PS+TF-TuM-1 Highly Selective and Isotropic Atomic Layer Etching using Dry Chemical Removal, Nobuya Miyoshi**, Hitachi High-Tech America, Inc. **INVITED**

As semiconductor devices shrink to sub-10 nm dimensions, the introduction of new device structures, integration schemes, and materials brings many challenges to device manufacturing processes. A new structure with gate-all-around (GAA) nanosheets has been introduced to reduce the power consumption of transistors and achieve higher transistor integration density. For advanced semiconductor memory devices, 3D NAND flash has been introduced to achieve higher bit densities. Fabricating these three-dimensional (3D) devices requires isotropic etching of thin films with atomic layer control, high selectivity to underlying materials, and high uniformity over high-aspect-ratio 3D structures. Thermal atomic layer etching (ALE) is a promising method for isotropic etching with atomic-level precision and high conformality over three-dimensional structures. We developed a dry chemical removal (DCR) tool with an infrared (IR) wafer annealing and quick cooling system to perform highly selective thermal ALE for various materials. Thermal ALE was demonstrated for Si_3N_4 and SiO_2 films using the formation and desorption of $(\text{NH}_4)_2\text{SiF}_6$ -based surface-modified layers. Thermal ALE processes for W and TiN films were also demonstrated by the formation and desorption of halogenated surface-modified layers. These ALE processes show a self-limiting formation of modified layers, enabling conformal and precisely controlled etching. In addition, spontaneous and highly selective etching of SiO_2 was demonstrated on the DCR tools using $\text{HF}/\text{CH}_3\text{OH}$ vapor. SiO_2 films can be etched spontaneously with high selectivity to SiN films when the temperature of the substrate is lower than -20°C .

8:30am **AP1+EM+PS+TF-TuM-3 Selective Si or Ge Dry, Thermal Spontaneous Etching Using HF Vapor, Marcel Junige, T. Collieran, S. George**, University of Colorado Boulder

Advanced 3D structures in microelectronics require novel self-aligned techniques. For example, selective etching may remove one specific material while leaving intact others in proximity. This multi-color challenge gets particularly difficult for selectivity between Si-based materials, as well as between Si and Ge. Instead of plasma activation, this work focused on developing gas-phase spontaneous etch pathways based on thermal chemistry using anhydrous hydrogen fluoride (HF) vapor.

In situ spectroscopic ellipsometry experiments discovered substantial spontaneous etching of Si by HF at 275°C . The Si etch rate was $12.2 \text{ \AA}/\text{min}$ at an HF pressure of 3 Torr. The Si etch rate increased further with higher HF pressures. In addition, Si etched selectively with an exceptionally high selectivity factor of $>1,000:1$ versus the retention of SiO_2 and stoichiometric Si_3N_4 .

Temperature-programmed quadrupole mass spectrometry (QMS) experiments confirmed the spontaneous etching of crystalline Si nanopowder by HF. SiF_4 and H_2 were observed as the main volatile etch products. QMS detected the SiF_4 product with a gradual onset above $\sim 175^\circ\text{C}$. This temperature dependency indicated that the etch reaction may be limited by SiF_4 desorption from the Si surface. SiF_4 desorption from fluorinated Si surfaces has been reported to occur at $>125^\circ\text{C}$.

Additional QMS experiments also observed the spontaneous etching of Ge nanopowder by HF. GeF_4 and H_2 were revealed as the main volatile etch products. QMS detected GeF_4 already at 25°C . The GeF_3^+ signal intensity increased with elevating temperature and exhibited a maximum at $\sim 80\text{--}85^\circ\text{C}$. Subsequently, the GeF_3^+ signal decreased below the noise level above $\sim 125^\circ\text{C}$.

These results suggest that Si etching could be achieved selectively over Ge retention at $>175^\circ\text{C}$. Likewise, Ge etching could be accomplished selectively over Si retention at $<125^\circ\text{C}$. This reciprocal selectivity between Si and Ge etching will depend on the influence of proximity effects resulting from the volatile etch products when Si and Ge are both present in the reactor.

8:45am **AP1+EM+PS+TF-TuM-4 Theoretically Designed Thermal Atomic Layer Etching Processes for Interconnect Metals, Miso Kim, H. Cho**, Hongik University, Republic of Korea; *D. Lee, J. Lee, J. Kim, W. Kim*, Hanyang University, Republic of Korea; *B. Shong*, Hongik University, Republic of Korea
Atomic layer etching (ALE) is emerging as a key technology for the precise and selective removal of materials at the atomic level, especially for manufacturing of nanoscale three-dimensional semiconductor devices. Previously known thermal ALE processes often involve two-step sequence of surface chemical reactions: surface modification of the substrate such as halogenation, followed by volatilization using another etchant. For example, a recent study reported a thermal ALE process for Ni, employing SO_2Cl_2 for halogenation and $\text{P}(\text{CH}_3)_3$ for volatilization via ligand addition [1]. Since ALE process is based on self-limiting surface chemical reactions, it is desirable to design ALE processes by understanding their surface reactions. However, the mechanistic aspects of such thermal ALE reactions remain significantly underexplored. In this work, we employed neural network potential (NNP) calculations to screen for suitable process conditions for thermal ALE process of metals, especially those considered as materials for nanoscale interconnects. Our findings demonstrate that several metals are capable of forming energetically stable volatile compounds via halogenation and ligand addition of thermal molecular etchants. Several novel thermal ALE processes that were theoretically predicted are experimentally demonstrated with varying etch rates and selectivity between the substrates. Overall our study show the applicability of theoretical analysis of the surface chemical reactions toward design of novel ALE processes.

References. (1) Murdzek, J. A.; Lii-Rosales, A.; George, S. M. *Chem. Mater.* 2021, 33 (23), 9174–9183.

Acknowledgments. This work was supported by Samsung Electronics.

9:00am **AP1+EM+PS+TF-TuM-5 X-ray Photoelectron Studies of Removal of Sputter Damage from InGaP Surfaces Using Thermal Atomic Layer Etching, Ross Edel**, University of Colorado Boulder; *E. Alexander*, MIT; *A. Cavanagh*, University of Colorado Boulder; *T. Nam*, Soonchunhyang University, Republic of Korea; *T. Van Voorhis*, MIT; *S. George*, University of Colorado Boulder

InGaP is widely used for red LED devices. Surface defects on LED devices can lead to non-radiative electron/hole pair recombination that reduces their light output. This light quenching effect is more severe for smaller μLEDs that have high surface-to-volume ratios. The surface defects are believed to be formed by energetic ion species during plasma processing that forms the μLEDs . Thermal ALE may provide a method to remove these defects.

To quantify the removal of surface damage, x-ray photoelectron (XPS) studies employed InGaP samples sputtered with argon as a model system. These InGaP samples simulate the μLED sidewalls that are exposed to energetic species during plasma processing. Thermal InGaP ALE was then performed using static, sequential HF and dimethylaluminum chloride (DMAC) exposures. This procedure yielded etch rates of $0.5\text{--}1.0 \text{ \AA}/\text{cycle}$ at temperatures from $300\text{--}330^\circ\text{C}$, respectively. This work was conducted using a new apparatus that combines a hot wall ALD/ALE reactor with *in vacuo* Auger spectroscopy to allow sample characterization without exposure to air.

InGaP samples damaged by Ar^+ ion sputtering were analyzed using *ex situ* X-ray photoelectron spectroscopy (XPS) before and after thermal ALE by tracking the shifted components in the P 2p XPS region that correspond to sputter damage. An *ex situ* XPS scan of a sputtered InGaP sample displayed two shifted doublets (Figure 1a) while an unsputtered sample showed only a bulk doublet (similar to Figure 1b). DFT simulations identified the higher energy doublet as phosphorus directly bound to three-coordinate indium or gallium and the lower energy doublet as three-coordinate phosphorus (Figure 2a). In contrast, the DFT simulations showed only a bulk doublet for InGaP without under-coordinated surface atoms (Figure 2b).

InGaP ALE can then remove the XPS features associated with the damaged lattice. A bulk-like XPS spectrum showing minimal damage was recovered after 50 ALE cycles for a sample initially exposed to 500 eV sputtering (Figure 1b). By contrast, annealing for 72 hours at 300°C without etching was not sufficient to eliminate the damage. AES analysis similarly showed that the argon implanted in the sample by sputtering was removed after etching but not annealing. Increasing the sputtering ion energy to 2 keV required more extensive etching to remove the sputter damage. In this case, 100 ALE cycles were able to largely remove the surface defects. The corresponding AES data showed a linear decrease in implanted argon and

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reached zero after 100 ALE cycles. The etch depth consistent with 100 ALE cycles indicates a damaged material depth of ~4 nm.

9:15am **AP1+EM+PS+TF-TuM-6 Temperature-Dependent Atomic Layer Etching of Polycrystalline, Epitaxial, and Doped ZnO Films: An *in situ* Spectroscopic Ellipsometry Investigation**, *Terrick McNealy-James, S. Berriel, B. Butkus, P. Banerjee*, University of Central Florida

Atomic layer etching (ALE) stands out as a remarkable technique for precise Angstrom-level control for material removal. With a growing demand in the semiconductor and nanotechnology sectors, ALE becomes a promising solution to address evolving challenges in patterning and in the shrinking of device dimensions.

In this work, we apply ALE to zinc oxide (ZnO) films, focusing on the influence of the film's structure (i.e., crystallinity and doping) on the etch rates. Utilizing *in situ* spectroscopic ellipsometry, we comprehensively map the etch rate as a function of temperature and pulse times for the reactants. The resulting 3D contour plot of etch rate vs. temperature and pulse time defines the process parameter 'window'. Notably, this plot is visually captivating and aids in the comprehension and optimization of the ALE process.

The ALE process employed for ZnO etching consists of alternate pulses of acetylacetone and O₂ plasma, spanning temperatures from 120 °C to 300 °C. The etch rates of epitaxial, single crystalline films are compared with polycrystalline ZnO. The effect of dopants, such as Al³⁺ on the etch rates of ZnO films are explored. The impact of ALE chemistry in determining etch rates in films with crystal facets, grain boundaries and dopants are discussed with implications to future device manufacturing.

References:

(1) A. Mameli, M. A. Verheijen, A. J. M. Mackus, W. M. M. Kessels, and F. Roozeboom, *ACS Appl. Mater. Interfaces*, vol. 10, 38588, (2018).

9:30am **AP1+EM+PS+TF-TuM-7 Examination of Atomic Layer Etch Mechanisms by Nuclear Magnetic Resonance Spectroscopy**, *T. Smith, Jane P. Chang*, University of California, Los Angeles

INVITED

As atomic layer etching (ALE) becomes more widespread, there is a need to better understand the underlying mechanisms by which it operates. Of particular interest is the removal half-cycle of thermal ALE wherein a vapor-solid reaction leads to the formation of a volatile etch product. Solid state magic angle spinning nuclear magnetic resonance (MAS-NMR) can provide a wealth of structural and chemical information, but it has not yet been used to examine ALE reaction mechanisms. In this work, MAS-NMR of CuO etched in solution phase formic acid (FA) is demonstrated and compared with prior density functional theory results¹. Although it may seem a simple system, the paramagnetic nature of CuO and the formation of many products with slightly different structures both lead to complicated NMR spectra. The issue of significant peak broadening by paramagnetic relaxation can be alleviated in part by spinning at very fast speeds (>30kHz). From the resulting spectra, confirmation of Cu(HCOO)₂·4H₂O as a product is possible by comparison to a commercial reference powder. However, assignment of other peaks requires correlation spectroscopy showing ¹³C-¹³C and ¹H-¹³C correlations to deduce the structures of the various products, illuminating the reaction landscape of CuO with FA. To extend these findings to the vapor-solid interactions present in ALE, a special heterogeneous NMR rotor can be used that was originally designed for use with high pressure gases. To adapt this rotor use with lower pressure FA vapor, a novel rotor packing method that separates the FA from the CuO prior to vaporization is presented.

Atomic Scale Processing Mini-Symposium Room 116 - Session AP2+EM+PS+TF-TuM

Atomic Layer Etching II: Energy-Enhanced Processes

Moderators: *Steven M. George*, University of Colorado at Boulder, *Austin Minnich*, California Institute of Technology

11:00am **AP2+EM+PS+TF-TuM-13 Atomic Layer Etching of Lithium Niobate for Quantum Photonics**, *Austin Minnich*, California Institute of Technology

INVITED

Lithium niobate (LiNbO₃, LN) is a ferroelectric crystal of interest for integrated photonics owing to its large second-order optical nonlinearity and the ability to impart periodic poling via an external electric field. However, on-chip device performance based on thin-film lithium niobate (TFLN) is presently limited by optical loss arising from corrugations between poled regions and sidewall surface roughness. Atomic layer etching (ALE)

could potentially smooth these features and thereby increase photonic performance, but no ALE process has been reported for LN. Here, we report a directional ALE process for x-cut MgO-doped LN using sequential exposures of H₂ and SF₆/Ar plasmas. We observe etch rates up to 1.01 +/- 0.05 nm/cycle with a synergy of 94%. We also demonstrate ALE can be achieved with SF₆/O₂ or Cl₂/BCl₃ plasma exposures in place of the SF₆/Ar plasma step with synergies above 90%. When combined with a wet post-process to remove redeposited compounds, the process yields a 50% decrease in surface roughness. With additional optimization to reduce the quantity of redeposited compounds, these processes could be used to smoothen surfaces of TFLN waveguides etched by physical Ar⁺ milling, thereby increasing the performance of TFLN nanophotonic devices or enabling new integrated photonic capabilities.

11:30am **AP2+EM+PS+TF-TuM-15 Tunable Electron Enhanced Etching of β -Ga₂O₃ Using HCl Reactive Background Gas and Positive Sample Voltage**, *Michael Collings*, University of Colorado Boulder; *J. Steele, D. Schlom, H. Xing*, Cornell University; *S. George*, University of Colorado Boulder

Crystalline β -Ga₂O₃ is an ultra-wide band gap material with important applications for high power electronics. High precision etching is required for β -Ga₂O₃ device fabrication. Previous thermal atomic layer etching (ALE) attempts to etch β -Ga₂O₃ have not been successful. Plasma etching of β -Ga₂O₃ using Cl-containing gases is difficult for Angstrom-level etching control and can leave surface damage. In this work, electron-enhanced etching of β -Ga₂O₃ is performed using a HCl reactive background gas (RBG) and positive sample bias. The β -Ga₂O₃ is a -oriented epitaxial film grown by suboxide molecular-beam epitaxy on a single-crystal (0001) Al₂O₃ substrate. The ~100 eV primary electrons from a hollow cathode plasma electron source (HC-PES) are incident on the β -Ga₂O₃ sample. The HC-PES is a chemically robust electron source capable of delivering >200 mA over an area >10 cm². The HCl reactive background gas (RBG) is present at ~1 mTorr. A small positive voltage of <50 V is applied to the sample stage.

The β -Ga₂O₃ film thickness was monitored using *in situ* spectroscopic ellipsometry during electron exposure. Figure 1 shows that the etching of β -Ga₂O₃ is tunable from 1-50 Å/min by varying the stage voltage from 0 to +40 V, respectively. No etching was monitored from electron exposures without the HCl RBG. Negligible etching was observed without a positive sample stage. The following mechanism can explain these results: (1) The primary electrons at ~100 eV can generate secondary electrons from the substrate. (2) The lower energy secondary electrons can attach to the HCl gas in the reactor. (3) The electron attachment then dissociates HCl into H + Cl⁻ through dissociative electron attachment ionization. (4) The Cl⁻ negative ions are attracted to the sample by the positive sample stage voltage. (5) The incoming Cl⁻ flux leads to an enhancement in etch rate resulting from the formation of volatile chloride species. An illustration of this proposed mechanism is shown in Figure 2.

The β -Ga₂O₃ etching was reproducible and only weakly dependent on the primary electron energy from 100-150 eV. The electron current going to ground through the sample also increased with positive sample voltages as expected if the secondary electrons are pulled back to the sample. Surface morphology of the β -Ga₂O₃ was also investigated after the electron enhanced etching. The RMS roughness decreased after etching. The RMS roughness decreased from 1.88 nm to 1.58 nm after the etching process removed 10 nm at +10 V stage voltage. In contrast, the surface roughness did not change after only electron exposures in the absence of HCl RBG.

11:45am **AP2+EM+PS+TF-TuM-16 Bias-Pulsed Atomic Layer Etching**, *Julian Michaels*, University of Illinois at Urbana-Champaign; *N. Deegan*, Argonne National Laboratory, USA; *Y. Tsaturyan*, University of Chicago; *R. Renzas*, University of Nevada Reno; *G. Eden*, University of Illinois at Urbana-Champaign; *D. Awschalom*, University of Chicago; *J. Heremans*, Argonne National Laboratory, USA

Atomic layer etching (ALE) is a binary cyclical process noted for its ability to controllably remove atomic monolayers for nanotechnological device fabrication; however, its relatively slow effective etch rate, often less than a monolayer each minute (tenths of an Angstrom per second), limits its applicability to niche devices that necessitate unmatched precision. If the process were slightly faster, semiconductor, optical, and quantum devices would be regularly implementing ALE because it can reach critical dimensions more consistently while simultaneously offering a smoother post-etch surface, both of which deliver superior device performance regardless of the application.

ALE is slow because the chemical reagent gas(es) is purged in and out of the chamber during each cycle. This is standard practice so that the binary steps, chemical and physical, are fully separated, but purge steps also tend

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to be the most time-consuming components of any ALE process. Thus, if shortening the cycle duration (speeding up the effective etch rate) is the aim, minimizing purge step duration is a sensible first pursuit.

Bias-pulsed atomic layer etching (BP-ALE) is the execution of the above goal with plasma etching in perhaps the simplest way possible. While traditional plasma ALE often pulses gas flows, plasma DC bias, chamber pressure, substrate temperature, and other parameters, BP-ALE achieves atomic precision by pulsing merely the plasma DC bias, hence "bias-pulsed" indicates that the plasma DC bias is the only parameter that distinguishes the steps, and the purge step duration is absolutely minimized as there is no gas purging whatsoever.

As of now, BP-ALE has been demonstrated in both 4H-SiC and diamond, where the usual ALE cycle duration that often exceeds a minute is superseded by the 6-second cycles of BP-ALE, and smoothing to subangstrom RMS surface roughness is achieved for both after etch treatment. This talk seeks to outline the main differences between BP-ALE in execution and potential applications, explain the material and chemistry characteristics needed for a viable BP-ALE method, and predict material/chemistry systems that are suitable for BP-ALE processing.

12:00pm AP2+EM+PS+TF-TuM-17 Atomic Layer Etching of 2D Transition Metal Dichalcogenides Semiconductors and Its 2D Device Application, Jeongmin Kim, J. Kim, Seoul National University, Republic of Korea

Transition metal dichalcogenides (TMDs), a class of 2D materials, possess a layered structure with individual layers bound by van der Waals forces. TMDs exhibit excellent electrical properties and have potential applications in various fields due to their low surface defect density. Moreover, TMDs possess a unique property where the bandgap varies with the number of layers, leading to changes in electrical characteristics depending on the thickness. Therefore, precise control of TMD thickness is crucial. Conventional etching methods, such as reactive ion etching, suffer from plasma-induced damage or difficulties in precise thickness control, making them unsuitable for accurate thickness control of TMDs. Consequently, atomic layer etching (ALE) utilizing self-limiting reactions has been devised to achieve precise thickness control at the atomic level.

We developed an ALE process for TMDs utilizing the adsorption of SF₆ gas, which exhibits minimal reactivity at room temperature. In a capacitively coupled plasma system, an etching with constant-thickness for each cycle was achieved by adsorbing SF₆ followed by Ar⁺ ion bombardment at an appropriate radio frequency (RF) power. The etch rate was controllable, and no change in the etching rate was observed within a specific RF power range. This was realized by the self-limiting reaction induced by the decomposition of SF₆ under Ar⁺ ion bombardment where further sputtering does not occur once all of the adsorbed SF₆ molecules are consumed. Using our ALE process, TMD-based recessed-channel FETs were fabricated. The electrical characteristics and device performance were evaluated, showing a decrease in off-current with reduced channel thickness and no significant deterioration in device performance. This ALE method enables precise thickness control while maintaining the crystallinity of the channel in TMD-based electronic devices, contributing to device performance enhancement. The ALE technology developed in this study paves the way of the advanced application with the TMD-based electronic devices.

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Plasma Science and Technology Room 124 - Session PS1-TuM

Plasma Processes for Advanced Memory

Moderators: Sebastian Engelmann, IBM T. J. Watson Research Center, Angeliqe Raley, TEL Technology Center America

8:00am PS1-TuM-1 Control of High Aspect Ratio Dielectric Etch Profile using Additive Etching Gases, Hyun Woo Tak, C. Choi, M. Park, J. Lee, B. Kim, J. Jang, E. Kim, D. Kim, G. Yeom, Sungkyunkwan University (SKKU), Republic of Korea

To form high-density memory devices, high aspect ratio contact (HARC) etching is critical as it determines the integration density of memory devices. Given that there is no standardized definition of "high" in high aspect ratio, it is crucial to continuously improve the HARC etching capability to meet the requirements of next generation memory devices. In this study, the effects of various additive etching gases added with only a

few standard cubic centimeters per minute (sccm) flow rates on etch characteristics of HARC structures were investigated. It is found that, by using a few sccm of various fluorine, sulfur and metal containing gases added to the process gases, etch characteristics such as etch selectivity, etch profile, and pattern charging can be controlled during the HARC etching. Detailed results on the effects of these gases such as etch rates, selectivity, and profiles, assessed through scanning electron microscopy (SEM) analyses will be provided in the presentation. Moreover, to understand the etch mechanism, the plasma and surface characteristics after addition of the additive gases were investigated by optical emission spectroscopy (OES), quadrupole mass spectrometry (QMS), and X-ray photoelectron spectroscopy (XPS). This research demonstrates that small additive gases in addition to main etch gases can significantly affect next-generation HARC etching processes, paving the way for advanced memory device fabrication.

8:15am PS1-TuM-2 Experimental and Molecular Dynamics Simulation Study of W and WSi Hard-Mask Etching by Fluorocarbon Plasmas, Hojun Kang, Osaka University, Japan, Republic of Korea; S. Kawabata, Osaka University, Japan; N. Mauchamp, Osaka University, Japan, France; E. Tinacba, Osaka University, Japan, Philippines; T. Ito, Osaka University, Japan; S. Kang, D. Lee, J. Son, Samsung Electronics, Republic of Korea; K. Karahashi, S. Hamaguchi, Osaka University, Japan

In response to the growing demand for high-density memory devices, driven by the advancement of smartphones, data centers, and AI technologies, the development of efficient fabrication techniques for complex structures of DRAM and 3D NAND devices has become increasingly critical. This necessitates the enhancement of plasma etching capabilities with high-energy ions, especially the development of mask materials with little erosion under high-energy ion irradiation. This study aims to clarify the etching characteristics of W-based hard masks under SiO₂ etching conditions with fluorocarbon plasmas. W-based hard masks are among the candidate materials to replace conventional Si or C-based hard masks. With a mass-selected ion beam system[1], W and WSi sample surfaces were irradiated with high-energy Ar⁺ and CF₃⁺ ions ranging from 500 to 4000 eV, with an ion dose of 1~2×10¹⁷ ions/cm². After ion irradiation, etched depths were measured with a surface profiler, and the etching yields were evaluated. Changes in the surface atomic compositions and chemical bonding were assessed through ex situ X-ray photoelectron spectroscopy (XPS). The depth profiles of the atomic composition below the etched surfaces were also measured with XPS employing 1,000 eV Ar⁺ ion etching. Our findings indicate that, below 1,000 eV, CF₃⁺ ions exhibit lower etching yields on W-Si masks compared to Ar⁺ ions; however, this trend reverses at energies exceeding 2000 eV. At lower energies, the formation of a W-C mixed layer inhibits the etching yield. Molecular dynamics (MD) simulations were also performed to evaluate the beam-surface interactions. The simulations used an embedded atom method (EAM) interatomic potential functions for W-W interactions [2], and Stillinger-Weber (SW)-type interatomic potential functions for W-C and W-Si interactions developed in this study. The study found good agreements between the experimental findings and simulated data. The force fields developed in this study allow further MD simulation of challenging etching scenarios that are hard to investigate by experiments only, such as etching with high incident angles, various ion energies, and high-aspect-ratio (HAR) etching with sidewall effects. This study underscores the potential of W-based hard masks in next-generation memory fabrication, offering critical insights into the surface reactions essential for optimizing the etching processes, supported by both experimental and simulation data.

References

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- [2] D. R. Mason, et al., J. Phys.: Condens. Matter **29** 505501 (2017)

8:30am PS1-TuM-3 3D NAND Dielectric Etch Technology Challenges and Breakthrough, Youn-Jin Oh, T. Lill, M. Wilcoxson, T. Kim, H. Singh, Lam Research Corporation

INVITED

Three-dimensional NAND technology has revolutionized the landscape of memory storage, enabled higher capacities and improved performance in semiconductor devices. However, the fabrication of 3D NAND structures presents unique challenges, particularly in the plasma etching. This presentation explores the challenges of plasma etching encountered and the indispensable role of new chemistries in cryogenic etch processes.

In 3D NAND device manufacturing, the vertical stacking of memory cells increases continuously, and lateral scaling has been tightened simultaneously, which brings more challenges to plasma etch process. The

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introduction of cryogenic etch has been able to breakthrough the critical challenges of vertical etch rate, mask selectivity, and critical dimension (CD) control, which enable us to scale up continuously.

In the cryogenic etch process, the role of chemical interactions on surfaces emerges as pivotal. In this presentation, the process breakthrough with various new chemistries will be discussed on the high aspect ratio $\text{SiO}_2/\text{Si}_3\text{N}_4$ (O/N) stacks in a capacitively coupled plasma (CCP) etcher which has high power, dual frequency, and high conductance capabilities. How cryogenic process performance is optimized with the synergy between new chemistries and advanced plasma modulation techniques will also be presented.

9:00am PS1-TuM-5 Patterning Challenges of Thick Tungsten Carbide Hard Mask Layers, Daniel Montero, K. Katcko, F. Lazzarino, IMEC, Belgium

Newer technology nodes are increasingly demanding the patterning and integration of High aspect ratio vias (HAR) with increasing aspect ratios (AR) to meet stricter chip design requirements. For some fields, as in memory applications, it comes at the cost of increasing the stack height to accommodate more memory layers, while in logic patterning, a reduction in the via critical dimension (CD) may also be necessary. High AR vias are challenging structures to pattern from the plasma etch point of view, as it requires a precise control of the plasma parameters to pattern straight HAR vias, while reducing the bowing, undercut and hard mask consumption. For most applications using HAR vias, the target layers to pattern are dielectrics, which require the use of a long plasma etch process, and hence a highly selective hard mask (HM) layer able to resist this process. Most hard mask layers may lack enough selectivity to achieve the desired dielectric HAR via patterning quality in terms of selectivity, bowing and uniformity.

Our previous work [1] demonstrated that Tungsten Carbide (WCx) HM layer may exhibit higher selectivity than other HM in Back End of Line applications. However, the results derived in [1] cover the development of thin WCx layers (up to 15 nm thick) for line-space patterns. In this work, we extend and detail the etch development of thick WCx layers, up to 350 nm thick, in the context of HAR via 3DNAND memhole patterning applications. Our test vehicle uses immersion lithography at 193 nm to pattern staggered vias at 480 nm pitch into a 1 μm thick silicon oxide layer, with expected AR of 8.0 and 5.3 for 60 and 90 nm CD vias respectively.

In a first approach, we used Continuous Wave (CW) plasma, derived from [1], with an adapted etch time to pattern the 350 nm thick WCx layer, but it showed limited performance. Hence, a redevelopment of the plasma etch process was needed to guarantee uniform, straight, and complete opening of the thick WCx HM layer. Different passivation and etching methods, as well as the use of Synchronized Pulsed Plasma, are proposed to improve the patterning performance of WCx layers. Then, the 300 mm wafers continue processing towards the oxide etch, and selectivity to WCx HM is evaluated. The results are then compared to the reference HM of the test vehicle, Amorphous Carbon Layer (ACL). WCx HM showed better selectivity and lower corner erosion than the ACL reference layer, proving that WCx layers may be a valuable candidate for HAR via patterning in 3DNAND memhole applications.

References: [1] D. Montero et al, *Exploring the use of Tungsten-based Hard Masks in BEOL interconnects for 3nm node and beyond*. AVS68 2022.

9:15am PS1-TuM-6 Sheath Uniformity with Pulsed Low Frequency Biases for High Aspect Ratio Plasma Etching, Evan Litch, M. Kushner, University of Michigan

Current roadmaps for microelectronics fabrication place focus on fabrication of 3-dimensional devices for higher functionality requiring increasing high aspect ratio (HAR) features. 3D-NAND memory structures containing hundreds of alternating layers of SiO_2 and Si_3N_4 require etching of vias having aspect ratios (ARs) exceeding 100. Deep trench isolation (DTI) for electrical isolation have similar HAR challenges. DTI etching of conductive substrates using halogen gas mixtures (e.g. HBr/Cl_2) is typically performed in inductively coupled plasmas (ICPs) with a substrate bias to facilitate highly anisotropic etching.

Plasma etching of HAR features requires ion energy and angular distributions (IEADs) that are high in energy, more than several keV, and narrow angular distribution. These requirements motivate the use of very low frequency biases (VLF) – 100s kHz. Concurrently, there is a transition to using pulsed biases to optimize the ratio of radical to ion fluxes. One of the motivations for pulsing is to gain the advantages of high peak power that produces higher energy ions with narrow angle distribution while lowering the average power deposition. However, pulsing at higher voltages thicken

the sheath while low frequencies charge focus rings (FR), that can lead to significant sheath curvature at substrate boundary thereby modifying IEADs away from desired characteristics.

In this presentation, results will be discussed from a computational investigation of IEADs incident onto wafers and remediation of edge exclusion when using pulsed VLF biases in ICPs for etching of trenches for DTI and TSVs (through silicon vias). Simulations were conducted using the Hybrid Plasma Equipment Model (HPEM). Operating conditions are tens of mTorr mixtures of $\text{Ar}/\text{Cl}_2/\text{O}_2$ with bias frequencies from 250 kHz to 5 MHz. Bias voltages are up to a few kV with pulse repetition frequencies of up to 10s kHz. The consequences of these operating conditions on etching DTI and TSV features were evaluated using the Monte Carlo Feature Profile Model (MCFPM). When using continuous wave biases, the charging of the FR is sensitive to frequency, and this charging produces sheath curvature at the edge of the wafer, which perturbs IEADs. With pulsed biasing, the FR is transiently charged both during the VLF cycle and during the pulsed cycle, adding additional challenges to minimizing edge exclusion. Comparisons for different reactor/FR properties will be discussed.

This work was supported by Samsung Electronics Co. and the US National Science Foundation (2009219).

9:30am PS1-TuM-7 Study of Electrode Material Effects on High Aspect Ratio SiO_2 Etching in CCP Etch Systems, Chanhyuk Choi, H. Tak, S. Kim, M. Park, J. Lee, B. Kim, J. Jang, E. Kim, D. Kim, G. Yeom, Sungkyunkwan University (SKKU), Republic of Korea

In semiconductor memory device manufacturing, plasma etching, particularly for high aspect ratio contact (HARC), has become increasingly crucial. A significant challenge is the uneven polymer deposition on the sidewalls of structures, leading to ion tilting, charging effects, and pattern distortion. Recent advancements have focused on integrating conductive materials, especially tungsten (W) by using WF_6 as an additive gas. WF_6 gas addition to the process gases has been effective in forming conductive polymers that resist etching, improving etch profiles, thus enhancing precision in etching. This study examines the use of a different showerhead material in addition to Si showerhead as an upper electrode with DC voltage for etching, comparing it to the traditional showerhead made of Si to assess their impacts on etching properties.

The SiO_2 etch rate was increased for all showerheads used in the experiment with increasing DC voltage, while the amorphous carbon layer (ACL) etch rate was remaining constant, indicating enhanced selectivity. The Si showerhead showed minimal improvement in removing charging with increased voltage, whereas the other showerhead significantly enhanced the bottom etch profile due to improved charge related issues. That is, Si showerhead showed bottom hole distortion, and which was not improved with increasing DC voltage to the showerhead while the other showerhead showed improved bottom hole shapes and profiles at higher DC voltages indicating improved charging related issues. XPS also showed a higher showerhead material atomic percent (at%) on the substrate for the -600V process compared to the 0V process when using the other showerhead, indicating more conductive polymer formation during the etching.

The etching with the other showerhead showed more anisotropic and undistorted etch profiles of ACL masked SiO_2 holes compared to the etching with Si showerhead due to lower charging related issues during the SiO_2 etching with polymer forming fluorocarbon gases due to the formation of more conductive polymer on the substrate during the etching. This research provides new insights into the role of electrode material reactivity in advanced etching processes of high aspect ratios in CCP systems.

9:45am PS1-TuM-8 Low GWP and Low Emission Gases for High Aspect Ratio Etching Application, Scott Biltek, N. Stafford, P. Nguyen, F. Qin, Air Liquide; P. Forest, Air Liquide, France

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. When it comes to manufacturing chips, plasma etch processes contribute significantly to emissions, especially in dielectric etching. High aspect ratio structures are commonly used in both memory (3D NAND and DRAM) as well as logic chip manufacturing processes. These structures are traditionally etched using fluorocarbon and hydrofluorocarbon gases to etch very challenging dielectric structures. Unfortunately these gases, such as C_4F_8 , CH_2F_2 , CHF_3 , CF_4 , etc have very high Global warming potentials (GWP) along with other gases like C_4F_6 and CH_3F which have low input GWP but potentially high GHG emissions.

However, while there has been a significant amount of work over the years to develop alternative low GWP etching gases, it is not only difficult to incorporate these chemistries in such very challenging etch processes but also understanding the emitted species from the plasma into the exhaust is rather limited. As the plasma dry etching is an extremely complex process involving chemical bond dissociation, recombination, side reactions, etc it is difficult to predict with any accuracy the post plasma exhaust stream and thus the CO₂ equivalence of the plasma byproducts.

In this work we will present novel low GWP etching gases to replace traditional high GWP gases such as C₄F₈ and CHF₃/CH₂F₂ that not only give improved etching performance but reduce the CO₂ equivalent (CO₂ eq) emissions from the etch chamber exhaust. This work utilizes Fourier Transform Infrared Spectroscopy (FTIR) to measure the exhaust stream of a 300mm CCP plasma etch chamber. Finally, we will present an etching recipe exclusively composed of low GWP etching gases.

Plasma Science and Technology Room 124 - Session PS2-TuM

Plasma Processing at Cryogenic Temperatures

Moderators: Angelique Raley, TEL Technology Center America, Mingmei Wang, TEL Technology Center, America, LLC

11:00am **PS2-TuM-13 Plasma Prize Award Talk: The Evolution of Cryogenic Etching Plasma Processes Since Their Introduction 35 Years Ago, Remi Dussart¹**, GREMI CNRS/Université d'Orléans, France **INVITED**

Cryoetching was first introduced in 1988 by Tachi's team to selectively etch silicon and form anisotropic trench profiles [1]. Since these very first experiments, etching at very low substrate temperature has been developed and studied. In particular, a passivation mechanism involving both fluorine and oxygen was found and characterized by in-situ diagnostics. [2] Cryogenic etching was also studied for other materials than silicon: metal and dielectric material cryoetching was also investigated. Due to the enhanced physisorption of some radicals on cold surfaces, it is possible to foster some reactions and modify the composition of the deposited layer at the sidewalls. One of the advantages relies on the low contamination of the reactor walls since deposition in cryoetching is efficient on low temperature surfaces only. Cryoetching was successfully used for porous ultra-low-k materials [3]. Experiments on cryo-Atomic Layer Etching were also carried out and self limiting etching was shown. [4] More recently, cryoetching was used to etch 3D NAND very high aspect ratio structures composed of thin SiO₂ and Si₃N₄ repetitively stacked layers. [5] A different chemistry involving HF was used and a new etching mechanism was proposed for both dielectrics.

The presentation will be focused on the evolution of the cryogenic etching process from its introduction to the most advanced developments that have been recently disclosed.

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 - [3] R. Chanson, L. Zhang, S. Naumov, Yu. A. Mankelevich, T. Tillocher, P. Lefauchaux, R. Dussart, S. De Gendt, J.-F. de Marneffe, Sci. Rep. 8:1886 (2018).
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11:30am **PS2-TuM-15 The Role of PF₃ on Etching Characteristics of SiO₂ and SiN Using HF-Based Cryogenic Plasma Etching Analyzed with in situ Monitoring Techniques, Shih-Nan Hsiao, M. Sekine**, Nagoya University, Japan; Y. Iijima, R. Suda, M. Yokoi, Y. Kihara, Tokyo Electron Ltd. Miyagi, Japan; M. Hori, Nagoya University, Japan

Since the introduction of 3D architecture in NAND Flash Memory technology in 2014, the areal density has significantly increased. With the stacking of more layers to enhance data capability, the fabrication of memory channel holes with very high aspect ratios becomes a major challenge. One of the most demanding etch processes for fabricating

advanced 3D NAND structures is the high-aspect-ratio contact (HARC) hole etch. Recently, cryogenic plasma etching containing hydrogen fluoride (HF)-containing species has been reported to mitigate surface charging effects while significantly increasing the throughput of SiO₂ etching [1, 2]. Furthermore, a significant enhancement of ONON etching by adding PF₃ to HF plasma has also been reported [3]. To understand the role of PF₃ in surface reactions and etching mechanisms, cryogenic etching of SiO₂ and SiN using HF diluted with PF₃ was investigated. A quasi-atomic layer etching (quasi-ALE) of SiO₂ and SiN film was conducted by using HF/PF₃/O₂ plasma for surface modification, followed by an Ar plasma for etching. *In situ* monitoring techniques, including spectroscopic ellipsometry and attenuated total reflectance Fourier transformation infrared spectroscopy (ATR-FTIR), were used to analyze the surface structure and etching characteristics. The substrate temperature (T_s) was controlled from 20 to -60 °C by circulating a coolant through the bottom electrode. At -20 °C, real-time thickness variation versus Ar sputter time exhibited a greater etched depth per cycle (EPC) after the Ar ion sputtering, compared to that at 20 °C. (see supplemental document for details). Surface structure observation using *in situ* ATR-FTIR revealed an increase in surface-adsorbed HF due to the presence of H₃PO₄ at -20 °C during the surface modification step, consistent with the results of density function theory simulations. This observation explains the increase in etched depth of SiO₂ attributed to the increased amount of surface-adsorbed HF. Conversely, the EPC vs T_s for the SiN exhibited an opposite tendency. Although more surface-adsorbed HF was also confirmed on the SiN surface using the plasma with PF₃ addition, the EPC was lower compared to pure HF. The surface structure observations reveal that the presence of P₃N₅ phase on the SiN surface, which might hinder the etching.

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- [2] S.N. Hsiao et al., Small methods (Under review).
- [3] Y. Kihara et al., VLSI symposium T3-2 (2023).

11:45am **PS2-TuM-16 MD Simulations of Cryogenic Etching of SiO₂ by HF Plasmas, Nicolas Mauchamp**, Osaka University, Japan; T. Lill, M. Wang, H. Singh, Lam Research Corporation; S. Hamaguchi, Osaka University, Japan

Plasma etching is a key technology for the manufacturing of semiconductor devices. Cryogenic etching, first introduced in 1988 by Tachi *et al.*, is an etching process at a very low material temperature (-50°C or lower). The extremely low surface temperature typically contributes to faster etching, a better control of etched profiles, and reduced contamination from the chamber walls. However, there seems an optimal temperature for the best etching results and too low a temperature can impede the desired etching process. This study attempts to clarify the surface reaction mechanisms of cryogenic etching of silicon dioxides (SiO₂) by hydrogen fluoride (HF) plasmas with molecular dynamics (MD) simulations. In the MD simulations, a SiO₂ material surface was thermalized at 200 K (-73.15°C) to emulate cryogenic conditions. Under such conditions, a relatively thick layer of gaseous species (HF molecules in our case) is formed on the material surface due to condensation. The surface is then exposed to highly energetic ions of Ar⁺ (or other ions from HF plasmas) with an incident energy of 1 keV or higher, together with a large flux of gaseous HF molecules that continue to condense on the material surface. The MD simulation results showed that the energetic ion impact caused the mixing of F and H atoms from the condensed layer in the material's subsurface layer and lead to efficient reactive ion etching of SiO₂. The material surface chemical composition, the sputtering yields, and desorbed species were analyzed under different etching conditions. It was found that, with an increasing flux ratio of HF molecules to incident ions, more F atoms accumulated in the material's subsurface layer and the sputtering yield of SiO₂ increased.

12:00pm **PS2-TuM-17 Mechanisms for Cryogenic Plasma Etching, Y. Yook, Mark J. Kushner**, University of Michigan

The increasing demands for high-aspect-ratio (HAR) plasma etching for 3-dimensional devices has produced a resurgence in innovations in cryogenic etching. Cryogenic plasma etching (CPE) is a process in which the substrate in an otherwise conventional capacitively coupled plasma is cooled temperatures as low as -90 C. The lower substrate temperature is thought to increase the rate of adsorption of precursor species to the degree of having a thin condensed layer. CPE of dielectric materials have produced etch rates of up to several times that of conventional etching for aspect ratios exceeding 100 though the mechanisms for this performance are unclear. Recipes for CPE of SiO₂ range from fluorocarbon gases with H₂ additives to Ar/HF mixtures. A common feature of such mixtures is production of HF and H₂O (the latter by either gas phase or surface

¹ PSTD Plasma Prize Winner

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processes) which is hypothesized to produce a condensed hydrofluoric acid-like layer at the surface which would normally produce isotropic etching. The lower temperature reduces the rate of isotropic etching, which then enables anisotropic etching by ion-bombardment. The use of additives such as PF_3 suggests that there may also be a catalytic component to the process. In gas mixtures that do not contain, for example, fluorocarbon species there is not a natural source of passivation for sidewall control, which suggests that passivation is in the form of etch products.

In this presentation, results will be discussed from a computational investigation of CPE of SiO_2 on reactor and feature scales using the Hybrid Plasma Equipment Model (HPEM) and Monte Carlo Feature Profile Model (MCFPM). The processing conditions are single- and dual-frequency capacitively coupled plasmas of tens of mTorr pressure. An investigation of surface kinetics during CPE was first performed while artificially specifying reactive fluxes to the wafer for Ar/HF gas mixtures. The consequences of adsorption probabilities, redeposition of etch products and enhanced yield on etch rate and profile control will be discussed. Results for coupled reactor and feature scale simulations for CPE of SiO_2 using CF_4/H_2 and Ar/HF mixtures will then be discussed with the goal of determining whether these proposed mechanisms are consistent with practice in high volume manufacturing.

Atomic Scale Processing Mini-Symposium Room 116 - Session AP+PS+TF-TuA

Atomic Layer Etching III: Plasma Processes

Moderators: Robert Bruce, IBM Research, T. J. Watson Research Center, Udyavara Sagar, Lam Research

2:15pm AP+PS+TF-TuA-1 Atomic Layer Etching with Plasma Processing for Semiconductor Device Fabrication, **Heeyeop Chae**, Sungkyunkwan University (SKKU), Republic of Korea

INVITED

The critical dimensions of semiconductor devices are continuously shrinking in nanometer and atomic scale with 3D device structure. The demand for dimension control in angstrom level is drastically increasing also in etching processes. Atomic layer etching (ALE) processes are being actively studied and developed for various metals, semiconductor, and dielectric materials. In this talk, plasma processes for atomic layer etching will be discussed for both isotropic and anisotropic patterning of metals and dielectric materials including molybdenum, ruthenium, cobalt, titanium nitride, tantalum nitride, hafnium oxide, zirconium oxides. [1-9] Typical ALE processes consist of surface a modification step and a removal step. For the surface modification, various fluorination, chlorination and oxidation schemes were applied including fluorocarbon deposition, halogenation, oxidation with radicals generated plasmas. For the removal or etching step, various schemes were applied including ion-bombardment, heating, ligand volatilization, ligand exchange, and halogenation. The surface characteristics such as surface roughness and surface residue after plasma-enhanced ALE processes will be also discussed.

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- 3) Y. Kim, S. Lee, Y. Cho, S. Kim, H. Chae, *J. Vac. Sci. Technol. A*, 38(2), 022606 (2020)
- 4) D. Shim, J. Kim, Y. Kim, H. Chae, *J. Vac. Sci. Technol. B.*, 40(2) 022208 (2022)
- 5) Y. Lee, Y. Kim, J. Son, H. Chae, *J. Vac. Sci. Technol. A.*, 40(2) 022602 (2022)
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2:45pm AP+PS+TF-TuA-3 Atomic Layer Etching in HBr/He/Ar/O₂ Plasmas, **Qinzhao Hao**, M. Elgarhy, University of Houston; P. Kim, S. Nam, S. Kang, Samsung Electronics Co., Republic of Korea; V. Donnelly, University of Houston

Atomic layer etching (ALE) of Si is reported in a radio frequency (RF) pulsed-power inductively-coupled plasma (ICP), with periodic injections of HBr into a continuous He/Ar carrier gas flow, sometimes with trace added O₂. Several pulsing schemes were investigated, with HBr injection simultaneous with or alternating with ICP power. The product removal step was induced by applying RF power to the substrate, in sync with ICP power. Etching and dosing were monitored with optical emission spectroscopy. Little or no chemically-enhanced ion-assisted etching was observed unless there was some overlap between HBr in the chamber and ICP power. This indicates that HBr dissociative chemisorption deposits much less Br on Si, compared with that from Br created by dissociation of HBr in the ICP. Chemically-assisted etching rates nearly saturate at 2.0 nm/cycle as a function of increasing HBr-containing ICP dose at -75 V_{DC} substrate self-bias. The coupled effects of O₂ addition and substrate self-bias DC voltage on etching rate were also explored. Etching slowed or stopped with increasing O₂ addition. As bias power was increased, more O₂ could be added before etching stopped.

3:00pm AP+PS+TF-TuA-4 Comparisons of Atomic Layer Etching of Silicon in Cl₂ and HBr-Containing Plasmas, **Mahmoud Elgarhy**, Q. Hao, University of Houston; P. Kim, S. Nam, S. Kang, Samsung Electronics Co.; V. Donnelly, University of Houston

This talk will report an experimental investigation of Cl₂ vs. HBr for plasma atomic layer etching (ALE) of silicon. An inductively coupled plasma (ICP) source with a constant flow of Ar (and sometimes He) carrier gases, and

HBr or Cl₂ as a dosing gas was used for etching Si (100) samples. Optical emission spectroscopy was used to follow relative yields of SiCl, SiCl₂, SiBr and SiBr₂, and scanning electron microscopy and profilometry were used to measure etching rates. HBr and Cl₂ residence times in the chamber were determined by measuring time-resolved pressure during gas dosing. It was found that the pressure rise and fall times were much longer for HBr compared to Cl₂, suggesting that HBr hangs up on the chamber wall after gas dosing. The effect of the delay time between gas dosing and the start of ICP power on the etching rate was also investigated. When HBr or Cl₂ were injected into the reactor with the plasma on, etching occurs for both sources, with Cl₂ having a higher etching rate. When HBr or Cl₂ were fed to the reactor with the plasma off, only Cl₂ etches. This indicates that the HBr does not chemisorb on Si, and bromination of the surface requires the plasma to form Br atoms, which do adsorb.

3:15pm AP+PS+TF-TuA-5 Atomic Layer Etching of Crystalline MoS₂ by Plasma Fluorination and Oxygenation, **Sanne Deijkers**, C. Palmer, N. Chittock, E. Kessels, A. Mackus, Eindhoven University of Technology, The Netherlands

Molybdenum disulfide (MoS₂) is a two-dimensional (2D) transition metal dichalcogenide (TMD) with applications in catalysis and nanoelectronics.¹⁻³ To enable integration of 2D materials in nanoelectronics, highly controlled and low-damage etching processes are required. One example of such a process is the atomic layer etching (ALE) of WSe₂.⁴ In this work, we present a plasma ALE process to etch crystalline MoS₂. The process involves plasma fluorination and oxygenation, targeting Mo-O-F as a volatile species. Previous work using the approach of fluorination and oxygenation involved thermal chemistries with an etch-per-cycle (EPC) of 0.5 Å for amorphous films and 0.2 Å for crystalline films.⁵ As plasmas are more reactive than their gaseous counterparts, they are expected to allow for etching crystalline materials.

Fluorination was performed by a SF₆-based plasma, and as removal step various oxygen sources were tested. To avoid continuous etching of the MoS₂, the plasma composition of the fluorination step had to be optimized.⁶ Addition of H₂ to the plasma mixture reduces F radical concentration by creating HF species *in situ*.⁷ With an adequate H₂ content using a ratio of SF₆:(SF₆+H₂) < 0.3, continuous etching is suppressed, and only modification of the top surface takes place. As second half-cycle, H₂O, O₂ gas and O₂ plasma exposures were tested. Of these only an O₂ plasma resulted in etching, while dosing H₂O or O₂ gas resulted in no measurable thickness change. Raman measurements showed a strong decrease in the characteristic E_{12g} and A_{1g} peaks, indicating etching of crystalline MoS₂. The complete ALE recipe with saturated SF₆-based plasma and O₂ plasma exposures had an EPC of 1.1 ± 0.2 Å at 300 °C table temperature.

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3. Deijkers, J. H. *et al. Adv. Mater. Interfaces* 4–9 (2023).
4. Nipane, A. *et al. ACS Appl. Mater. Interfaces*13, 1930–1942 (2021).
5. Soares, J. *et al. Chem. Mater.*35, 927–936 (2023).
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7. Hossain, A. A. *et al. J. Vac. Sci. Technol. A*41, (2023).

4:00pm AP+PS+TF-TuA-8 A Reduced Order Model of Plasma-Surface Interactions in Atomic Layer Etching, **David Graves**, Princeton University; J. Vella, TEL Technology Center, America, LLC

Any future physics-based, rather than purely data-driven, digital twin of a plasma tool and process will need a reduced order model (ROM) of the effects of the plasma on the surface being processed. In this talk, I present one possible version of a ROM for simulating a plasma atomic layer etching (ALE) process. The ROM is based on a transient version of a surface site balance model that was first applied in the 1980s for plasma etching. Classical molecular dynamics (MD) simulations of ALE of Si using Cl₂/Ar⁺ cycles are first validated with experimental measurements and then used to provide values for parameters (e.g., ion energy dependent etch yields) for a transient site balance model of the process. The ROM is computationally much faster than the MD simulations and is shown to reproduce additional, and previously unexplained, experimental results. Future applications of MD to plasma-surface interactions in semiconductor device fabrication will likely use another type of ROM. MD methods require interatomic potentials or force fields for all simulated atomic interactions. The force field parameters can be inferred from higher level methods such as density functional theory (DFT), coupled with neural net data-driven algorithms. I

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will conclude with preliminary results using one such approach, namely Deep Potential MD (DeePMD), to develop illustrative force fields.

4:15pm AP+PS+TF-TuA-9 Atomic Layer Etching of SiO₂ using Sequential Exposures of Al(CH₃)₃ and H₂/SF₆ Plasma, David Catherall, A. Hossain, A. Minnich, California Institute of Technology

On-chip photonic devices based on SiO₂ are of interest for applications such as microresonator gyroscopes and microwave sources. Although SiO₂ microdisk resonators have achieved quality factors exceeding one billion, this value remains an order of magnitude less than the intrinsic limit due to surface roughness scattering. Atomic layer etching (ALE) has potential to mitigate this scattering because of its ability to smooth surfaces to sub-nanometer length scales. While isotropic ALE processes for SiO₂ have been reported, they are not generally compatible with commercial reactors, and the effect on surface roughness has not been studied. Here, we report an ALE process for SiO₂ using sequential exposures of Al(CH₃)₃ (trimethylaluminum, TMA) and Ar/H₂/SF₆ plasma. We find that each process step is self-limiting, and that the overall process exhibits a synergy of 100%. We observe etch rates up to 0.58 Å per cycle for thermally-grown SiO₂ and higher rates for ALD, PECVD, and sputtered SiO₂ up to 2.38 Å per cycle. Furthermore, we observe a decrease in surface roughness by 62% on a roughened film. The residual concentration of Al and F is around 1-2%, which can be further decreased by O₂ plasma treatment. This process could find applications in smoothing of SiO₂ optical devices and thereby enabling device quality factors to approach limits set by intrinsic dissipation.

4:30pm AP+PS+TF-TuA-10 Atomic Layer Etching of Cu Using Alternating Cycles of Hexafluoroacetylacetone and O₂ Plasma, Yusuke Nakatani, Hitachi High-Tech, Japan; A. Kaye, Colorado School of Mines, USA; Y. Sonoda, M. Tanaka, K. Maeda, Hitachi High-Tech, Japan; S. Agarwal, Colorado School of Mines, USA

Atomic layer etching (ALE) is a critical technology in semiconductor device fabrication, including for interconnect metals such as Cu and Co. Previously, thermal ALE of Cu has been reported using alternating half-cycles of hexafluoroacetylacetone (hfacH) and O₂ or O₃ at ~275 °C. It has also been shown that hfacH cannot spontaneously etch Cu, and peroxidation of the Cu surface is required. In this presentation, we will report on ALE of Cu at a much lower temperature of 150 °C using hfacH and O₂/Ar plasma half-cycles.

The ALE process was monitored using in situ reflection-absorption infrared spectroscopy (RAIRS). Prior to ALE, the Cu wafers were cleaned using a H₂ plasma at a temperature of 300 °C to reduce the native oxide, and to remove the surface carbonates and adsorbed hydrocarbons. Initially, we tested the reactivity of hfacH at 150 °C with a reduced Cu surface, and after re-oxidation with an O₂ plasma. In both cases, in the infrared spectra, we observed absorption bands related to CF₃ (1240 cm⁻¹), C=C, and C=O (1645 cm⁻¹) vibrations. On a reduced Cu surface, the C=C and C=O bands were much weaker indicating decomposition of hfacH. Since hfacH does not spontaneously etch Cu, this indicates that an oxidized Cu surface is required for the adsorption of hfacH. Our infrared data also show that the ALE window is very narrow, and the etch rate could only be measured at 125 and 150 °C. At temperatures lower than 125 °C, our infrared data shows that hfacH does adsorb onto the CuOx surface, but the temperature is likely too low for the formation of the etch products— Cu(hfac)₂ and H₂O. The subsequent O₂ plasma half-cycle simply removes the hfac ligand and oxidizes the surface further. At 150 °C, a balance is established between surface oxidation and removal of CuOx from the surface as Cu(hfac)₂ and H₂O. The etch per cycle at 125 and 150 °C were 0.1 and 0.7 Å, respectively. At temperatures higher than 150 °C, atomic force microscopy shows that the Cu surface roughens due to severe oxidation, and the Cu film thickness cannot be measured with ellipsometry.

4:45pm AP+PS+TF-TuA-11 Enabling Anisotropic and Selective Etch Through Surface Modification of Ru, Owen Watkins, UCLA; H. Simka, Samsung Electronics; J. Chang, UCLA

Ruthenium is a potential replacement for copper in metal interconnects below 10 nm, where the grain boundary scattering and the need for a barrier layer increases the effective resistivity of Cu. Unlike Cu, Ru can be directly etched using O₂-plasma-based processes, allowing a subtractive metal patterning to be used. Current Ru etching processes largely rely on O₂/Cl₂-based RIE. While this process is able to anisotropically etch Ru, it requires Cl₂ and damages the hard mask, resulting in ballooning and low selectivity. A cyclic process that is halogen-free, anisotropic, and selective has been proposed. The process consists of a nitrogen plasma passivation step, hydrogen plasma reduction step, and oxygen plasma etching step. The passivating layer of RuN formed by N₂ plasma exposure can be reduced in

H₂ plasma. Bias applied to the substrate during the H₂ step results in the selective reduction of RuN on the vertically-exposed surface, leaving a layer of RuN on the sidewalls. During the O₂ plasma step, RuN passivates the sidewall from O radicals that would otherwise etch the sidewall. The two surface modification steps cause the normally isotropic O₂ plasma etch to become anisotropic, while maintaining a high selectivity vs. SiO₂ and SiN used as the hard mask. The sequential process has been experimentally shown to be anisotropic and selective, and results in lower resistivity and surface roughness vs. O₂ plasma alone. To understand the effects of the surface modification steps on the overall process, each step of the sequential process has been examined, including the surface composition and structure of the Ru film after each plasma exposure. RuO₂ and RuN thin films were deposited as references, allowing the presence of RuN after nitridation to be confirmed using XPS and XRD. The etch rate of nitridated Ru films was found to be 0.4 nm per minute in O₂ plasma, more than 15 times less than the etch rate of Ru in O₂ plasma at the same conditions. Removal of the N₂ plasma step from the process resulted in isotropic etching, confirming that nitridation is responsible for sidewall passivation. XPS was used to confirm that most, but not all of the RuN surface layer is reduced after exposure to H₂ plasma. H₂ plasma was also found to significantly affect the etching of hard mask SiO₂. Reduction of the plasma density by lowering the power and increasing the pressure was necessary to reduce SiO₂ etching and corner faceting during the H₂ step. The combination of surface modification techniques results in a process that has been demonstrated for features down to 32 nm pitch.

5:00pm AP+PS+TF-TuA-12 Enhanced Control of Plasma Surface Interaction to Etch Alloys Using Transient Assisted Plasma Etching (TAPE), Atefeh Fathzadeh, KU Leuven/IMEC, Belgium; P. Bezaud, IMEC Belgium; T. Conard, F. Holsteyns, IMEC, Belgium; S. De Gendt, KU Leuven/Imec, Belgium

A novel plasma process design called transient-assisted plasma process (TAPP) has been recently introduced to tackle multiple patterning challenges brought by the introduction of 3D devices, new ultra-thin films, and compound materials without suffering from the poor throughput of Atomic layer etching. In the realm of dry-etching, it has exhibited promising patterning capabilities at etch rates compatible with high-volume manufacturing. In deposition applications, it also has demonstrated superior control over precursor dosage and fragmentation for in-situ hard-mask deposition compared to conventional methods. Moreover, from a sustainability perspective, Transient-assisted processing (TAP) presents considerable advantages by notably reducing the consumption of problematic gases. TAPE operates in cycles, involving at least two phases: Time-limited injection of the reactant (with or without plasma), and when the injection is stopped, a gas transient happens in the plasma, where the reactant concentration diminishes over time, as shown in Figure 1. The fluence of reactive species is regulated by the gas pulse characteristics (partial pressure, etc.) and its associated plasma transient, while ion fluence is governed by the duration of the plasma phase. This segregation yields significantly enhanced control over plasma-surface interactions compared to conventional plasma etching techniques. This design is compatible with any gas mixture, and energy sources (ions, photons, electrons, fast neutral species/clusters, etc.).

Enhancing control over plasma-surface interactions holds promise in rectifying the uneven etching observed in multicomponent materials like alloys. This imbalance in etching induces a compositional drift, thereby impeding the process and deteriorating material characteristics as shown in Figure 2a. Typically, one component undergoes predominantly chemical etching, while the other experiences primarily physical etching. In TAPE, most chemically-driven etching occurs early during the plasma step when a substantial amount of etchant is present. The modified surface/profile will then be exposed to a reduced etchant quantity and a continued ion bombardment. Each cycle is thus capable of providing the necessary species for a balanced etching of the compound's elements. Figure 2b compares the chemical composition of InGaZnO after conventional etching and TAPE, while Figure 2c compares the etch rate, and profile relative to a previously published ALE process. Meanwhile, TAPE consumes 25 times less CH₄ than the ALE process.

5:15pm AP+PS+TF-TuA-13 Leveraging Plasma Nitridation for Atomic Layer Etching of Ni₃Al, Taylor G. Smith, University of California, Los Angeles; J. de Marneffe, imec, Belgium; J. Chang, University of California, Los Angeles

Extreme ultraviolet (EUV) lithography is entering a new era with high numerical aperture (NA) EUV, increasing the importance of integrating new absorber layer materials like Ni₃Al to mitigate mask 3D effects. However, Ni₃Al adoption has been limited by difficulties in anisotropically etching

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Ni₃Al with high selectivity to the underlying Ru capping layer. A previously reported ALE based on plasma oxidation was shown effective at etching Ni₃Al but had poor selectivity to Ru, which etches spontaneously in oxygen plasma. An atomic layer etch (ALE) based on plasma nitridation and formic acid (FA) vapor exposure was previously demonstrated to etch Ni²⁺, and in this work the nitridation-based ALE process is extended to the more complex and industrially relevant Ni₃Al. X-ray photoelectron spectroscopy (XPS) is used to analyze the surface composition of blanket Ni₃Al films after plasma nitridation, showing the nitrided films have a stoichiometry of Ni_{2.4}AlN. The effects of plasma power, from 200 to 700 W, and pressure, from 8 to 50 mTorr, on plasma nitridation are examined, with current results indicating that high power and low pressure lead to the greatest amount of surface nitridation. Langmuir probe measurements are used to correlate these effects with changes in plasma density and electron temperature. For the removal half-cycle, FA vapor was shown to remove the nitride layer as indicated by the disappearance of the characteristic metal nitride peak in the N 1s spectrum at 397.2 eV. XPS also shows depletion of Ni as successive ALE cycles are applied, an effect that can be mitigated using basic etchants due to their selective removal of Al over Ni. Selectivity to Ru is measured by etching blanket Ru films and measuring the thickness with SEM, with a current selectivity of 2.4. To assess anisotropy, Ni₃Al is first conformally deposited over a patterned Si substrate by physical vapor deposition (PVD), and the samples are subsequently processed by ALE. The ion energy of the nitrogen plasma is varied by changing the voltage applied to an ion extraction grid from -100 to +100 V, with the sidewall Ni₃Al etch compared to the vertical Ni₃Al etch using scanning electron microscopy (SEM).

¹ T.G. Smith, A.M. Ali, J.F. de Marneffe, J.P. Chang, J. Vac. Sci. Technol. A 42, 022602 (2024).

5:30pm **AP+PS+TF-TuA-14 Precision Etching for Vertical GaN Nanowire Transistor Fabrication: A Focus on Atomic Layer Etching**, *Amin Karimi, R. Jafari Jam, I. Sharma, O. Danielsson, M. Asif, Y. Ilarionova*, AlixLabs A.B., Sweden; *A. Kumar, P. Ramvall*, RISE Research Institutes of Sweden; *D. Suyatin, J. Sundqvist*, AlixLabs A.B., Sweden

Power electronics are essential for our daily lives, driving everything from consumer gadgets to industrial machinery. Gallium Nitride (GaN) stands out in this domain for its superior electrical properties, offering higher efficiency and power density compared to traditional silicon-based devices. Vertical GaN nanowire (NW) high-electron-mobility transistors (HEMTs) represent the forefront of GaN-based technologies, boosting advantages such as increased power density, reduced switching losses, improved heat dissipation, enhanced breakdown voltage, scalability, and radiation hardness. Despite these benefits, conventional fabrication techniques for GaN NW transistors face challenges. Non-uniform mask etching can lead to variations in NW diameters, impacting device performance. Reactive ion etching (RIE), which is often used for mask etching, may damage the substrate surface, compromising interface quality and device functionality. Surface irregularities exacerbate electron scattering, increasing energy dissipation and degrading electrical interfaces. Addressing these issues, atomic layer etching (ALE) emerges as a solution. ALE operates at the atomic level, removing one layer at a time without harming the substrate. Unlike traditional methods, ALE ensures a high-quality interface for improved device performance.

In our study, we utilize ALE to enhance the fabrication of GaN NW-based HEMT transistors. Our method employs fluorine-based chemistry for uniform SiN mask etching, enabling precise pattern transfer, and facilitating uniform NW growth. Additionally, we introduce chlorine-based ALE to refine substrate surfaces, reducing roughness and improving device performance. AFM characterization reveals a substantial decrease in surface roughness, directly contributing to enhanced electrical performance. We use Retarding Field Energy Analyzer (RFEA) data to optimize ALE parameters for different etching steps, and enhancing device fabrication.

In conclusion, our study highlights the potential for ALE processes to improve GaN NW-based HEMT transistor fabrication. By addressing mask uniformity and substrate surface roughness issues, ALE enables the production of GaN devices with superior interface quality and enhanced electrical performance.

Acknowledgment The ALL2GaN Project (Grant Agreement No 101111890) is supported by the Chips Joint Undertaking and its members including the top-up funding by Austria, Belgium, Czech Republic, Denmark, Germany, Greece, Netherlands, Norway, Slovakia, Spain, Sweden and Switzerland.

Plasma Science and Technology

Room 124 - Session PS-TuA

Plasma Chemistry and Catalysis II

Moderators: **Michael Gordon**, University of California at Santa Barbara, **François Reniers**, Université Libre de Bruxelles, Belgium

2:15pm **PS-TuA-1 Nonthermal Plasmas for Advanced Nanomanufacturing**, **Rebecca Anthony**, Michigan State University **INVITED**

Advanced manufacturing strategies have immense potential to reduce time and production costs for a range of applications. Meanwhile, the multiple functionalities and small size of nanomaterials can influence the versatility and capabilities of many devices including solar cells and solid-state lighting, energy conversion technologies and batteries, wearable electronics, and coatings. Combining advanced manufacturing with nanotechnology opens the door to exciting applications based on thin films and microstructures, with on-demand tunable functionality.

One promising route to achieving advanced nanomanufacturing is to use low-temperature plasmas for synthesis of nanoparticles, together with additive manufacturing methods which are compatible with roll-to-roll or additive printing methods. Here, synthesis of nanocrystals from semiconductor materials such as Gallium Nitride (GaN), Indium Nitride (InN), Silicon, and Carbon using low-temperature flow-through plasma reactors is presented. By tuning frequency, power, pressure, and gas composition, nonthermal plasmas open the door to allowing tuning of physical nanoparticle properties including size and surface defect concentration, as observed via x-ray diffraction (XRD), transmission electron microscopy (TEM), and electron paramagnetic spin resonance (EPR). Additionally, the tunable reactor parameters open the door to controlling bonding configuration in some materials, such as carbon. This is a promising prospect, as the ratio of sp² / sp³ hybridization represents significant changes in the properties of carbon materials, and in nanoparticles these changes can be paired with size-induced shifts in physical and optoelectronic properties. Nonthermal plasma synthesis can also be merged with an additive manufacturing approach to deposit tunable-property nanoparticle layers and patterns. The low-temperature synthesis of otherwise difficult-to-make semiconductor nanoparticles can thereby be uniquely paired with direct deposition onto arbitrarily chosen substrates – including temperature-sensitive materials such as polymers – for versatile deposition with on-demand property modulation.

2:45pm **PS-TuA-3 Understanding Olefin Selectivity in Light Hydrocarbon DBD Plasmas**, **Ibukunoluwa Akintola, J. Yang, J. Hicks, D. Go**, University of Notre Dame

The conversion of light hydrocarbons into higher-order species, such as olefins and aromatics, offers the potential to upgrade natural gas into other chemicals that are essential to a wide variety of consumer products. This can be achieved using thermal catalysis but there is a need for alternative carbon-efficient, environmentally friendly, sustainable processes. Low-temperature, atmospheric plasmas (LTPs) produce highly reactive chemical environments and present the potential for an electrical approach to light hydrocarbon conversion into valuable products as a part of the electrification of the chemicals industry. Preliminary findings show plasma activation of methane directly forms C₂+ olefins and alkynes with high selectivities at relatively low temperatures and atmospheric pressure, which when combined with certain catalysts can create aromatics or higher molecular weight products. In this work, we use a dielectric barrier discharge (DBD) to systematically study the selectivity of olefins to alkanes for various light hydrocarbon plasmas, including methane (CH₄), ethane (C₂H₆), and propane (C₃H₈). We explore changing operating conditions (temperature, plasma power, and gas composition) and their effect on the plasma and reaction pathways. We utilize optical emission spectroscopy (OES) and electrical characterization to investigate changes to specific gas phase species densities (C₂ and CH) and analyze both gas and liquid phase products to elucidate the mechanisms directing olefin selectivity and identify key parameters affecting product distribution. Complementary plasma simulations also provide a better interpretation of reaction mechanisms that influence observed product formation.

3:00pm **PS-TuA-4 Pulsing a Methane Discharge for Temperature Control and Better Energy Efficiency for Hydrogen Production**, **Thomas Fontaine, L. Nyssen, D. Petitjean**, Université libre de Bruxelles, Belgium; **N. De Geyter**, Ghent University, Belgium; **R. Snyders**, University of Mons, Belgium; **F. Reniers**, Université libre de Bruxelles, Belgium

In the quest for CO₂-free energy, new fuels and energy storage media are gaining attention. The hydrogen molecule is of interest, as it presents

industrial potential and can serve as an energy carrier. H₂ is mainly obtained from CH₄ steam reforming and water gas shift reactions, emitting CO₂. Cracking of CH₄ is an alternative route for H₂ production, with competitive theoretical energetical cost (standard enthalpy of the reaction at 0°C: 37.5 kJ for 1 mol of hydrogen, i.e. 7.5 times less than H₂O splitting) and no direct CO₂ emission. Various plasma processes can form H₂, but all struggle to enhance energy efficiency.

Tuning the shape of the voltage applied to the system is known to have beneficial impact on the energy efficiency, mostly by allowing a better control of the discharge energy. It is indeed well known that temperature of the discharge is a key factor, as some dehydrogenation steps are favored by higher temperatures, but elevated temperatures also lead to thermal losses. [1]

We investigate pulsing at different time scales (ms (AC pulses, called “burst”), μs, ns) in an atmospheric pressure discharge. A dielectric barrier discharge reactor is used to investigate the energy efficiency. DBD notably allows for operation with different high voltage sources. The reactor is composed of a central copper rod (high voltage electrode), a borosilicate glass tube (dielectric) and a stainless-steel mesh wrapped around the glass (ground electrode). Conversion is measured over time by mass spectrometry. Interesting conditions were further investigated by optical emission spectroscopy. Rotational temperatures during the pulses are derived from the Swan band. A T_{rot} increase is measured for shorter duty cycle in burst mode. Switching from burst to nanosecond pulses also increases T_{rot}. Impact of the pulse energy on the temperature is studied by tuning the pulse energy (voltage tuning) and the total power (frequency tuning). T_{rot} is linked to the pulse energy, but not to the total power. Conversion for same SEI through different pulse lengths is compared in identical experimental conditions, which is rarely observed in the literature. We conclude that ms and ns pulses lead to similar energy efficiencies and perform better than ms pulses.

This study is funded by the FNRS-FWO Excellence of Science program, PlaSyntH2 project O.0023.22F.

[1] M. Scapinello *et al.*, *Chem. Eng. Process. Process Intensif.*, vol. 117, pp. 120–140, Jul. 2017, doi: 10.1016/j.cep.2017.03.024

3:15pm PS-TuA-5 Conversion of Liquid Hydrocarbons to H₂ and C₂ Olefins in AC Plasma Discharges, Norleakvisoth Lim, M. Gordon, UCSB Chemical Engineering

Growing concerns regarding fossil fuel depletion, coupled with efforts to transition towards sustainable and low-carbon energy sources, have prompted innovative solutions for sustainable and efficient utilization of natural resources. This has led to increasing interest in developing technologies to transform light and heavy hydrocarbons to H₂ and more valuable hydrocarbons, such as ethylene and acetylene. Direct plasma-based conversion of liquid hydrocarbons offers a new approach to hydrocarbon reforming. It leverages the high energy density of the liquid phase to achieve fast reaction rates and compact reactor design, and may enable selective production of intermediate products through quenching at the gas-liquid interface. In this work, we explore the use of low current AC discharges in liquid hydrocarbon jets (**Figure 1**) to produce gaseous hydrogen, C₂ olefins, and separable solid carbon.

This talk will examine the influence of discharge frequency, liquid jet velocity and hydrocarbon feedstock on production rates, specific energy requirements and gaseous and liquid product distributions (**Figure 2**). Direct discharges in liquid hexanes predominantly produced H₂ (56.6 mol %), C₂H₂ (23.6 mol %), C₂H₄ (13.1 mol %) and CH₄ (6.7 mol %) under 60 Hz AC frequency. As the AC frequency increased to 17.3 kHz, the energy efficiency improved by a factor of two or more, owing to the change in plasma-generated bubble formation and transport dynamics surrounding the electrode region. A single-shot multi-frame imaging system was developed for consecutive nanosecond shadowgraph acquisitions, which allows us to further investigate the changes in bubble dynamics due to discharge duration and frequency. Decrease in bubble formation/contact time was shown to improve energy efficiency. For a liquid jet flow velocity of ~270 cm/s, the specific energy requirements (SER) for H₂, C₂H₄ and C₂H₂ production were 24 kWh/kg H₂, 3.2 kWh/kg C₂H₄ and 4.9 kWh/kg C₂H₂, respectively. We also examined the reactivities and product distributions of cyclohexane, benzene, toluene and xylene (BTX) feedstocks and ultimately demonstrate the potential of using AC discharges to upgrade less valuable hydrocarbon reformat. Additional characterization of the liquid (GC-MS) and solid (SEM, TEM and Raman) products will be discussed.

4:00pm PS-TuA-8 Integrated Reactor Models of Diamond Growth: Advancing Towards Low-Temperature CVD, Yuri Barsukov, I. Kaganovich, M. Mokrov, PPPL; A. Khrabry, Princeton University

In modern diamond chemical vapor deposition (CVD) techniques, substrates are commonly exposed to temperatures above 1200K. This high-temperature requirement restricts the selection of substrate materials to those that can withstand such extreme conditions. Low-temperature diamond CVD attracts major interest because it enables broader applications, e.g., utilization of diamond materials in the architecture of three-dimensional integrated circuits.

The objective of this study is to identify conditions that would allow to significantly reduce the substrate temperature for diamond CVD growth. To investigate the potential for reducing the substrate temperatures, we developed a comprehensive reaction kinetic model of (100) diamond surface growth from a CH₄/H₂ gases, which are typical feed gases [1]. This model involves 91 surface reactions, which were investigated using quantum chemistry methods. Subsequently, we integrated this reaction kinetic model with a gas-phase chemistry model of typical hot-filament and microwave reactors. The models were validated against previously reported experimental data, accurately predicting the measured diamond growth rates under various operating conditions.

Our results show that the effect of C₂H₂ on diamond growth is minor at temperatures above 1200 K, as previously reported. For temperatures below a critical value predicted by our model, C₂H₂ molecules nucleate the sp²-phase (soot) instead of diamond, thus hampering diamond growth. At temperatures above the critical, C₂H₂ does not nucleate the sp²-phase (soot) and its effect on the diamond growth is not important (compared to the main precursor CH₃). However, for a low-temperature CVD regime, C₂H₂ deleteriously affects the diamond growth, and its presence in the CVD mixture is highly undesirable.

Using ab initio quantum chemistry methods coupled with a numerical plasma model, we developed an integrated model that not only reproduces the experimental results but also identifies a critical bottleneck in modern CVD reactors. Our findings suggest that an optimization of low-temperature CVD reactor design implies maximizing the CH₃ radical production and minimizing the generation of C₂H₂ and other sp and sp² hydrocarbons.

[1] Y. Barsukov, I. D. Kaganovich, M. Mokrov, and A. Khrabry, *Quantum Chemistry Model of Surface Reactions and Kinetic Model of Diamond Growth: Effects of CH₃ Radicals and C₂H₂ Molecules at Low-Temperatures CVD*, (2024). <https://doi.org/10.48550/ARXIV.2405.03050>

4:15pm PS-TuA-9 Solid State Generated Microwave Power for Hydrogen Plasma Reduction of Iron Oxide, Daniel Ellis, J. Rebolgar, University of Illinois Urbana-Champaign; *B. Jurczyk*, Starfire Industries; *J. Krogstad, M. Sankaran*, University of Illinois Urbana-Champaign

The reduction of iron ore is a key step in steel production. Current approaches lead to substantial carbon dioxide emission and there has been growing interest in low-temperature hydrogen plasmas that would avoid carbon-based feedstocks and lower the heating required by increasing reactivity. Microwave excitation is of particular interest because of the potential to energy efficiently generate reactive plasma species. However, microwave power is typically generated by magnetrons, which utilize rigid and bulky waveguides to couple the microwave radiation to a cavity, and the plasmas that are formed at atmospheric pressure are filamentary, hot, and confined to cavities.

Here, we studied a low-temperature, atmospheric-pressure hydrogen plasma for iron oxide reduction powered by microwave generated from solid state amplifiers. Solid state technology allows the microwave power to be transmitted by standard coaxial cables to an antenna. By configuring the antenna in a coaxial geometry where gas flow is simultaneously coupled, a plasma jet free from any surface is generated which can be used to treat a material surface downstream. To demonstrate the applicability of this unique plasma to iron oxide reduction, films of iron oxide prepared from hematite powder were prepared and treated. The effect of various process parameters, including plasma power, treatment time, distance between the plasma electrode and substrate, and feed composition, on reduction were investigated. The reduction of the iron oxide samples was evaluated ex-situ by mass loss measurements, X-ray diffraction, and scanning electron microscopy. The reduction was found to especially depend on the distance of the plasma and the concentration of molecular hydrogen in a background of argon gas. In support of these experimental results, an advection-diffusion-recombination model was developed to calculate the hydrogen radical concentration in the gas phase. The study clarifies

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opportunities and challenges for iron oxide reduction by low temperature plasmas.

4:30pm **PS-TuA-10 Plasma Synthesis of Hydrogen from Ethanol Solution: A Mechanistic Study**, *D. Lojen, T. Fontaine, L. Nyssen, N. Roy*, Université Libre de Bruxelles, Belgium; *R. Snyders*, Université de Mons, Belgium; *N. De Geyter*, Ghent University, Belgium; **François Reniers**, Université libre de Bruxelles, Belgium

Routes to produce hydrogen at low energy cost and without emission of carbon dioxide are extensively studied nowadays, going from methane splitting (either thermal or plasma) to water electrolysis. In a previous preliminary study, we showed that production of hydrogen from liquid ethanol could be a possible route of interest, although the energy cost was still too high. In this paper, we present new results of the plasma induced splitting of liquid ethanol, using a nanopulsed generator. The plasma reactor consists of a 6 pin-to-plate electrode geometry, with the plate electrode being submerged in an ethanol-water solution. The gaseous products of reaction were analysed and quantified by atmospheric mass spectrometry (Hiden), after appropriate calibration, and the discharge is characterized using a high speed Photron camera, electrical measurements, and optical emission spectrometry. Ethanol – water solutions of different concentrations and liquid thicknesses have been investigated. In our previous study we focused on the drastic effect of the liquid thickness on the plasma regime (DBD-like for high thicknesses, hot plasma for small thicknesses). Here we focus on the hot plasma regime. We show that, together with hydrogen, valuable gaseous byproducts are formed, namely acetylene, ethylene, and carbon monoxide, most often without any detectable CO₂ release. Compared to methane splitting, the deposition of solid carbon on the electrodes is also strongly reduced. OES characterization of the plasma reveals that the plasma temperature, the electron density and the electron average energy depend on the composition of the solution. The amount of hydrogen produced as a function of the solution composition is also investigated, leading to a proposed mechanism for hydrogen formation in such conditions.

Acknowledgements:

This project is funded by the EoS PlaSynH2 project (FNRS-FWO Excellence of Science, Belgium, project EOS O.0023.22F).

4:45pm **PS-TuA-11 Study of Plasma-Catalyst Surface Interactions for Coking Reduction**, *Michael Hinshelwood, G. Oehrlein*, University of Maryland, College Park

Methane reforming is important for the production of both pure hydrogen and syngas (H₂ + CO) which can be used to produce other valuable chemicals. Dry methane reforming (DRM) with CO₂ is a promising technique for converting greenhouse gases into syngas. However, catalyst deactivation by carbon deposition on the catalyst surface (coking) is an issue. Non-thermal plasma may be a useful technique for mitigating coke formation in DRM performed at atmospheric pressure. Reactive species generated by the plasma may react with coke deposits, regenerating the catalyst. To better understand this plasma-surface interaction, we use in-situ IR spectroscopy techniques with a remote plasma-catalysis setup. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is used to probe surface adsorbates formed during the reaction, while Fourier Transform Infrared Spectroscopy (FTIR) is used to quantify the product species downstream of the reaction. A nickel catalyst supported by SiO₂/Al₂O₃, commonly used for dry reforming reactions, is used as a test material. By exposing the catalyst to Ar/CH₄ plasma, or just Ar/CH₄ at elevated temperatures, the catalyst's dry-reforming activity is reduced, and a lower product concentration is measured downstream. Surface characterization under the same conditions reveals a growth of adsorbed C-H species, CH₂ (2930 cm⁻¹) and CH₃ (2960 cm⁻¹, 2860 cm⁻¹), suggesting that they are responsible for this deactivation. Subsequent exposure to Ar/CO₂ plasma results in the removal of the adsorbed CH_n surface species on the timescale of minutes. The experimental setup allows for variation of the catalyst temperature to test the reactivity of the plasma produced flux with surface carbon at different temperatures. CH_n removal is seen to be more effective at high temperatures and plasma powers, suggesting a synergistic effect of temperature and reactive species flux to the surface. At lower plasma powers or catalyst temperatures, both the removal rate and amount removed are less. For surface cleaning experiments using high temperature and high plasma power, the bulk of the CH_n removal takes place during the first minutes of CO₂ plasma exposure. By comparing the effect of CO₂ plasma on surface CH_n to its effect on the subsequent dry reforming performance, the potential of plasma to reduce catalytic deactivation during dry reforming will be demonstrated. Increased

understanding of this time-dependent relationship will help inform future development of plasma enhanced DRM systems.

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Atomic Scale Processing Mini-Symposium

Room 116 - Session AP1+EM+PS+TF-WeM

Energy-Enhanced Atomic Layer Processing

Moderators: Ashley Bielinski, Argonne National Laboratory, USA, John F. Conley, Jr., Oregon State University

8:00am AP1+EM+PS+TF-WeM-1 Low-Temperature Synthesis of Crystalline $\text{In}_x\text{Ga}_{1-x}\text{N}$ Films via Plasma-Assisted Atomic Layer Alloying, S. Allaby, F. Bayansal, H. Silva, B. Willis, Necmi Biyikli, University of Connecticut

Based on our first demonstration of crystalline III-nitride film growth via hollow-cathode plasma-assisted atomic layer deposition (HCP-ALD) at substrate temperatures as low as 200 °C, this technique is attracting increasing interest for the low-temperature deposition of various semiconductor layers. Despite its success for binary III-nitride films, ternary III-nitrides pose additional challenges including limitation on fine stoichiometry control, potential incompatibility of plasma gas mixtures, and complexity of in-situ ellipsometry analysis of the growing film. In this work, we share our experimental findings on the self-limiting growth of $\text{In}_x\text{Ga}_{1-x}\text{N}$ films on SiO_2/Si , quartz, and sapphire substrates using digital alloying technique in an HCP-ALD reactor at 200 °C.

The $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy films were deposited using conventional metal-alkyl precursors (triethylgallium, trimethylindium) and two different nitrogen plasmas (N_2/H_2 , N_2/Ar) as metal precursor and nitrogen co-reactant, respectively. GaN and InN unit ALD cycle parameters have been determined using the saturation curves for each binary compound. Digital alloying technique was used by forming ALD supercycles with the following GaN:InN cycle ratios: (9:1), (6:1), (3:1). The targeted indium concentrations ranged within (10% – 50%) range. $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy films with different stoichiometries and thickness values around 50 nm were synthesized to further characterize the structural, chemical, optical, and electrical film properties.

In-situ ellipsometry was employed to monitor the surface ligand-exchange reactions and plasma surface interactions. XRD, XRR, XPS, spectroscopic ellipsometer, UV/Vis spectroscopy, and Hall-effect measurements are carried out to characterize the crystal structure, average crystal grain size, film density, stoichiometry (Ga:In ratio), impurity content, complex refractive index, optical bandgap, film resistivity, carrier concentration and electron mobility, respectively. The experimental results will be discussed along with faced challenges, potential solutions and follow-up studies.

8:15am AP1+EM+PS+TF-WeM-2 Comparison of Low Temperature Methods for Crystallization of Vanadium Oxide Produced by Atomic Layer Deposition, Peter Litwin, Naval Research Laboratory, USA; M. Currie, N. Nepal, M. Sales, D. Boris, S. Walton, V. Wheeler, US Naval Research Laboratory

Crystalline VO_2 (c- VO_2) undergoes a phase transformation between two crystalline states near room temperature (≈ 68 °C), which is accompanied by a metal-to-insulator transition (MIT). This favorable MIT in stoichiometric c- VO_2 is of interest for numerous applications such as passive thermal regulation (e.g. energy efficient windows), thermal sensors, and passive radio frequency components. Current VO_2 films deposited by thermal atomic layer deposition (ALD) processes are amorphous and require a high temperature post-deposition annealing step (≥ 400 °C) to crystallize, which often limits the application space of ALD VO_2 due to thermal budget constraints. Thus, the development of processes to produce ALD c- VO_2 without the need of a high-temperature annealing step are desired.

Two possible routes to c- VO_2 are plasma-enhanced ALD (PEALD) and femtosecond laser processing (fsLP). PEALD offers increased kinetics through the simultaneous delivery of a flux of both energetic and reactive plasma species to the growth surface, allowing for deposition and crystallization at lower processing temperatures. However, the enhanced reactivity of oxidizing-plasma sources poses challenges not present in thermal ALD processes of VO_2 . For example, the oxidation state of the V in the metal-organic precursor is less of a driver for stoichiometric control often resulting in the more stable V_2O_5 with plasma processes. In fsLP, crystallization is initiated as a result of non-equilibrium excited-state dynamics in the film occurring on sub-ps timescales. This produces a combination of athermal and thermal annealing expected to promote the formation of c- VO_2 , even under ambient conditions. Both methodologies maintain sub-200 °C temperature windows which facilitate the use of c- VO_2 in a wider range of applications. For example, high-temperature annealing

of VO_2 on metal substrates often results in the dewetting of VO_2 films; both PEALD and fsLP are potential solutions.

Here we report on investigations into the efficacy of PEALD and fsLP to produce c- VO_2 . A focal point of the PEALD studies is correlating plasma properties, including plasma power, Ar/ O_2 ratio, system pressure, and total gas flow during the plasma step, with the control of the VO_x stoichiometry and crystallinity. We demonstrate control of the amorphous to crystalline transition as a function of PEALD parameters and comment on control of the $\text{V}^{4+}/\text{V}^{5+}$ ratio. fsLP is shown effective at producing c- VO_2 from amorphous ALD films under ambient conditions. We also discuss the ability of the technique to produce c- VO_2 on polymer and metal substrates, an application space often incompatible with high-temperature annealing.

8:30am AP1+EM+PS+TF-WeM-3 Temperature-Dependent Dielectric Function of Plasma-Enhanced ZnO Atomic Layer Deposition using in-Situ Spectroscopic Ellipsometry, Youssa Traouli, U. Kilić, University of Nebraska-Lincoln, USA; M. Schubert, University of Nebraska - Lincoln; E. Schubert, University of Nebraska-Lincoln, USA

In this study, in-situ spectroscopic is employed to real-time monitor the growth of ZnO thin films fabricated by plasma-enhanced atomic layer deposition for different temperatures. The process involves dimethylzinc, $\text{Zn}(\text{CH}_3)_2$, organometallic precursor and oxygen plasma as the primary reactant and co-reactant, respectively. We investigate the cyclic surface modifications and growth mechanisms of ZnO for different substrate temperatures. Subsequently, the deposition chamber is then used as an thermal annealing chamber to investigate the evolution of dielectric function of ZnO ultra-thin films for different temperature values ($22^\circ\text{C} \leq T \leq 300^\circ\text{C}$).

Hence, the temperature-dependent complex dielectric function spectra of ZnO ultra-thin film is obtained. Complementary x-ray photoelectron spectroscopy, x-ray diffraction, and atomic force microscopy are also used to provide the compositional, structural, and morphological characteristics of the ZnO films, respectively. These findings highlight the critical role of precise thermal management in ALD processes for tailoring the dielectric properties of ZnO thin films. The insights gained from this study are crucial for the development and optimization of ZnO PE-ALD recipe but also for optoelectronic devices, ensuring enhanced performance and reliability.

8:45am AP1+EM+PS+TF-WeM-4 Optical Properties and Carrier Transport Characteristics of NiO Films Grown via Low-Temperature Hollow-cathode Plasma-assisted Atomic Layer Deposition, Fatih Bayansal, S. Allaby, H. Mousa, H. Silva, B. Willis, N. Biyikli, University of Connecticut

While there is an abundance of as-grown unintentionally doped n-type semiconductor materials, only a few alternative materials exhibit p-type conduction without requiring additional high-temperature doping processes. NiO is of particular interest mainly due to its relative stability and promising performance as hole-transport layers in emerging solar cell device structures. However, the stability of film properties including carrier concentration and mobility of NiO needs to be substantially improved for its use as reliable transistor channel layers. While low-temperature thermal, plasma, and ozone-assisted ALD efforts have resulted in NiO films with p-type behavior, degrading film properties over time and at higher temperatures, and low hole mobility values prevent the usage of these layers for devices.

To enhance film properties in low-temperature as-grown NiO layers, our study conducts a comprehensive investigation on plasma-enhanced ALD (PEALD) of NiO films on Si, SiO_2/Si , glass, sapphire, and quartz substrates. This process utilizes nickelocene (NiCp_2) and O_2 plasmas within a plasma-ALD reactor featuring a stainless steel-based hollow-cathode plasma (HCP) source, equipped with an in-situ ellipsometer. 800-cycle deposition runs at 100 – 250 °C substrate temperatures were carried out to achieve at least 30 nm thick films for further characterization.

The resulting as-grown crystalline (c-NiO) films are characterized for their optical and electrical properties. Films grown at 200 °C exhibited higher refractive index values reaching 2.3, which is in good agreement with reported values for the best polycrystalline NiO films in the literature. NiO films deposited on sapphire and quartz substrates showed strong absorption in the UV region ($\lambda=190\text{-}380$ nm) yet demonstrated minimal absorption in the visible and near-IR regions. As a result of the analysis using the Tauc relation, it was found that the band gaps of all films were close to the bulk value of 3.6 eV. Furthermore, we will also present the results of Hall-effect measurements conducted at room temperature to determine the film resistivity, type of conduction mechanism, Hall mobility, and carrier concentration. The long-term stability of the NiO films will be investigated at ambient and higher temperature annealing conditions.

Wednesday Morning, November 6, 2024

9:00am **AP1+EM+PS+TF-WeM-5 Characterizing Inductively Coupled Plasmas in Ar/SF₆ Mixtures for Atomic Layer Deposition, David Boris, V. Wheeler, U.S. Naval Research Laboratory; M. Sales, NRC Research Associateship Program; L. Rodriguez de Marcos, J. Del Hoyo, NASA Goddard Space Flight Center; A. Lang, U.S. Naval Research Laboratory; E. Wollack, M. Quijada, NASA Goddard Space Flight Center; M. Meyer, NRC Research Associateship Program; S. Walton, U.S. Naval Research Laboratory**

Low temperature plasmas containing sulphur hexafluoride (SF₆) are particularly rich plasmas from the perspective of gas phase chemistry and plasma physics. They possess a wide range of positive and negative ion (SF_x⁺, SF_y⁻, F⁻, F₂⁺, etc.) and reactive neutral species (SF_x, F, F₂, etc.) that play important roles in materials processing applications ranging from semiconductor etching [1] to the formation of fluoride based optical thin films [2]. Understanding the physical mechanisms at play in these plasmas is often challenging and requires a comprehensive approach employing multiple diagnostic tools.

In this work, we use a combination of Langmuir probes and optical emission spectroscopy to examine the effects of varying process parameters on the physical characteristics of Ar/SF₆ plasmas generated in a remote, inductively coupled plasma (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 F density, plasma density, plasma potential, and the ratio of positive to negative ions in the plasma. These changes in plasma properties are then tied to changes in the material characteristics of aluminum tri-fluoride (AlF₃) thin films grown via plasma-enhanced ALD using a remote ICP employing Ar/SF₆ gas mixtures. This work is supported by NASA Astrophysical Research and Analysis (APRA) grant 20-APRA20-0093/ N0017322GTC0044. This work was also partially supported by the NRL Base program through the Office of Naval Research.

[1] D.C. Messina et al, J. Vac. Sci. Technol. A 41, 022603 (2023)

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9:15am **AP1+EM+PS+TF-WeM-6 Dynamic Global Model of Cl₂/Ar Plasmas: In-Depth Investigations on Plasma Kinetics, Tojo Rasoanarivo, C. Mannequin, Institut des Matériaux de Nantes Jean ROUXEL - Nantes Université, France; F. Roqueta, M. Boufnichel, ST Microelectronics, France; A. Rhallabi, Institut des Matériaux de Nantes Jean ROUXEL - Nantes Université, France**

Plasma processes such as Atomic Layer Etching (ALE) using Cl₂/Ar gas mixture are often reported in the literature as chlorine chemistry is suitable for a wide variety of materials [1]. ALE is a cyclic process and Cl₂ and Ar plasmas are implemented for the adsorption and activation steps, respectively, through alternating feedgas overtime or overspace. However, these studies mostly focus on experimental approaches and modeling investigations are scarce. Some others ALE recipes rely on plasma kinetics through specific recipes [2] and to better understand plasma/surface interactions at atomic scale, we must first precisely investigate plasma behavior especially during the switching durations.

In most cases, global models have been well implemented to determine the plasma composition at specific plasma reactor parameters, with good computational time effectiveness [3] in steady-states conditions [4]. We have implemented the dynamic mode to investigate the plasma kinetics during the transitions between the modifying Cl₂ plasma and the Ar activation plasma.

We closely investigate the influence of the switch duration between the Cl₂ to/from Ar feedgas, for different RF powers. We found that under a critical switch duration there is a competition between the plasmas kinetics mainly governed by electrons collisions with the neutrals and the physical residence time depending of the working pressure. For short switch duration from Cl₂ rich plasma toward Ar plasma, we observed discrepancies compared to equivalent steady-state composition on chlorine species. These differences are associated with longer characteristics time reactions than the switch duration. In the case of RF power source switch, we observed for switch duration lower than 100 ms, overshoots of the electron temperature (T_e). These stiff T_e variations observed are assumed to originate from quasi-instantaneous electrons acceleration before first collisions with neutrals.

These results may be used to predict plasma behavior during ALE transitions steps or for fast-paced plasma etching processes.

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9:30am **AP1+EM+PS+TF-WeM-7 Precise Growth and Removal of Carbon Films by Electron-Enhanced Chemical Vapor Deposition (EE-CVD) and Chemical Vapor Etching (EE-CVE), Z. Sobell, Steven George, University of Colorado at Boulder**

Electron-enhanced chemical vapor deposition (EE-CVD) was used to grow carbon films at T < 70 °C. EE-CVD employs a continuous flux of low energy (~100 eV) electrons that are incident on the sample through a methane (CH₄) reactive background gas (RBG). Electron-enhanced chemical vapor etching (EE-CVE) was also used to etch carbon films at < 70 °C. EE-CVE employs a continuous flux of low energy electrons that are incident on the sample through an oxygen (O₂), ammonia (NH₃), or hydrogen (H₂) RBG. Both EE-CVD and EE-CVE were accomplished with precise rate control.

The EE-CVD and EE-CVE used an electron beam from a hollow cathode plasma electron source with currents on the sample of ~30 mA over ~10 cm². The electron beam can desorb surface species by electron stimulated desorption. The electron beam also travels through the RBG in the reactor at pressures of ~1-3 mTorr. Electron induced dissociation can form radicals and ions that facilitate the growth or removal of the carbon film. In addition, a negative voltage (-30 V) on the substrate (sample bias) was observed to greatly enhance both the deposition and etching of carbon films. The negative voltage is believed to pull positive ions to the substrate to enhance the growth or removal.

With no applied sample bias, carbon deposition proceeded at ~22 Å/min for a CH₄ flowrate of 10 SCCM (Fig. 1). The introduction of a sample bias of -30 V increased the deposition rate by >20 times to ~480 Å/min. In contrast, carbon deposition with a +30 V sample bias proceeded at a similar rate to carbon deposition with no sample bias. For etching of carbon films with a -30 V sample bias and RBG flow rates of 4 SCCM, O₂ produced the highest carbon etch rate at ~225 Å/min (Fig. 2). In contrast, NH₃ displayed a slower carbon etch rate of ~48 Å/min and H₂ had an even slower carbon etch rate of ~18 Å/min.

Raman spectroscopy was used to characterize the carbon films grown at different sample biases. At negative substrate voltage, the carbon films displayed faster growth, were more disordered (D:G peak ratio=2.29), and exhibited faster etching. At zero substrate voltage, the carbon films displayed slower growth, were more ordered (D:G peak ratio=1.18), and exhibited slower etching.

Many applications are possible for the EE-CVD and EE-CVE of carbon films. More ordered carbon films may find use as hard masks or diffusion barriers. Amorphous carbon films may be employed as channel materials. Carbon hard masks are currently removed with an O₂ plasma which also oxidizes the surrounding and underlying material. Using H₂ and electrons may allow for a single-step oxygen-less hard mask removal.

9:45am **AP1+EM+PS+TF-WeM-8 Microwave Enhanced ALD of Al₂O₃, Benjamin Kupp, J. Haglund, S. Witsell, J. Conley, Oregon State University**

The low deposition temperatures typical of ALD are advantageous for many applications. However, low deposition temperatures can allow incorporation of -OH groups or residual impurities from unreacted ligands which can lead to non-ideal stoichiometry and sub-optimal physical, optical, and electrical properties. Although increasing the deposition temperature and post deposition annealing can both help drive off impurities and improve film properties, the temperatures required may (i) move a process out of the ALD regime or (ii) exceed the thermal budget, respectively. To maintain a low ALD temperature while maximizing film properties, adding energy in-situ during each ALD cycle or supercycle can help drive/speed reactions and reduce impurity incorporation. For example, including rapid thermal annealing as part of the ALD cycle have been shown to improve density, stoichiometry, electrical, and optical properties that cannot be achieved by post deposition annealing alone [1-4]. Other reported in-situ energy enhanced EE-ALD methods include flash lamp annealing, plasma, UV, and laser exposure, electric fields, and electron-beams [5-15]. Here, we introduce microwave enhanced MWE-ALD.

Al₂O₃ films were deposited at 300 °C using TMA and H₂O in a Picosun R200 PE-ALD chamber integrated with a custom microwave antenna and an MKS SG 1024 solid state microwave (MW) generator. Film thickness and

refractive index, n , were modeled using a Film Sense FS-1 mapping ellipsometer. A 30 s in-situ 400 W MW exposure (*without* plasma generation) during either the TMA or H₂O purge part of each ALD cycle reduced film thickness by ~7% and ~25%, and increased n by ~2% and ~6%, respectively, across a 150 mm Si wafer as compared to a control without MWs (Fig. 1). Preliminary electrical measurements on MOS devices indicate an associated reduction in low field leakage. Additional electrical and analytical data will be presented, including MWE-ALD deposition temperatures.

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Atomic Scale Processing Mini-Symposium Room 116 - Session AP2+EM+PS+TF-WeM

New Advances in Atomic Layer Deposition

Moderators: Ashley Bielinski, Argonne National Laboratory, USA, John F. Conley, Jr., Oregon State University

11:00am **AP2+EM+PS+TF-WeM-13 Direct Atomic Layer Processing (μ DALP™): Revolutionizing Precision Coatings for Emerging Device Technologies**, S. Santucci, M. Akbari, B. Borie, **Mira Baraket**, I. Kundrata, M. Plakhotnyuk, ATLANT 3D Nanosystems, Denmark

As the microelectronics sector advances towards further miniaturization, precision in thin film deposition becomes crucial. Traditional Atomic Layer Deposition (ALD) techniques, vital for semiconductor manufacturing, often require extensive surface preparation, limiting throughput. ATLANT 3D's μ DALP™ technology adapts ALD using microreactor technology for localized thin film deposition with accuracy down to a few hundred microns, maintaining all conventional ALD benefits. This approach uses micronozzles for precise delivery of precursors, allowing rapid film formation on targeted substrate areas under atmospheric conditions. The μ DALP™ achieves a vertical resolution of 0.2 nm, offering exceptional precision.

This technology enhances conventional ALD's capabilities in selective patterning for microfluidic channels, optical gratings, and nanostructured surfaces, improving its use in next-generation device fabrication. This presentation will discuss how μ DALP™ retains ALD's core advantages while enhancing scalability, processing speed, and cost-efficiency. We will highlight the transformative impact of μ DALP™ on thin-film manufacturing across optics, photonics, MEMS, and advanced electronics, underscoring its potential to propel future innovations in energy storage and conversion, quantum computing, and advanced packaging solutions.

Keywords: Atomic Layer Deposition, μ DALP™, Nanotechnology, Thin Film, Microelectronics.

Fig. 1. (a) Top view of aligned Si trenches (aligned horizontally) coated with a perpendicular line of TiO₂ (low magnification SEM). (b) Microfluidic precursor delivery concept: Schematic view of the delivery nozzle in frontal view (top) and in cross-section (lower panel).

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11:15am **AP2+EM+PS+TF-WeM-14 Ceramic Thin-Film Composite Membranes with Tunable Subnanometer Pores for Molecular Sieving by Atomic Layer Deposition**, X. Zhou, Yale University; R. Shevate, A. Mane, Jeffrey Elam, Argonne National Laboratory; J. Kim, M. Elimelech, Yale University

Membranes with tunable, sub-nanometer pores are needed for molecular separations in applications including water treatment, critical mineral extraction, and recycling. Ceramic membranes are a promising alternative to the polymeric membranes typically used in such applications due to their robust operation under harsh chemical conditions. However, current fabrication technologies fail to construct ceramic membranes suitable for selective molecular separations. In this presentation, we describe a ceramic thin film composite (TFC) membrane fabrication method that achieves sub-nanometer pore size control using atomic layer deposition (ALD) by incorporating a molecular-scale porogen. By co-dosing alkyl alcohols along with the H₂O coreactant during Al₂O₃ ALD, we incorporate alkoxide species in the film which create a continuous network of pores upon calcination. Varying the alkyl alcohol (methanol, ethanol, isopropanol) tunes the pore size. We use Fourier transform infrared absorption spectroscopy, X-ray photoelectron spectroscopy, and scanning electron microscopy to elucidate the surface chemistry and growth during the alcohol-modulated ALD as well as the subsequent pore formation. We evaluate the transport and separations properties of the ALD TFC membranes using a two-chamber diffusion cell with aqueous salt solutions. We measured a remarkable enhancement in the transport of Cl⁻ compared to SO₄²⁻ (8.6 times faster) matching the selectivity of state-of-the-art polymer membranes. We attribute this selectivity to the dehydration of the large divalent ions within the subnanometer pores. In addition, permeation studies using neutral adsorbates revealed average pore sizes of ~7 Å, 13 Å, and 19 Å for ALD TFC membranes prepared using methanol, ethanol, and isopropanol, respectively. This work provides the scientific basis for the design of ceramic membranes with subnanometer pores for molecular sieving using ALD.

11:30am **AP2+EM+PS+TF-WeM-15 Electrical and Optical Properties of Macroscopic Nanocomposites Fabricated by ALD Infiltration and Pressure-Assisted Sintering of Nanoparticle Compacts**, Benjamin Greenberg, K. Anderson, A. Jacobs, U.S. Naval Research Laboratory; A. Cendegas, American Society for Engineering Education; E. Patterson, J. Freitas, J. Wollmershauser, B. Feigelson, U.S. Naval Research Laboratory

Over the past 20+ years, a wide variety of nanocomposite thin films with unique property combinations have been produced by atomic layer deposition (ALD) infiltration of nanoparticle (NP) films. Examples include electrochromic WO_{3-x} NP films with photochemical stability enhanced by Ta₂O₅ ALD¹ and superhydrophilic and antireflective TiO₂/SiO₂ NP films with elastic modulus and hardness enhanced by Al₂O₃ ALD.² Applications of such nanocomposite films, however, are limited by their small thickness (typically a few μ m or thinner), reliance on substrates, and/or residual porosity that can remain after ALD infiltration.

In this work, we explore fabrication of macroscopic, freestanding, dense nanocomposites—pucks with ~1 mm thickness, ~10 mm diameter, and solid volume fraction that can exceed 99%—via ALD infiltration of NP compacts followed by pressure-assisted sintering. For a prototype, we use monodisperse 100 nm SiO₂ NPs and an ALD coating of Al-doped ZnO to form electrically conductive ceramic nanocomposites with electrical and optical properties dependent on the coating thickness. Infiltration of the ultra-high-aspect-ratio (>10,000) SiO₂ NP compacts with ZnO:Al is accomplished via a recently developed cyclical-temperature ALD process.³ The ZnO:Al-coated SiO₂ compacts are then densified via environmentally controlled pressure-assisted sintering (EC-PAS), wherein NPs are cleaned and kept in an inert atmosphere to maintain high surface energy, which enables low-temperature densification with minimal grain growth.⁴ An EC-PAS process with a maximum pressure of ~2 GPa and a maximum temperature of 450 °C yields dense SiO₂/ZnO:Al nanocomposites that contain nanocrystalline ZnO:Al networks and exhibit low electrical resistivity, ρ . At nominal ZnO:Al coating thicknesses, t , of ~3 nm and ~6 nm, ρ is on the order of 1 and 0.1 Ω -cm, respectively, at 300 K. Moreover, at $t \approx 6$ nm, the Hall mobility approaches 1 cm²V⁻¹s⁻¹ at 300 K, and ρ increases by less than a factor of 3 upon cooling to 10 K, suggesting proximity to the metallic/band-like charge transport regime. Interestingly, the nanocomposites are blue in color with transparency and hue apparently dependent on t . Characterization techniques employed in our investigation into these electrical and optical properties include X-ray diffractometry, scanning electron microscopy, Hall and Seebeck effect measurements, absorption/transmission/reflection spectroscopy, and photoluminescence spectroscopy and imaging.

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11:45am **AP2+EM+PS+TF-WeM-16 Tunable Growth of Layered Double Hydroxide Nanosheets through Hydrothermal Conversion of ALD Seed Layers**, *Daniel Delgado Cornejo*, *A. Ortiz-Ortiz*, *K. Fuelling*, University of Michigan, Ann Arbor; *A. Bielinski*, Argonne National Laboratory, USA; *T. Ma*, *N. Dasgupta*, University of Michigan, Ann Arbor

Nano-architected materials have seen a rise in recent years and have produced advancements in a variety of fields including biomedicine, energy storage, and catalysis. As such, there is great motivation to develop novel synthesis and processing methods designed to improve the degree of fine control over the material's geometric parameters. In this study, we explore a method known as surface-directed assembly which makes use of the synergy between atomic layer deposition (ALD) and hydrothermal synthesis to grow layered-double hydroxide (LDH) nanosheets. The formation of the LDH product stems from the interaction between the deposited ALD Al_2O_3 film and an aqueous zinc solution. Unlike other reported seeded hydrothermal syntheses, which rely on epitaxial growth from a seed layer, this interaction results in the consumption and conversion of the initial ALD film into the LDH product, where aluminum from the ALD film serves as a limiting reagent in the kinetic processes of nucleation and growth. Geometric parameters such as the nanosheet inter-spacing and length can be tuned by varying the thickness of the ALD film with sub-nanometer precision. A non-linear trend in nanosheet length is observed and characterized within three regimes: (I) depletion limited, (II) length independent, and (III) steric hindrance. In addition, we observe an inverse relationship between the nanosheet inter-spacing and the ALD film thickness. Finally, this process enables the formation of hierarchical nanostructured surfaces onto three-dimensional substrates including microposts, paper fibers, and porous ceramic supports. By leveraging the tunability and conformality of the ALD process, this work enables the programmable control of nano-architected material geometries for a variety of applications, including for energy and medical devices.

12:00pm **AP2+EM+PS+TF-WeM-17 Passivation Strategies for Far-Ultraviolet Al Mirrors Using Plasma-Based AlF_3 Processing**, *Maria Gabriela Sales*, *D. Boris*, U.S. Naval Research Laboratory; *L. Rodriguez de Marcos*, NASA Goddard Space Flight Center; *J. Hart*, *A. Lang*, *B. Albright*, *T. Kessler*, U.S. Naval Research Laboratory; *E. Wollack*, *M. Quijada*, NASA Goddard Space Flight Center; *S. Walton*, *V. Wheeler*, U.S. Naval Research Laboratory
Far-ultraviolet (FUV) astronomy ($\lambda = 100\text{-}200$ nm) relies on efficient Al mirrors because Al has a very high theoretical reflectance in this region. However, since Al readily oxidizes in air, the strongly absorbing native oxide layer appreciably degrades its FUV performance. A novel surface passivation technique for Al mirrors was previously demonstrated using an electron beam (e-beam) generated SF_6/Ar plasma, which proceeds via a combined etching of the native oxide and simultaneous fluorination of the Al surface [1].

In our present work, this novel e-beam plasma technique is integrated into a plasma-enhanced atomic layer deposition (PEALD) system. We use a Veeco Fiji G2 reactor, equipped with substrate biasing, that has been uniquely modified to include an on-axis e-beam generated plasma source. Trimethylaluminum (TMA) and SF_6/Ar plasma, produced with an inductively coupled plasma (ICP) source, were used as our precursor and reactant for the ALD AlF_3 process. Optimization of the ALD parameters was performed, and our best ALD AlF_3 films ($F/\text{Al} \approx 3$, $\sim 1\%$ oxygen content, and roughness < 1 nm) were attained using 100 W ICP power and total plasma gas flows > 30 sccm. Our ALD AlF_3 films provide improved FUV reflectivity compared to oxidized bare Al, however, these optical properties are still limited by Al oxide at the AlF_3/Al interface. To overcome this, we utilize our in-situ e-beam plasma, produced in a gas mixture of SF_6/Ar , to minimize the native oxide layer prior to ALD.

In this talk, we discuss the processing parameters of the in-situ e-beam plasma (SF_6/Ar ratio and flow, sample bias) and how they affect the AlF_3 growth rate, film/interface chemistry, and surface roughness. These material properties are related to optical performance, which compares favorably to state-of-the-art coatings ($\approx 90\%$ at 121 nm). We then discuss hybrid AlF_3 films, in which the growth is initiated by e-beam plasma, and then continued using an optimized ALD AlF_3 recipe. For the initial step, pre-treatments using the in-situ e-beam plasma and the previously developed ex-situ e-beam plasma [1] are compared. We show that both in-situ and ex-situ hybrid techniques significantly reduce the interfacial oxygen compared

to ALD AlF_3 alone (no pre-treatment), which enhances the FUV reflectivity. This work highlights the importance of the interface quality of passivated Al mirrors on their optical performance in the FUV range.

This work is supported by NASA Astrophysical Research and Analysis (APRA) grant 20-APRA20-0093/ N0017322GTC0044 and is partially supported by the NRL Base program through the Office of Naval Research.

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Plasma Science and Technology

Room 124 - Session PS-WeM

Plasma Modelling

Moderators: Pingshan Luan, TEL Technology Center America, Kenji Maeda, Hitachi High Technologies America Inc.

8:00am **PS-WeM-1 Challenges and Opportunities of a Holistic Approach toward Simulation-Assisted Plasma Etch Technology Development**, *Du Zhang*, *Y. Tsai*, TEL Technology Center, America, LLC; *T. Nishizuka*, Tokyo Electron Miyagi Limited, Japan; *A. Ko*, *P. Biolsi*, TEL Technology Center, America, LLC

Technological advancements in plasma etching crucially rely on the synergy of various areas of expertise due to its highly interdisciplinary nature, requiring subject matter knowledge ranging from plasma physics and surface chemistry, to transport, metrology, etc. Many simulation techniques exist, each targeting a different scope, and each with its own limitations and advantages; therefore, none should be considered the silver bullet. Nevertheless, from a pragmatic point of view, if the ultimate goal is to accelerate process and product development, the foremost priority is to identify the key issues and variables, then use suitable simulation tools to test out hypotheses and determine next action plans in an organized workflow. In this paper, focusing on the very thought process, we examine several examples of process and product development in which computational simulations provide insights to complement experimental techniques. We also discuss requirements for further simulation technology development in accordance with such industry needs.

8:15am **PS-WeM-2 Some Lessons from Particle-in-Cell Modeling of Intermediate Pressure Capacitively Coupled Plasmas**, *Shahid Rauf*, *A. Verma*, *R. Sahu*, *N. Nuwal*, *K. Bera*, Applied Materials, Inc.

Capacitively coupled plasmas (CCPs) are widely used for thin film etching and deposition in the semiconductor industry. The pressure in these plasmas varies over a broad range, from a few mTorr to tens of Torr. At low pressure, non-local phenomena are important in both plasma production and charged species transport, necessitating the use of kinetic or hybrid kinetic-fluid models for accurately capturing the CCP physics. Fluid plasma models are typically used at intermediate pressures (> 100 s of mTorr). It is important to understand how well fluid plasma models capture the behavior of intermediate-pressure CCPs and what improvements in the fluid models would render them more accurate. 1-dimensional particle-in-cell (PIC) simulations are done for 13.56 MHz N_2 and Ar CCPs between 100 mTorr – 1.5 Torr. Once the time-dependent simulation reaches steady state, the particle data is analyzed to obtain all the terms in the continuity, momentum conservation, and energy balance equations for the charged species. The potential and current in the plasma are also processed to determine the spatially resolved impedance in the plasma and sheaths. Comparison of PIC results to fluid plasma model under the same conditions and using the same plasma chemistry shows significant differences. This disparity between the two models can be linked to the assumptions about the electron energy distribution function (EEDF) and the electron transport coefficients in the fluid plasma model. In addition, the PIC simulations indicate that the EEDF is not spatially uniform. The drift-diffusion approximation appears reasonable for electron transport. However, it is necessary to solve the ion momentum equation as ion inertia effects are important. Analysis of the electron energy equation highlights that energy transport mechanisms such as the Dufour effect should be included in fluid plasma models.

8:30am **PS-WeM-3 Modeling to Inform Optimization of Radiofrequency Plasma Sources**, *Amanda Lietz*, *C. Wagoner*, *S. Zulqarnain*, *S. Bin Amir*, *M. Hossain*, North Carolina State University

INVITED

Radiofrequency (RF) plasmas are essential for the processing of semiconductors, but also are used in other applications, including medical treatments and auxiliary heating devices for fusion. In this work, we will discuss the role of computational modeling in informing the design

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and operation of RF plasmas sources, including examples of hydrogen inductively coupled and argon capacitively coupled plasmas. These plasma sources often operate in a regime where the commonly used fluid approximations (e.g. the local mean energy approximation) fail. Because there are insufficient collisions compared to the rate of acceleration by the electric field, the electron energy distributions are no longer a function of only local quantities like the electric field and the electron energy. First the failures of the fluid approach will be discussed with an example of particle-in-cell simulations investigating tailored voltage waveforms applied to argon capacitively coupled plasmas at the low pressures relevant for plasma etching (<20 mTorr). The fully kinetic approach is used for a detailed mechanistic understanding of the plasma dynamics in this system, though the timescales and chemistry are limited. The kinetic approach and results will be contrasted with fluid and hybrid modeling of hydrogen inductively coupled plasma sources for fusion. In this example, some fluid approximations are necessary to address neutral dissociation dynamics and flow timescales. These approximations also facilitate the rapid turnaround required in a design cycle. Finally, a new approach to use machine learning to incorporate non-local information into a fluid closure will be discussed and applied to a capacitively coupled plasma. As pressure decreases, an increasing amount of non-local information is required to obtain accurate fluid fluxes. The potential advantages and challenges of this approach will be discussed for a 1-dimensional, single frequency, capacitively coupled plasma.

9:00am **PS-WeM-5 Stability Model for Capacitively Coupled Radiofrequency Argon Plasma at Moderate Pressures***, *Omar Alsaed*, NCSU - Nuclear Engineering Department; *A. Lietz*, North Carolina State University; *B. Yee*, *B. Scheiner*, *M. Mamunuru*, *C. Qu*, Lam Research Corporation

Wafer-scale uniformity is essential in semiconductor manufacturing but can be disrupted by plasma instabilities due to energy transport phenomena that are not well understood. This work reports on the operational conditions that can lead to plasma instabilities and thus self-organization in plane-parallel radiofrequency capacitively coupled argon plasmas at moderate pressures (0.1-10 Torr). Plasma processing equipment often employs this simple configuration and striations in the direction transverse to the electric field have not been theoretically analyzed using a linear stability analysis. We use a fluid description that relies on the drift-diffusion approximation and includes the thermoelectric electron energy which proves essential in describing the pattern formation mechanism¹ and is critical for plasmoid formation in capacitively coupled plasmas². The equilibrium electron density and temperature solutions are derived using the inhomogeneous model for a capacitive discharge³. The ionization rates and electron transport coefficients are computed using a multi-term Boltzmann equation solver, MultiBolt⁴. A stability criterion dictating the allowed values of the thermoelectric electron energy transport coefficient as a function of discharge parameters is analyzed. Stable plasma processing windows are theoretically established as a function of background gas pressure, gas composition (He), and inter-electrode gap size.

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* Work funded by Lam Research Corp.

9:15am **PS-WeM-6 Plasma Modeling Guided Process Development and Optimization for High Density Plasma Sources**, *Qiang Wang*, *G. Hartmann*, *P. Conlin*, *R. Longo*, *S. Sirdhar*, *P. Ventzek*, Tokyo Electron America, Inc.

High density plasmas have been demonstrated to be robust tools for advanced node logic/memory device fabrication. With a plethora of plasma operating parameters, optimizing an etch process is quite complex, requiring a significant investment of time and resources. Plasma modeling guided process development is aiming to provide clear and prompt guidelines in the development of etch recipes. We present our approach on pairing first principle-based multi-scale plasma modeling with advanced surrogate optimization techniques in selecting optimized pulsing recipes for conductor etch applications. The modeling framework integrates a zero-

dimensional global model, a circuit/sheath dynamic model and a surface/etch model, allowing rapid calculations of in-chamber (e.g., ions and radicals densities and fluxes), on-wafer (e.g., Ion Energy and Angular Distribution) and in-feature (e.g., surface site coverage) during etching. An advanced methodology of surrogate modeling with a machine learning (ML) technique is applied to reduce computation time of simulation-based optimization and enhance prediction reliability. Using this integrated modeling approach, the pulsing sequence was optimized for a single objective (e.g., minimizing aspect ratio dependent etch, minimizing bow CD etc.), or to optimize trade-offs among multiple objectives. We will further demonstrate examples of applying the developed modeling framework in handling increasingly challenging problems in conductor etch applications and its validation with process experiments.

9:30am **PS-WeM-7 Investigating Instabilities in Magnetized Low-Pressure Asymmetric Capacitively Coupled Plasma Sources**, *Sathya Ganta*, *K. Bera*, *S. Rauf*, Applied Materials, Inc.; *I. Kaganovich*, *A. Khrabrov*, *A. Powis*, Princeton University Plasma Physics Lab; *D. Sydorenko*, University of Alberta, Canada; *L. Xu*, Soochow University (SUDA), Suzhou, Jiangsu, China

Asymmetric capacitively coupled plasma (CCP) chambers at low pressures (< 100 mTorr) are used in the semiconductor industry for thin film deposition and etch applications. Low pressure ensures low collisionality in the sheaths resulting in high energy ions. Low pressure plasma with relatively lower collisions diffuses towards the chamber center creating a center high non-uniformity in the deposition thickness or etch profile on the wafer. An external magnetic field can be used to make the plasma more uniform and mitigate the center high non-uniformity on the wafer. We performed an investigation previously of magnetized low pressure RF plasma in asymmetric CCP chambers using Particle in Cell (PIC) plasma model which indicated the possibility of instabilities at high magnetic field strengths (≥ 75 Gauss for 10 mTorr). These instabilities could adversely affect process uniformity on the wafer. This investigation was done at 40 MHz radio frequency (RF) with a vacuum gap between ground and RF powered electrodes. The effects of changing magnetic field strength, pressure, ground to RF powered electrode area ratio and an external capacitor were examined. The investigation provided guidelines for the upper limit of magnetic field strength to have an instability-free operation within the range of design and operating parameters studied. It was found that only pressure affected such upper limit of magnetic field strength as the increasing collisions dampened instabilities at higher pressure. In this paper, we continue the investigation in low pressure magnetized CCPs to observe the effect of changing frequency; dielectric boundary between electrodes instead of a vacuum boundary; and the chamber geometry on instabilities at high magnetic field strengths. The previous investigation showed waves of instabilities that had a continuous spectrum with peak frequency at around 1.9 MHz. We investigate if there is an enhancement in instabilities if the RF source frequency is around this peak frequency.

9:45am **PS-WeM-8 Fast Kinetic Modeling of Magnetron Sputtering**, *Daniel Main*, *T. Jenkins*, Tech-X Corporation; *J. Theiss*, *G. Werner*, University of Colorado Boulder; *S. Kruger*, *J. Cary*, Tech-X Corporation

Magnetron sputtering devices have a wide range of uses in the coatings industry, where they are used for optical coatings, metallization in integrated circuits, and coatings for wear resistance. Numerical simulations can aid in the design of such systems, as computation can allow one to predict the figures of merit, eliminating the need to test each conceived configuration on the path to the final design. Such figures of merit include the uniformity and extent of the distribution of sputtered material, the power consumption of the system, and the erosion of the cathode. Such computations must be self-consistent and kinetic, i.e., they must follow particle trajectories, since fluid approximations make simplifying assumptions that may not be valid (especially at low pressure) and only a kinetic approach can properly account for the critical physics, including the energy-angle distribution of the impacting sputters and the resulting distribution. The Particle-In-Cell, Monte Carlo Collision (PIC-MCC method) is ideal for this, as it can properly account for the above physics as well as the physics involved in plasma creation, electron trapping by the magnetic field, and even dynamics that occurs in High Power Impulse Magnetron Sputtering (HIPIMS). Unfortunately, these calculations can take significant computing time, as the time scales for relaxation to steady-state are long compared with plasma processes. This talk presents computations using multiple techniques to speed up these calculations. The methods include using a circuit model that allows one to rapidly reach the final state, steady-state relaunch (where the results of one simulation that has reached steady-state are used to initialize another), and physics minimization, where initial analysis using a global model minimizes the number of

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included collisional processes. We also present a method that reduces the calculation of the deposition rate onto the substrate. Using our approach, we first use VSim to evolve the plasma and sheath dynamics over electron time scales. Then after reaching steady state, we then maintain the discharge and sheath while computing the spatially dependent deposition rate onto the substrate over longer time scales. Results are compared with those available in the literature.

Acknowledgements: NSF Grant No. PHY2206904

11:00am **PS-WeM-13 Advancements in Multiscale Simulation of Silicon Etching: Broader Implications for Plasma Processing**, *Rim Ettouri, A. Rhallabi*, Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, France

The Bosch process [1] is fundamental in semiconductor manufacturing, enabling precise etching of deep, high-aspect-ratio silicon structures through alternating etching and passivation cycles. It uses sulfur hexafluoride (SF_6) for etching and octafluorocyclobutane (C_4F_8) for sidewall polymer films, maintaining etch precision and integrity.

Recent studies [2], [3], experimentally explore variations in C_4F_8 plasma parameters and their effects on passivation films, our research approaches these phenomena through advanced simulation [4]. Our research employs a sophisticated Bosch simulator using a multiscale approach, composed of three modules: **global plasma kinetics** for SF_6 and C_4F_8 , a **sheet module**, and a **surface module**. This simulation framework allows us to dissect the plasma-assisted etching dynamics [5], examining how operating conditions affect etch profiles and rates.

Building on analyses of oxygen's impact on C_4F_8 plasma [4], we use updated tools to study broader plasma compositions' influences on etching behavior. These studies reveal subtle yet critical shifts in plasma behavior from variations in component ratios, emphasizing the importance of atomic and molecular interactions. Our Monte Carlo cellular approach investigates how changes in machine parameters such as pressure, gas flow, and duty cycle affect scalloping—irregularities in the sidewalls of etched structures—enabling detailed predictions on optimizing etching cycles to minimize these defects. Our findings enhance the understanding of the Bosch process, providing theoretical insights that can inform practical adjustments to improve etch precision and efficiency in semiconductor manufacturing. The implications of this work suggest new avenues for research and application, potentially setting new industry standards.

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11:15am **PS-WeM-14 Modeling of Modern Plasma Processing Reactors Using Particle-in-Cell Codes**, *Igor Kaganovich*, Princeton Plasma Physics Laboratory, Princeton University; *D. Sydorenko*, University of Alberta, Canada; *A. Khrabrov*, Princeton Plasma Physics Laboratory, Princeton University; *S. Sharma*, Institute for Plasma Research, India; *S. Jubin*, A. Powis, W. Villafana, S. Ethier, Princeton Plasma Physics Laboratory, Princeton University

For plasma processing, there is a need to simulate large plasma devices via kinetic means, because the Electron Velocity Distribution Function in these devices is non-Maxwellian and therefore a fluid treatment is insufficient to accurately capture the physics. The method of choice for many fully kinetic simulations has been the particle-in-cell (PIC) technique due to relatively ease of implementation of the method and that it can be parallelized effectively over many processors and accelerated on GPUs. However, PIC codes that use standard explicit schemes are constrained by the requirement to resolve the short length and time scales associated with the plasma Debye radius and plasma frequency respectively [1]. This makes it

extremely challenging to perform long time 2D PIC simulations for large plasma devices. For this reason, many 2D kinetic simulations of plasmas have been limited to small or artificially scaled systems. Energy conserving [2] or implicit methods [3] must be used to remove these limitations. Effects of numerical noise in simulations using PIC code need to be analyzed and taken into account [1]. The PIC codes have been applied to study plasma processing applications, such as capacitively coupled plasmas, electron beam produced plasmas, inductively coupled, hollow cathodes [4-9]. The Darwin scheme was implemented for simulations of inductive discharges.

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11:30am **PS-WeM-15 Intermediate Pressure Capacitively Coupled Ar/ N_2 Plasmas – Experimental Diagnostics and Modeling**, *Abhishek Verma, K. Bera, S. Rauf*, Applied Materials Inc.; *S. Hussain, M. Goeckner*, University of Texas at Dallas

Intermediate pressure (1-10 Torr) capacitively coupled plasmas are used for numerous deposition and etch applications in the semiconductor industry. In this work, we describe experiments in a modified Gaseous Electronics Conference (mGEC) reference cell. These measurements are used to validate an in-house hybrid fluid plasma modeling framework for Ar/ N_2 capacitively coupled plasmas (CCP) operating at intermediate pressures. The model validation is critical for providing confidence in the model as a predictive tool for development of semiconductor applications as well as elucidate the underlying physics behind the complex mechanisms associated with the plasma processes. For this study, we focused model validation for Ar/ N_2 CCP processes in an asymmetric electrode chamber configuration with complex electrical connections. As part of model validation process, the experimental measurements are performed over a range of pressures and powers. The model includes fluid plasma equations for charged and neutral species and a Monte Carlo model for secondary electrons, coupled with Poisson's equation for self-consistent electrostatic plasma description. The model validation study accompanies sensitivity analysis of critical model input parameters for overall uncertainty of model output as well as discussion on experimental uncertainties. Our findings include the model performance over a range of parameters and plasma characterization of Ar/ N_2 CCP.

11:45am **PS-WeM-16 Controlling the Etch Process by Changing the Plasma Chemistry Through Pulsing**, *Evrin Solmaz, D. Zhang*, TEL Technology Center America; *B. Lane*, Tokyo Electron America; *Y. Sakakibara, S. Uda, M. Yamazaki, C. Thomas, T. Saito*, Tokyo Electron, Japan; *Y. Tsai*, TEL Technology Center America; *T. Hisamatsu, Y. Yamazawa*, Tokyo Electron, Japan

Plasma etching has been a key part of modern integrated circuit fabrication technology. The plasma etch process can be both material-selective and directional, enabling significant control of etch profiles. Among various plasma tuning features, the pulsed power operation has emerged as an effective option to provide additional controls to plasma properties for improving the etch results. A challenge of optimizing the pulse setting for each target, no different from other conditions, is the tremendous number of possible combinations which makes the purely empirical process development costly. As a remedy, we show that the pulsed plasma modeling can guide not only the process development but also real time control. Pulsing changes the plasma chemistry through the differences in the timescales of important phenomena. We identify and exploit these timescales to enhance the process control and address challenges associated with high aspect ratios and small CDs (critical dimensions). We show how the pulse repetition frequency (PRF) affects individual radical neutral fluxes, hence the F/C ratio in fluorocarbon plasmas. The result implies a possible etch/deposition flavor change as the differences in the generation and decay times of F and C radicals (C, CF, CF_2 , CF_3) are the culprits for the lean and polymerizing regimes. Pulsing also affects electronegativity by separating the electron and ion decay timescales. In

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addition to the radical ratio, we show simulation results of an ion-ion chlorine plasma where the electrons are depleted quickly in the afterglow of the pulsed discharge. The formation of an ion-ion plasma explains the mechanism by which etching continues into the afterglow, as evidenced by recent experimental data. With an offset bias pulse, we observe a continued albeit slower directional etch process. Electrons are long gone in the source afterglow, but vertical etching still carries on, which shows that there are still ions present. This finding suggests that it is possible to control the electronegativity and the vertical etch rate by selecting when to employ the offset bias pulse.

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Room 124 - Session PS1-WeA

Plasma Modelling AI/ML

Moderator: Amanda Lietz, North Carolina State University

2:15pm **PS1-WeA-1 Sequential Plasma Process Design by Genetic Algorithm**, *Patrick Conlin, G. Hartmann, Q. Wang, R. Longo, S. Sridhar, P. Ventzek*, Tokyo Electron America, Inc.

The complexity of modern semiconductor device fabrication has caused the parameter space of plasma process design to balloon to levels which are untenable to navigate without algorithmic guidance. The degrees of freedom provided by so-called process knobs alone present a substantial optimization challenge. "Time" is by far the most flexible process knob and the sequencing of plasma processes is the largest source of complexity, next to the choice of process chemistry. Understanding the interval scheduling problem in the context of plasma-surface interactions is hindered by a sparse fundamental knowledge of species-surface site interactions, and the computational and experimental effort required to elucidate these relationships. An alternative approach to the scheduling problem is to employ phenomenological models to establish guiding principles for how a process is sequenced, i.e. the problem may be split into more tractable parts. For example, how flux and energy interact on a surface can be used to order sequences of fluxes. From sequences of flux and energy, one can work backwards to understand plasma conditions that can be used practically. Many different optimization approaches are available for the scheduling problem. Here we describe the use of a genetic algorithm (GA) to study the impact of time series of plasma-generated species and energy flux on basic surface evolution parameters like etch depth, selectivity, and profile. GAs are well-established in the study of optimization and are considered especially well-suited for solving interval scheduling problems. We encode Langmuir-Hinshelwood plasma-surface interaction kinetics, which form the fundamental basis for plasma processes, into our GA. We recover the intuitive limits where continuous and atomic layer etch equivalents of radical pre-loading are optimal sequences. Models of increasing complexity are demonstrated with different objective functions. The limitations of GAs, generally and in this specific context, are discussed.

2:30pm **PS1-WeA-2 Machine-Learning-Based Force Fields for Molecular Dynamics Simulation of Silicon and Silicon Dioxide Ion Beam Etching**, *Shunya Tanaka, S. Hamaguchi*, Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, Japan; *H. Kino*, National Institute for Materials Science (NIMS), Japan

Recently machine-learning (ML) techniques have been developed to create interatomic force fields and potentials for classical molecular dynamics (MD) simulations in the field of materials science. The ML-based force fields are the surrogate model of the realistic interatomic force fields, where the surrogate model can offer the force fields far more quickly than the corresponding density-functional-theory (DFT)-based quantum mechanical calculation by interpolating a large amount of force-field data with a large number of possible atomic configurations evaluated in advance by the DFT-based calculations. The ML-based force fields are expected to be far more accurate than the widely used classical interatomic force-field models and can be as accurate as those obtained from the DFT-based calculations. However, unlike typical MD simulations in thermodynamical equilibrium widely used in materials science, sputtering/etching simulations require special attention in the development of such force fields; in typical sputtering simulations with high-ion-energy impacts, some interatomic distances can become extremely small and the standard DFT-based force-field data do not cover such cases. Therefore, in our study, the Ziegler-Biersack-Littmark (ZBL) potential functions were used to represent the short-range repulsive interaction whereas the ML-based force fields were employed otherwise. The ML-based force fields were developed with the Behler-Parinello Neural Network (BPNN) and the Graph Neural Network (GNN) with active learning based on query by committee sampling. MD simulations with the newly obtained MD-based force fields were performed for ion beam sputtering/etching of Si and SiO₂ and the results were compared with the beam experimental data as well as the existing classical MD simulation results.

2:45pm **PS1-WeA-3 Machine Learning Interatomic Potentials for Plasma-Surface Interaction Simulations**, *Jack Draney, A. Panagiotopoulos, D. Graves*, Princeton University

Results of molecular dynamics (MD) simulations of nonequilibrium plasma-surface interactions are highly sensitive to the accuracy of the underlying interatomic potential. Increasingly complex interatomic potentials, such as ReaxFF [1], have been developed to capture more and more of the underlying physics of atomic forces. The most flexible and accurate potentials are often the slowest, requiring significant computing power to reach the long timescales typical in simulations of plasma-surface interactions. Machine learning potentials (MLP) such as DeePMD [2], originally developed to fit quantum density functional theory (DFT) data, represent maximally flexible models and run quickly on GPUs. In this work, we show how MLPs can not only be derived from DFT, but also from classical potentials like ReaxFF. We demonstrate the quality of the derived MLPs by comparing them to their classical counterparts in simulations of oxygen, hydrogen, and argon plasma interactions with diamond and amorphous carbon surfaces. We use what we've learned from this process to fit MLPs to DFT data for the same system and compare the results to those from classical potentials. Finally, we outline some of the possible pitfalls associated with the successful production and use of MLPs for plasma-surface interactions.

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3:00pm **PS1-WeA-4 Dry Etching Process with NLD Plasma Distribution Determined by Machine Learning**, *Keiichiro Asakawa, K. Doi, Y. Morikawa*, ULVAC, Inc., Japan

A magnetic neutral line discharge (NLD) is an inductively coupled plasma generated along a magnetic neutral loop (NL). NLD can generate high-density plasma with low electron temperature at low gas pressure, and is used for dry etching of various device structures such as optical devices and MEMS (Micro Electro Mechanical System). Typically, a magnetic field is induced by three electromagnetic coils placed around the chamber, and the NL region is formed in a ring shape where the magnetic fields cancel each other out and become zero. The radius of NL depends on the current value of each electromagnetic coil. Therefore, by adjusting the current values of the electromagnetic coils, the size of the NL radius can be modified and the spatial distribution of plasma can be optimized for the required etching distribution across a wafer. Conventionally, it was time-consuming to optimize the current values of each electromagnetic coils so that the resultant magnetic field for a given NL radius would be zero. Therefore, we developed a new application that applies machine learning (gradient descent method), and made it possible to instantly output the coil current values for each input NL radius and Z-axis position. This has become an effective means of spatial and temporal control of the NLD plasma distribution, potentially realizing uniform etching condition, i.e., radicals and ions contributions, across a wafer.

3:15pm **PS1-WeA-5 Accelerating Plasma-based Process Development and Chamber Productivity with Artificial Intelligence**, *Meghali Chopra, S. Sirard*, SandBox Semiconductor Incorporated

Developing advanced semiconductor chips is becoming more expensive and time consuming due to the growing sophistication of processing tools, recipes, and chip architectures. Traditional brute force trial-and-error approaches for optimizing recipes are becoming unsustainable as it is impractical for human process engineers to experimentally explore the trillions of possible recipe combinations on advanced fabrication tools. Furthermore, many of the recipe parameters for plasma etch and deposition processes display complex, non-linear interactions. Here we showcase a software platform, SandBox Studio™ AI, that efficiently generates optimal recipes for plasma etch and deposition processes in less than 75% of the time of statistical experimental design approaches. Superior performance is achieved by using a hybrid physics-based model coupled with artificial intelligence (AI), thus requiring far fewer experiments to calibrate. The platform is tool agnostic and automatically maps the multi-dimensional process space and provides recipe recommendations to achieve desired feature profile and uniformity targets. The AI-driven approach has been applied across a wide variety of applications and development phases. Successful examples of plasma etch and deposition recipe predictions that optimize both feature profiles and wafer uniformity for logic and memory applications will be discussed. Additionally, we

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demonstrate how co-optimized multi-step etch and deposition recipes capture step interactions, leading to a larger process window compared to sequentially optimizing each step separately. Beyond process engineering, SandBox Studio™ AI can be used to improve fab tool productivity. The AI toolset has been used to identify the root causes of process drift by correlating tool sensor data to on-wafer results. The software has addressed other common tool issues such as chamber-to-chamber matching and can predict optimal recipe conditions to maximize yield across multiple chambers. An optimized model may be used to make new recipe predictions when minor fluctuations or adjustments are made to the incoming chip stack dimensions. In summary, our approach enables engineers to streamline plasma-based recipe development, cut costs, and enhance manufacturing productivity.

Plasma Science and Technology

Room 124 - Session PS2-WeA

Plasma Processes for Emerging Device Technologies

Moderator: Phillipe Bezdard, IMEC Belgium

4:15pm **PS2-WeA-9 Low Damaged GaN Surface Through Passivating Plasma Etching and Post-Etch Treatments for Improved GaN-MOS Capacitor Performance**, *David Cascales*, CEA-LETI & LTM, France; *P. Pimenta-Barros*, *E. Martinez*, CEA-LETI, France; *B. Salem*, LTM - MINATEC - CEA/LETI, France

The power electronics industry is facing new challenges to meet the increasing needs of electrical power in modern devices [1]. These needs require an efficiency rise of power converters, also accompanied by higher operating voltages, currents and frequencies. Wide bandgap materials such as GaN are then investigated and preferred to Si-IGBT converters due to silicon limits being reached [2]. Lateral and vertical GaN-based power devices have emerged such as the vertical MOSFET or the lateral MOS-channel High Electron Mobility Transistor (MOSc-HEMT). With both technologies, normally OFF properties are needed and can be achieved with a gate recess, while a MOS gate controls the channel operation.

Plasma processing is crucial for channel and gate performance [3]. For instance, the recess shape can directly affect channel conducting properties and gate leakage, while the damaged GaN layer can influence the gate's behavior by deteriorating the flat band voltage. Indeed, flat band voltage is driven by charge generation that is caused by lattice amorphization, nitrogen depletion, element implantation or etching by-products deposition [4].

This study aims to investigate negative charge generation at the GaN/dielectric interface in order to shift threshold voltages towards greater values. Plasma etchings and post etch treatments (PET) were performed in an ICP chamber, together with pre-deposition treatments in the ALD chamber prior to dielectric deposition to limit nitrogen depletion and lattice amorphization.

First, thanks to X-ray Photoelectron Spectroscopy measurements, we will discuss the chemical modifications induced by silicon introduction (SiCl_4) in a Cl_2 plasma etching chemistry. A Si-based layer protecting GaN from ion bombardment is present at the $\text{Al}_2\text{O}_3/\text{GaN}$ interface. The Si-layer and GaN evolution through the MOS capacitor fabrication steps will then be analyzed, including the O_2 PET, and the Al_2O_3 ALD preceded by an HCl gallium oxide removal. SiCl_4 addition shows a significant flat band voltage improvement with C-V measurements. As well, HCl replacement by a dry *in situ* N_2/H_2 pre-deposition treatment for high SiCl_4 etching ratios will also be examined.

Finally, we will explore the impact of PET chemistry variations after $\text{SiCl}_4/\text{Cl}_2$ etching with addition of N_2 to the O_2 chemistry, giving a better understanding of the plasma interactions with GaN, the SiN holder and chamber walls. The goal is to restore the N/Ga ratio with nitrogen supply.

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4:30pm **PS2-WeA-10 Anisotropic and Sub-Micrometric InGaP Plasma Etching for High Efficiency Photovoltaics**, *Alison Clarke*, *M. de Lafontaine*, University of Ottawa, Canada; *R. King*, *C. Honsberg*, Arizona State University; *K. Hinzer*, University of Ottawa, Canada

Nanoscale III-V semiconductor etching enhances light trapping, enabling low cost and efficient photovoltaic devices [1]. Mitigating sidewall erosion

and chlorine-based defects is crucial for increased device performance. However, anisotropic III-V patterning with sub-micrometric definition has many challenges, such as sidewall erosion and surface damage [2]. Room-temperature InGaP plasma etching is challenging due to non-volatile InCl_x subproducts. Chlorine-based plasmas lead to defects which can be passivated by introducing hydrogen-based plasma chemistries [3].

InGaP nanotextures with vertical sidewalls were patterned using electron-beam lithography and inductively coupled plasma etching. Circular nanotextures with 850 nm diameter and 150 nm minimum spacing were patterned in a hexagonal array. The etch was performed at room temperature to limit sidewall erosion [3], using the resist as a mask. To assess the impact of chlorine and hydrogen, four plasma chemistries were investigated: Cl_2/Ar , Cl_2/H_2 , $\text{Cl}_2/\text{Ar}/\text{H}_2$, and Ar/H_2 . The etched InGaP was investigated with atomic force microscopy. The Cl_2/H_2 plasma produced the fastest average etch rate (150 nm/min), with aspect ratio of 0.66. The Ar/H_2 plasma had the slowest average etch rate (75 nm/min) due to the absence of Cl-based chemical etching. All etch rates were low due to the high (~25%) In content in the InGaP which creates poor volatility byproducts. Hydrogen improved the etching process, suppressing chlorine-based defects and decreasing the line edge roughness by up to 48% compared to the plasma without hydrogen.

These results show that hydrogen-based plasma chemistries improve pattern transfer for photovoltaics applications, where precise control of critical dimensions is required to improve conversion efficiencies. Ongoing work on top view and cross-sectional scanning electron microscopy will also be presented along with device performance measurements to confirm light-trapping properties. Complimentary characterizations such as energy-dispersive X-ray spectroscopy will be performed to benchmark the passivation properties of hydrogen plasmas.

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4:45pm **PS2-WeA-11 On the Plasma Etching Mechanisms of Patterned Aluminum Nitride Nanowires with High Aspect Ratio**, *Saron Sales de Mello*, *L. Jaloustre*, University Grenoble Alpes, CNRS, LTM, France; *S. Labau*, *C. Petit-Etienne*, University Grenoble Alpes, CNRS, LTM, France; *G. Jacopin*, University Grenoble Alpes, CNRS, Institut Néel, France; *E. Pargon*, University Grenoble Alpes, CNRS, LTM, France

III-nitride (III-N) semiconductor light-emitting diodes (LEDs) are a particularly promising alternative to mercury vapor lamps as ultra violet (UV) sources [1]. However, the external quantum efficiency (EQE) of current planar $\text{Al}_x\text{Ga}_y\text{N}$ well-based UV LEDs is extremely low (<1% for wavelengths below 250 nm) [2]. Three-dimensional (3D) core-shell architecture offers some promising solutions to increase UV LED efficiency up to 50%. This approach consists in radially growing emissive quantum wells on predefined aluminum nitride (AlN) nanowires (Fig.1) [3]. The top-down combining lithography and plasma etching transfer is the only viable approach to fabricate the well-organized arrays of high Aspect Ratio (AR) AlN nanowires required.

This study aims to develop a chlorine (Cl_2) plasma etching process in a Inductively Coupled Plasma (ICP) reactor dedicated to high AR AlN nanowires (AR>10, i.e. sub-500nm diameters, 4µm-high) fabrication, based on a fundamental understanding of the etching mechanisms involved. The samples are AlN (4µm) grown on sapphire substrate with a silicon oxide (SiO_2) 1.4µm thick hard mask on top. Electron beam lithography is used to design dots with several diameters, densities and shape. We investigate the impact of the plasma parameters (source, bias and pressure) on the AlN etch rates, AlN/ SiO_2 etch selectivity, pattern profiles and sidewalls roughness. We observe that the carrier wafer (CW) chemical nature (Si or Si_3N_4) affects the nanowire profile. Under the same plasma conditions, the use of Si_3N_4 CW always leads to passivation layer formation on the AlN sidewalls, which creates more tapered AlN pillars than using Si CW (Fig. 2). In both cases SiCl_x etch by products coming from the CW are present in the plasma and are likely to redeposit on AlN sidewalls [4]. However, with Si_3N_4 CW, the presence of N helps to fix the SiCl_x and to form a SiNCl passivation layer.

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Ion flux, ion angular distribution and ion energy measurements show that, the plasma conditions that favor high ion flux over radical flux (higher source power, lower pressure, higher bias) enhance the AlN etching, suggesting an ion-enhanced chemical etching mechanism. In addition, conditions for which the physical component of the plasma dominates lead to tapered profiles, while anisotropic ones can be obtained when the chemical component dominates. Fig. 3 shows the source power impact on the profiles. Charging and ion angular distribution effects also affect the pattern profiles. Finally, we also observe a crystal orientation preferential etching phenomenon. Cl₂ plasma etching tends to reveal nonpolar a-planes, suggesting that they are the most stable in this process.

5:00pm **PS2-WeA-12 Room Temperature ICP Plasma Passivation for SiC MOS Capacitor**, *Rodrigo Cesar*, Center for Electronic Components and Nanotechnology - CCSNano, Brazil

Studies on silicon carbide (SiC) began in the late 1980s. Initially used as an abrasive material in cutting tools, it has become a highly promising material in the microelectronics industry due to its properties such as high thermal conductivity, high breakdown voltage, large band gap, high electron saturation velocity, and high thermal conductivity. Therefore, it is ideal for developing devices that will be used in extreme power and temperature conditions.

A crucial point in the process of manufacturing devices with SiC substrate is surface passivation. This process completes the open bonds of carbon ions, reducing the surface defects and charge density, resulting in devices with better performances. There are several passivation methods such as oxidation, nitridation, doping with phosphorus ions, among others. However, all these processes occur at high temperatures, with the most commonly used being treatment in a furnace at 1500°C. In this work, we propose a passivation process where the great advantage is to carry out the process at room temperature. For this, we employ an inductively coupled plasma – ICP, and different tests, using plasmas with N₂ and N₂+O₂ gases in an ICP LAM equipment.

In order to evaluate these passivation processes, we manufacture MOS capacitors using HfO₂ as the gate dielectric and Si wafers previously passivated, which were electrically characterized using C×V curves. Here we determined the best time and gas combination that results in the best passivation and consequently the best device performance. Table 1 presents a summary of the tests carried out and table 2 shows the parameters used during the tests.

In Fig. 1A we can see a clear difference between the C×V curve of the sample with only N₂ plasma and the others. In this way, this curve was removed, as shown in Fig. 1B, where we can observe that the curve improvements occurred post-oxidation annealing (POA), with the best treatment being N₂+O₂+POA.

With the best passivation determined, two SiC capacitors were manufactured, one with passivation and the other without. Fig. 2 shows the C×V curves of these capacitors. It can be seen that there was a significant difference between the curves. The one without passivation has a VFB of 9V, twice the size of the curve with passivation. The curve with passivation demonstrates the efficiency of the passivation process, presenting a well-defined C×V curve with a smaller range than that without passivation, in addition to the fact that the VFB value is 4V.

This indicates that room temperature passivation by ICP plasma is effective.

Plasma Science and Technology Room 124 - Session PS-ThM

Plasma Sources, Diagnostics and Control I

Moderators: Michael Gordon, University of California at Santa Barbara, Steven Vitale, MIT Lincoln Laboratory

8:00am **PS-ThM-1 Radio-frequency Hollow Cathode Discharge: Modeling and Experimental Diagnostics**, **Kallol Bera**, Applied Materials, Inc.; **H. Luo**, Applied Materials, Inc., Canada; **X. Shi**, Applied Materials, Inc.; **I. Korolov**, Ruhr Universität Bochum, Germany; **A. Verma**, **S. Rauf**, Applied Materials, Inc.; **J. Guttman**, **J. Schulze**, Ruhr Universität Bochum, Germany

Low to intermediate pressure radio-frequency (RF) hollow cathode discharges (HCDs) have gained significance for advanced plasma processing in the semiconductor industry. HCDs form in the cavities in the cathode that is separated from the anode by a dielectric. In the HCD, RF sheath heating as well as secondary electron acceleration can lead to plasma production. Complementary modeling and experimental studies are performed for slotted hollow cathode discharge to validate plasma model as well as to elucidate discharge physics behavior at various operating conditions in several designs. The design parameters include the slot width (10 - 20 mm), angle (0 - 10°) and shape (linear and curvilinear), while the process parameters are pressure (2.5 - 100 Pa), RF voltage (200 - 500 V) and gas mixture. Electropositive Ar, electronegative O₂, and their mixtures are considered. For the experiments, slot structures are constructed in the cathode, and Phase Resolved Optical Emission Spectroscopy (PROES) is performed for Ar I emission. From the emission spectrum, spatio-temporal distribution of excitation rate is obtained. A hairpin probe is utilized to diagnose plasma density in the transverse direction. For plasma modeling, a 2-dimensional planar computational domain in transverse plane to the slot is considered. At low-pressure (tens of mTorr), where kinetic effects are important, particle-in-cell Monte Carlo collision (PIC-MCC) modeling scheme is used. The PIC-MCC model includes evolution of charge densities from charged particles and electrostatic field and charged particle collisions with each other and with neutral fluid using a Monte Carlo model. At intermediate pressure (several hundreds of mTorr), due to high collisionality, the PIC-MCC modeling becomes computationally prohibitive. Therefore, hybrid-fluid plasma model is used that includes fluid plasma equations for charged and neutral species, and a Monte Carlo model for secondary electrons, coupled with Poisson's equation for self-consistent electrostatic plasma simulation. At low pressure the behavior of excitation rate using PIC-MCC simulation matches reasonably well with experimental data. However, excitation rate distribution at moderate pressure using the hybrid-fluid model has some discrepancies. The plasma density profiles from PIC-MCC and fluid simulations are consistent with the experiments. Based on our analysis, the hybrid-fluid plasma model is being improved to better describe RF hollow cathode characteristics.

8:15am **PS-ThM-2 Advancing In situ Transmission Electron Microscopy to Study Plasma-Nanomaterials Interactions**, **Jae Hyun Nam**, University of Minnesota, USA; **D. Alesm**, Hummingbird Scientific; **P. Bruggeman**, University of Minnesota, USA

Non-thermal plasma (NTP) has been increasingly recognized as a promising alternative to conventional technologies in diverse fields due to its high reactivity and non-equilibrium characteristics. These properties make NTP particularly effective for material interactions, such as materials synthesis, etching, deposition, and chemical redox processes. Although NTP is extensively employed for the synthesis and functionalization of nanomaterials, the direct observation and mechanistic understanding of these interactions have been limited due to the significant technical challenges associated with the development of *in situ* diagnostic capabilities.

Significant advances have been made in *operando* environmental Transmission Electron Microscopy (TEM) enabling the monitoring of nanoparticle growth in solutions in an environmental TEM configuration. Despite these advancements, applications of *in situ* TEM in the NTP field have been sparse, primarily due to the challenges of integrating the necessary vacuum conditions and microscale requirements of TEM with the gaseous environment and high-voltage requirements of NTP. A decade ago, an integration of microplasma within a TEM was performed by demonstrating gold sputtering by argon plasma, albeit with a spatial resolution restricted to approximately 100 nm. Our recent new developments have successfully overcome these limitations, establishing an

in-situ plasma TEM capability with a spatial resolution of less than 1 nm. This was achieved through the introduction of micron-sized electrodes in a gas environmental TEM cell enabling atmospheric micro-plasmas directly inside an electron microscope. The new device allows us to sustain atmospheric plasma steadily for several hours.

We demonstrate our *in situ* TEM capability through the real-time observation of morphological changes in iron oxide nanoparticles (magnetite, Fe₃O₄), likely induced by reduction processes, under DC hydrogen microplasma (He/H₂, 0.5 %) exposure with a temporal resolution of 1 s. This novel technique not only deepens our understanding of plasma and material interactions on a small scale, but also significantly expands the potential for *in situ* TEM studies in the NTP field.

Acknowledgement: This material was also based upon work supported by the Army Research Office accomplished under Grants No. W911NF-20-1-0322 and W911NF-20-1-0105.

8:30am **PS-ThM-3 Sensing and Control of Radio-Frequency Driven Plasmas**, **Timo Gans**, Dublin City University, Ireland **INVITED**

Sensing and control of radio-frequency driven plasmas is crucial for next-generation plasma manufacturing. Surface interactions and negative ions play key roles in the properties of reactive molecular processing plasmas. Radio-frequency driven oxygen and hydrogen plasmas are ideal test-beds for investigations into the role of surface interactions for the chemical kinetics of the plasma and associated negative ion formation. Oxygen containing plasmas can exhibit either mostly electro-negative or mostly electro-positive characters [1, 2]. Oxygen negative ions can be efficiently destroyed by singlet oxygen which in turn is itself strongly influenced by surface reactions and surface properties [3]. Atomic oxygen, as a key reactive species, can also be dependent on surface properties [4]. In hydrogen plasmas, negative ions can be produced through surface processes as well as volume processes [5]. Nitrogen doped diamond surfaces are promising candidates for enhanced surface production of negative hydrogen ions [6,7,8]. Volume processes are determined by dissociative attachment involving vibrationally excited hydrogen molecules. These in turn are also dependent on surface properties [5]. This interplay between surface properties and the plasma chemical kinetics as well as plasma dynamics will be discussed for the examples of single [1, 3, 4, 5, 6, 7, 11] and multi-frequency [2, 9, 10] driven oxygen and hydrogen plasmas.

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9:00am **PS-ThM-5 AVS National Student Award Finalist Talk: Time Resolved Diagnostics of HiPIMS Discharges With Positive Cathode Reversal**, **Zachary Jeckel¹**, University of Illinois at Urbana Champaign; **T. Choi**, **N. Connolly**, University of Illinois Urbana-Champaign; **S. Das**, University of Illinois at Urbana Champaign, India; **M. Hossain**, University of Illinois Urbana-Champaign, Bangladesh; **D. Kapelyan**, **N. Vishnoi**, **R. Pickering**, University of Illinois at Urbana Champaign; **D. Qerimi**, University of Illinois Urbana-Champaign; **D. Ruzic**, University of Illinois at Urbana-Champaign

This work investigates the temporal evolution of a high-power impulse magnetron sputtering (HiPIMS), with a positive cathode reversal, discharge by using a number of different diagnostics such as gated fast cameras, time resolved Langmuir probes, and time and energy resolved mass spectrometers acquired using the plasma sampling mass spectrometer (PSM). Using time resolved Langmuir probes we have studied that the rise time of the plasma potential is 1-2 μs which correlates to the time scale over which the ion energy distribution function (IEDF) is seen to increase. This, paired with PSM data collected where the magnetron and PSM are 90 degrees off axis

¹ AVS National Student Award Finalist

from each other still showing an increase in the Ag^+ energy suggests that the plasma potential commuting throughout the volume is one of the primary causes of increased ion energy after the positive cathode reversal. The Langmuir probe setup also allows for the creation of time resolved electron energy distribution functions (EEDF) both near the substrate and near the target which offers valuable insight into the discharge physics. Using the PSM we have shown that at early stages of the positive cathode reversal there is an elevated population of metal ions and that the overall fraction of metal to working gas fraction is at its highest. Time and energy resolved mass spec data was collected on this system for a variety of conditions such as pulse lengths, pressures, and target material with the objective of developing a better understanding for the energetics at play. Additionally, it was discovered that for the reactive sputtering of TiN that the IEDF of the N^+ species has a high energy tail of 40 eV at a pressure of 4 mTorr. This distribution mirrors that of Ti^+ which indicates that the target poisoning is responsible for an increase in the energy of the nitrogen species and that target poisoning could be the source of nitrogen in the film. Gated fast camera measurements taken with the PI-MAX 4 camera have been performed to investigate the formation of hot spots and observed that the formation of hot spots occurs above the critical current density for silver. Fast camera measurements are also taken on and off axis to visualize the 3-D structure of spokes, and to visualize how the discharge changes when the positive cathode reversal occurs. Additionally, it was found that for cases with current four times higher than the critical current threshold that the hot spots seem to disappear, however, coupling PSM measurements with the fast camera we can see linear correlation between discharge current and counts of Ag^{+2} which suggests that the hot spots have disappeared due to rarefaction of the working gas.

9:15am **PS-ThM-6 Understanding Plasma Surface Dynamics Through Time Resolved Ion Energy Analysis for Deposition/Etch Processes, Angus McCarter**, Impedans Ltd., Ireland; A. Verma, Impedans Ltd., India

As semiconductor critical dimensions are decreasing rapidly, reproducible control of etching and deposition processes has become crucial. These processes are heavily dependent on the chemical/physical processes occurring on the wafer surface. Like any other surface in contact with plasma, a sheath usually develops on the wafer which pulls down the ions out of bulk plasma necessary to complete the process on the wafer. Furthermore, external RF/DC/tailored waveform biases are applied to the wafer to modify the ion behaviors as it can affect the chemical composition, microstructure and the associated electrical properties of the thin films during plasma assisted deposition processes as well as the selectivity and anisotropy of high aspect ratio trenches in etching processes. Therefore, the characterization of only bulk plasma is not sufficient in providing insights necessary to understand the plasma surface interactions. A high-speed monitoring of the ion energy distribution function and ion flux can lead to enhanced understanding of the plasma surface interactions and improved process performance.

We will highlight the successful measurements done by the *Semion* RFEA diagnostic under different chamber and bias conditions. Such applications enabling accurate and precise control of etching profiles on different materials and various plasma chemistries. The *Semion* measures the ion energies hitting a surface, the ion flux, negative ions and bias voltage at any position inside a plasma chamber using an array of integrated sensors. On the other hand, the *Semion pDC system* measures these parameters in real time over an energy range up to 2000 eV (process dependent). It can do sub-microsecond time resolved measurements, for studying pulsed ICPs, or pulsed DC biases, as well as floating and grounded substrate conditions. The *Semion Pulsed DC system* is the key instrument used to measure the temporal evolution of the ion energy and flux at different times through the pulse period of a pulsed DC plasma process. These measurements are essential for establishing the correlation between the plasma inputs and the ion energy/flux which, in-turn, determines the effectiveness of the surface treatment.

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9:30am **PS-ThM-7 The Plasma Dynamics of Dual Frequency Capacitively Coupled Argon Discharge using Tailored Voltage Waveforms, Syed M Zulqarnain, A. Lietz**, North Carolina State University; J. Prager, T. Ziemba, J. Perry, P. Melnik, EHT Semi

Ion energy and flux represent the primary factors of significance for etching and deposition plasmas in the semiconductor industry. The independent control over ion energy and flux to some degree can be achieved by harnessing the dual-frequency capacitively coupled plasmas. Tailoring the voltage waveform shape beyond simple sinusoids has unlocked a regime where ion energy distributions can be controlled. In this work, we simulate a dual-frequency capacitively coupled argon discharge employing a high-frequency (60 MHz) sinusoidal voltage waveform at the upper electrode and low-frequency (400 kHz) tailored triangular-shaped waveform at the lower electrode using a Monte-Carlo collision-based, particle-in-cell simulation (EDIPIC³). This exploration entailed a comprehensive assessment of plasma dynamics in response to alterations in the shape (including peak width and slope of the negative and positive regions) of the tailored voltage waveform. The temporal control of ion energies, synchronized with the shape of the tailored voltage waveform, was observed, offering potential benefits for regulating the chemistry during processing. The ion energies exhibited a correlation with the cumulative effects of the two applied waveforms. The low-frequency waveform dominated ion acceleration and temporal variations of ion energies. However, the energetic ions were slightly influenced by the high-frequency component leading to the emergence of two energetic peaks. The most power was delivered to the ions primarily during the negative cycle, especially after the positive pulse ended, while the electrons gained power mostly in the sheath edge with most power delivered during the positive pulse. The rate of rise of the positive portion of the waveform had minimal impact on ion distribution, but it did result in an increase in the number of electrons (of energies between 20-40 eV) reaching the lower electrode. This outcome could potentially aid in addressing charging concerns in the process of semiconductor etching of high aspect ratio features.

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9:45am **PS-ThM-8 A Real-Time 2-D Gas Temperature Monitoring Sensor Based on Molecular Emission Spectroscopy, Dhruval Patel**, University of Illinois at Urbana-Champaign; D. Jacobson, Lyten; D. Qerimi, University of Illinois at Urbana-Champaign; M. Stowell, Lyten; D. Ruzic, University of Illinois at Urbana-Champaign

Recent trends have indicated a growth in the usage of thermal and non-thermal plasmas for material processing applications. In these processes, gas temperature is a critical thermodynamic state variable, but sensors suitable for monitoring its fluctuations in plasmas are few and often not applicable. The most straightforward method is to estimate the gas temperature based on the rotational temperatures obtained from molecular transitions in plasma. Not only does this require access to a spectrometer, but analysis can often be time-consuming. This study aims to address this by designing and testing a stand-alone 2-D optical sensor capable of simultaneous *in-operando* measurements of rotational and vibrational temperatures.

The proposed optical sensor monitors the emission intensity of specific rovibronic transitions of the $\Delta v = 0$ and $+1$ sequences of C_2 Swan system. The light collected from a point source is split into three different color channels using beam-splitters and carefully selected bandpass filters. The net intensity of light from each channel is monitored with photodiodes/CCD sensors. The rotational and vibrational temperatures are inferred by comparing relative intensity of light collected from each channel to those predicted by simulations. The simulations used in this work assume that the rotational and vibrational states follow Boltzmann statistics to minimize the number of channels required in this device. The applicability of this sensor is limited to cases which satisfy this assumption. As a result, it is necessary to test the feasibility of this sensor in various discharge conditions on a case-by-case basis. For the scope of this work, we limit ourselves surface wave microwave discharges, operated at low and high pressures.

The accuracy in temperature measurements is evaluated by comparing them to those obtained using the well-known Boltzmann analysis technique. A high-resolution Czerny-Turner spectrometer is employed to obtain well-resolved ro-vibronic transitions of the $\Delta v = +1$ sequence. Boltzmann analysis of these transitions is not only used to estimate the rotational and vibrational temperatures, but also monitor any departure from expected density distributions. In addition, rotational temperatures

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are also compared to gas temperature measurements obtained from the doppler broadening of the H β line. Combined these results will demonstrate the viability of this sensor for its usage as a gas temperature monitoring device.

11:00am PS-ThM-13 Fiber PROES: Phase-Resolved Optical Emission Spectroscopy by Time-Correlated Photon Counting Through Optical Fibers, Florian Beckfeld, I. Korolov, Ruhr University Bochum, Germany; M. Höfner, SENTECH Instruments GmbH, Germany; J. Schulze, Ruhr University Bochum, Germany

Phase-resolved optical emission spectroscopy (PROES) is a powerful, non-intrusive plasma diagnostic tool that can give useful insight into plasma parameters like the electron density or surface coefficients by visualizing the dynamic of the highly energetic electrons in the plasma. Furthermore, PROES may also be used to calculate the energy distribution function of these highly energetic electrons by applying a rate equation model. Despite these benefits, PROES has not been able to make a transition into the industry, as it requires optical access to wide regions of the discharge, which is not given in industrial plasma chambers. Additionally, the intensified charged-coupled device (ICCD) cameras commonly used for the diagnostic require expensive investments. To address these issues, we propose a technique for PROES based on photon counting. This brings several benefits: photon counting can be realized with a photomultiplier tube (PMT), which has fractions of the cost of an ICCD camera. This PMT can then be connected to the plasma chamber with an optical fiber, making the diagnostic easy to integrate into existing structures. In this work, measurements of the heating mode in a geometrically symmetric capacitively coupled plasma will be shown to demonstrate the capability of the approach to PROES with a PMT compared to measurements with an ICCD camera.

11:15am PS-ThM-14 Atomic Hydrogen Density, Electron Density and Ion Flux Energy Distribution of an Ar/H₂ Remote CCP Plasma Source for Atomic Scale Processing, M. van Gorp, Thomas van den Biggelaar, A. Salden, H. Knoops, E. Kessels, Eindhoven University of Technology, Netherlands

A remote CCP source (Oxford Instruments PlasmaPro ASP) has been developed for higher throughputs for atomic layer deposition (ALD) processes, by generating high radical fluxes combined with controlled ion bombardment. In a previous study [1], it has been shown that this plasma source is well suited for Al₂O₃ deposition on GaN when operated with Ar/O₂ plasmas. This work uses a testbed setup containing the remote CCP source. The setup has optical access that allows extensive studies on plasma-surface interaction (PSI), relevant for ALD, atomic layer etching (ALE) and 2D material modification. Ar/H₂ plasmas can generate hydrogen atoms that, combined with ions, could modify materials synergistically. In this study, an Ar/H₂ (95%/5%) plasma is characterized by three diagnostics as a starting point for PSI studies. First, two-photon absorption laser induced fluorescence (TALIF) has been employed to measure the absolute atomic hydrogen density as a function of distance to the substrate surface for different pressures (38-375 mTorr). In this pressure range, a constant dissociation degree of 10% has been found, with $n_H = 10^{12} - 10^{13} \text{ cm}^{-3}$. Second, a Langmuir probe has been used to spatially measure the electron density, which is in the order of 10^{10} cm^{-3} . Third, a retarding field energy analyzer (RFEA) probe has been employed to determine the ion flux energy distribution, ion energies and ion fluxes at the substrate table. The measured ion flux energy distribution has been found to be bimodal, with ion energies and fluxes that are dependent on pressure and power. Both the Langmuir probe and the RFEA probe show that the electron density at the substrate table rapidly drops at pressures greater than 263 mTorr. Since the hydrogen dissociation degree remains constant in this region, it is hypothesized that the plasma source becomes remote at pressures above 263 mTorr, i.e. the plasma becomes confined near the electrodes instead of filling the whole reactor. Given the outcomes, PSI for atomic scale processing will be further investigated specifically for hydrogen atoms and ions.

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11:30am PS-ThM-15 Spatially Resolved Measurement of Fluorine Radical Density Using Reactive Radical Probes, Jeremy Mettler, University of Illinois at Urbana-Champaign; T. Tohara, Tokyo Electron; D. Qerimi, D. Ruzic, University of Illinois at Urbana-Champaign

Plasma etching kinetics and reaction mechanisms often involve complex interactions between radical and charged species. Characterization of these

mechanisms requires accurate measurement of reactant concentrations, which is often achieved using spectroscopic techniques. While nonintrusive, these techniques have significant limitations in their spatial resolution and ability to produce absolute measurements. For complex plasma and reactor geometries, spatial distribution of radical species can play a key role in the observed etching characteristics.

In this work we discuss the development of etching based, nonequilibrium radical probes for measuring fluorine radical densities across industry relevant pressures, powers, and radical densities. Tungsten pellets are used as the active probe surface and to preserve probe lifetime a nonequilibrium analysis method was developed. The tungsten etching rate is determined in-situ by measuring the rate of energy deposition to the probe via temperature response. Fluorine radical density is determined from the etching rate, independently of ion exposure, due to the purely chemical nature of tungsten etching at high temperatures. Results from the radical probe are compared against actinometry in spatially uniform and nonuniform plasmas to validate the probe technique and highlight its spatial resolution. Fluorine density profiles are then characterized for SF₆, NF₃, and CF₄ plasmas to demonstrate the generality of the technique to multiple fluorine process gases. Measured fluorine densities ranged from $1.4 \times 10^{20} \pm .2 \times 10^{20} \text{ (#/m}^3\text{)}$ to $3.9 \times 10^{21} \pm .6 \times 10^{21} \text{ (#/m}^3\text{)}$.

11:45am PS-ThM-16 The Applicability of a Microwave Resonant Probe to the Plasma Processing of Silicon Oxide, D. White, G. Hassall, James Ellis, Oxford Instruments Plasma Technology, UK

In-situ diagnostics for industrial scale plasma processing represents a sizeable challenge for multiple semiconductor hardware companies. Simple, robust, and inexpensive sensors are required both to understand process development challenges and for real-time monitoring of the plasma process; the advent of machine learning only enhances the importance of such sensor development. A microwave enhanced resonance probe with a spiral-shaped slot design, also known as a curling probe¹⁻³, has been used to measure relative electron densities in the edge region of a Plasma Pro 100 Oxford Instruments Plasma Technology reactor. Etch tests were run across a broad range of plasmas processing parameters centred around a CF₄/O₂ plasma chemistry to ascertain the potential impact of the curling probe on the process. It was confirmed through both global and localised etch rate measurements that the curling probe was not observed to have any impact on the wafer outcomes. The sensitivity of the curling probe enabled changes in the plasma conditions to be tracked in real time with failure modes clearly visible from the measured shift in the resonant frequency.

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[3] F. Boni *et al.*, *Rev. Sci. Instrum.*, **92**, 033507 (2021)

12:00pm PS-ThM-17 Terahertz Absorption Spectroscopy for Measuring Atomic Oxygen Densities: A Comparison with ps-TALIF and CRDS, Jente Wubs, U. Macherius, A. Nave, Leibniz Institute for Plasma Science and Technology (INP), Germany; L. Invernizzi, K. Gazeli, G. Lombardi, Laboratoire des Sciences des Procédés et des Matériaux (LSPM), CNRS, France; X. Lü, L. Schrottke, Paul-Drude-Institut für Festkörperelektronik Leibniz-Institut im Forschungsverbund Berlin, Germany; K. Weltmann, J. van Helden, Leibniz Institute for Plasma Science and Technology (INP), Germany

Oxygen-containing plasmas are widely used in industry for a variety of applications, including etching, thin-film deposition, and other surface modification processes. Atomic oxygen is a key species in most of these applications. An accurate method for determining atomic oxygen densities is therefore of great importance, not only to gain a fundamental understanding of the plasma chemistry, but also to improve industrial processes. However, existing techniques, such as two-photon laser induced fluorescence (TALIF), vacuum ultraviolet (VUV) absorption spectroscopy, cavity ring-down spectroscopy (CRDS), and optical emission spectroscopy (OES), are all either bulky and expensive, experimentally challenging, or indirect and relying on a multitude of assumptions.

Terahertz (THz) absorption spectroscopy with quantum cascade lasers (QCLs) has recently been developed and implemented as a novel diagnostic technique for determining atomic oxygen densities. It is based on detecting the ³P₁ ← ³P₂ fine structure transition of ground-state atomic oxygen at approximately 4.75 THz (i.e. approximately 63 μm). THz absorption spectroscopy allows for direct measurements (i.e. no calibration is required) of absolute ground-state atomic oxygen densities, and its accuracy depends almost exclusively on the accuracy to which the line

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strength of the transition is known. Furthermore, the narrow laser linewidth of QCLs makes it possible to determine the temperature from the detected absorption profiles as well. In addition, the experimental setup for THz absorption spectroscopy is relatively compact (especially compared to TALIF setups that typically involve bulky laser systems), vacuum conditions are not essential (as opposed to when working in the VUV), and the requirements for the optical alignment are not as strict as for CRDS. These features make THz absorption spectroscopy an attractive alternative to existing diagnostic techniques.

To confirm the accuracy of THz absorption spectroscopy, we performed picosecond TALIF (ps-TALIF) and CRDS measurements of atomic oxygen densities on the same capacitively coupled radio frequency (CCRF) oxygen discharge, for a variation of the applied power (20 to 100 W) and the gas pressure (0.7 and 1.3 mbar). The obtained atomic oxygen densities (all of the order of 10^{14} cm⁻³) were found to be in excellent agreement, both qualitatively and quantitatively. This demonstrates that the three different diagnostic techniques all allow for accurate measurements and can be used interchangeably, provided that no spatial resolution is required.

Plasma Science and Technology

Room 124 - Session PS-ThA

Plasma Sources, Diagnostics and Control II

Moderators: Sumit Agarwal, Colorado School of Mines, Necip Uner, Middle East Technical University, Turkey

2:15pm PS-ThA-1 Si Etch Characteristics in an Ultra-Low Electron Temperature CF₄ Plasma, C. Chung, Junyoung Park, N. Kim, J. Choi, U. Jung, J. Jung, M. Kim, Hanyang University, Korea

The etching characteristics of Si in an ultra-low electron temperature (ULET, $T_e \sim 0.7$ eV) CF₄ plasma using a grid are investigated. Si etching is performed in the ULET CF₄ plasma, and the etch profile of Si is obtained by a Field Emission Scanning Electron Microscope (FE-SEM). When the substrate bias power is not applied, the etch profile of Si in an inductively coupled plasma (ICP, $T_e \sim 2$ V) shows a rounded shape of the trench, while the etch profile of Si in the ULET plasma shows a flat shape. When a DC pulse bias voltage is applied to the ULET plasma, the etch profile shows a flat shape trench. However, when a substrate bias voltage frequency is 12.56 MHz, the electron temperature is increased and then the etch profile at the bottom of the trench shows a rounded shape as the bias voltage increases. These results show that the ULET plasma has a significant impact on the etch profile, which seems to be the reduction in charge accumulation in the trench due to the low electron temperature.

2:30pm PS-ThA-2 Temporal Evolution of Plasma Parameters and Electron Energy Distribution in a Pulsed-Modulated Capacitively Coupled Plasma, Satadal Das, University of Illinois at Urbana-Champaign; D. Ruzic, University of Illinois at Urbana Champaign

Electron energy distribution function (EEDF) controls the production of any radical/species in plasma and the ion energy distribution on the substrate. In recent years, the pulsed-modulated capacitively coupled rf (PM-CCRF) plasma has gained much attention in the semiconductor industry due to the variations of electron temperature and plasma density over a wide range with the operating controls, i.e., the pulse repetition frequency, duty cycle and pulse shape. Recently, our group in CPMI, UIUC proposed a novel concept for controlling the time resolved EEDF at the substrate in a high-power impulse magnetron sputtering (HiPIMS) discharge. In our present work, we study the time resolved plasma parameters and EEDF for various rf powers and working gas pressures in the steady-state plasma and the effect of PM-CCRF on time resolved EEDF.

In our experiment, argon plasma is produced between two parallel-plates with 13.56 MHz rf supply. An external function generator is used for pulsing the rf power supply. An in-house developed single cylindrical Langmuir probe and two different measuring circuits are used to collect the I-V characteristics of plasma. We observe that in the steady-state condition both the plasma potential and density increase four times over the rf cycle. For the argon pressure of 5.7 mTorr (~ 0.76 Pa), the plasma potential and density reach at 33 ± 0.65 Volts and $(4.2 \pm 0.5) \times 10^{15} / \text{m}^3$ respectively. We also measure the time resolved EEDF over the complete rf cycle and it does not change with rf times. However, the shapes are broadly like Maxwellian curve. From the EEDF we calculate the effective electron temperatures (T_{eff}) and it remains constant at 12 ± 0.24 eV over the rf cycle. We also observe that both the plasma density and potential increase with increasing the rf power over the complete rf cycle; however, T_{eff} reduces. During the PM-CCRF, we measure the higher T_{eff} than the steady-state, i.e., 14.67 ± 0.36 eV and it also does not change over the rf cycle. It is important that our measured EEDF gives the density of high energetic tail electrons (up to 50 eV) which are present in plasma. The experimental observations will be discussed in detail during the presentation.

2:45pm PS-ThA-3 Probing Microwave-Driven Plasmas: Investigating Ar Metastable Densities in Ar/N₂ Mixtures via LIF Technique, Nafisa Tabassum, C. Dechant, North Carolina State University; A. Zafar, Applied Materials; D. Peterson, T. Chen, Applied Materials; S. Shannon, North Carolina State University

The spatial and time-resolved density of metastable Ar species in microwave-driven plasmas operating at 2.45 GHz is systematically investigated by Laser-Induced Fluorescence (LIF). Effects of gas pressure and microwave power are investigated in the range of 70-200 mTorr and 25-150 W. LIF measurements involve the targeted excitation of metastable atoms using a tunable Nd:YAG laser producing nanosecond duration laser pulses at 100 Hz. The laser is tuned at 696.73 nm to pump the metastable (${}^2P_{3/2}4s \ 2[3/2]^0$, J=2 level to the (${}^2P_{1/2}4p \ 2[1/2]$, J=1 level. The fluorescence

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is observed from decay to the (${}^2P_{3/2}4s \ 2[3/2]^0$, J=1 level at 727.49 nm. The fluorescence is captured using an ICCD camera along with a bandpass filter centered at a wavelength of 730 nm with 10 nm FWHM bandwidth. The LIF intensity correlates with the expected variation in metastable density. A large density gradient is observed that correlates with power and pressure. Furthermore, the study extends to mapping the population density of metastable atoms by introducing nitrogen admixture (ranging from 0 to 20 %) into the argon plasma environment. The natural lifetime of fluorescence for pure argon and the impact of introducing nitrogen is examined. The effects of varying pressure, power levels and the quenching rate, are examined through fluorescence decay. Additionally, the experimental findings are compared with simulations conducted using the Multiphysics Object Oriented Simulation Environment (MOOSE) platform.

3:00pm PS-ThA-4 Diagnostics of Plasma Parameters and Surface Impedance by Measuring AC Probe Current at Harmonic Frequencies, Junki Morozumi, K. Eriguchi, K. Urabe, Kyoto University, Japan

To understand the physical and chemical interaction between plasma and material, a methodology to diagnose both plasma and surface properties is necessary. From a physical point of view, the system consisting of bulk plasma, ion sheath, surface (modified) layer, and bulk material can be electrically modeled by a series of nonlinear resistance of the ion sheath and RC parallel circuit of the surface [1]. We have demonstrated that the impedance of the surface layer can be characterized during plasma exposure by measuring the amplitude and phase of the current flowing in the material with applying an AC voltage at various frequencies [2]. To obtain the plasma parameters, a method to analyze the nonlinear resistance of the ion sheath by measuring the current at harmonic frequencies of the applied AC voltage has been developed [3]. In recent years, we have studied the influence of the impedance of surface-modified layers on the generation of harmonic currents to develop a method to monitor plasma parameters and surface impedance simultaneously. In this study, we performed simultaneous monitoring of the plasma parameters and the surface resistance using a single metal probe in a reactive plasma generated in low-pressure Ar/O₂ gas. First, we analyze the nonlinear resistance of the ion sheath by applying AC voltage to the probe at a frequency where the surface impedance can be negligible. (>10 kHz in our system) Then, we calculate a relationship between the surface resistance and the amplitudes of harmonic currents at a frequency where the RC parallel circuit of the surface layer can be considered as a resistance. (<100 Hz) From these analyses and measurement data of the harmonic currents at the low frequency, we decide the surface resistance. By applying the AC voltage at the high and low frequencies alternately, we continuously measured the plasma parameters (electron temperature and ion density) and the surface resistance with a temporal resolution of approximately 10 s. The experimental results obtained in various discharge conditions indicate that the developed method can contribute to advanced control of plasma processing by providing data on plasma and surface properties.

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3:15pm PS-ThA-5 Plasma Diagnostics with a Transparent(ITO) Probe Based on the Floating Harmonic Method, C. Chung, Beom-Jun Seo, H. Nahm, D. Kim, Hanyang University, Korea

The floating harmonic method is commonly employed for plasma diagnostics in semiconductor processing. From the ratio of harmonic currents flowing through a floating probe in the plasma, parameters such as electron temperature and ion density can be measured. This technique is effective even when the probe is contaminated or coated with a thin dielectric film. In this study, we propose a diagnostic method that uses a floating probe with a tip made of ITO glass. By applying nonlinear circuit analysis and high-frequency voltage, we could have developed this novel approach. The primary advantage of our method is the ability to acquire both electrical and optical measurements simultaneously at the same location on the chamber wall. This dual measurement capability compensates for the inherent limitations of each individual measurement type, thereby significantly improving the accuracy and comprehensiveness of plasma diagnostics. We measured plasma parameters using the floating probe and performed optical emission spectroscopy measurements through the ITO glass.

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3:30pm **PS-ThA-6 Time-Resolved Ion and Neutral Energy Distribution Function Study of High-Power Impulse Magnetron Sputtering with Positive Cathode Reversal using a Linear Magnetron**, *Tag Choi, Z. Jeckell, S. Pickholtz, J. Miles, D. Qerimi, D. Ruzic*, University of Illinois at Urbana-Champaign

High-Power Impulse Magnetron Sputtering (HiPIMS) plasma is one of the physical vapor deposition (PVD) techniques that utilizes very short voltage pulses and a high peak currents. It can produce higher ionization fraction and denser plasma compared to conventional DC or pulsed DC magnetron sputtering, resulting in higher quality thin films such as denser films, smoother film surfaces, and better adhesion. Several years ago, positive cathode reversal technique was introduced to the HiPIMS sources, which reverses the polarity of the cathode to increase the energy of ions. This work aims to investigate the time-resolved ion and neutral energy distribution functions (IEDF/NEDF) of HiPIMS with positive cathode reversal discharge on a large area linear magnetron using Plasma Sampling Mass spectrometer (PSM) from Hiden Analytical Inc. This work includes IV traces of each pulse, which is used to confirm that the plasma produced is in HiPIMS plasma regime. Ultimately, a better understanding of HiPIMS plasma can contribute to improving film quality such as increasing uniformity, reducing stress, enhancing conductivity, and improving crystallinity. In this study, titanium (Ti) and tungsten (W) targets are utilized while parameters such as main pulse length between 10 – 100 us, peak current between 40 – 400 A, positive pulse length between 20 – 200 us, with/without positive voltage of the cathode, etc. are varied to understand how HiPIMS plasma properties vary.

3:45pm **PS-ThA-7 A Plasma Diagnostic Based Approach to Enabling Low Run-In for Sputter Deposited MoS₂ Solid Lubricants**, *Steven Larson, A. Ming, T. Babuska, M. Dugger, F. DelRio, M. Rodriguez, R. Kolasinski, J. Curry*, Sandia National Laboratories

Sputter deposited molybdenum disulfide (MoS₂) coatings have long been utilized as dry lubricants for aerospace applications because of their ultra-low friction and high performance in vacuum. Historically, sputter deposited MoS₂ films have faced challenges such as low density, poor aging resistance, and inconsistent performance across batches due to variability in material properties. To overcome these issues, the industry resorted to doping MoS₂ coatings with various metals (Ni, Ti, Al, Pb, Au, WSe) and nonmetals (Sb₂O₃, PbO, C), which, while improving density and consistency, undesirably increased initial friction, particularly after aging. In this study we present using a modern, plasma diagnostic based approach to develop high performance undoped MoS₂ coatings. Using these methods, we tie deposition parameters directly to ion flux and energy, and eventually to the resulting material properties (crystallinity, hardness, modulus, and stoichiometry) and tribological performance (friction, run-in, and wear rate) of the of the deposited films. The resulting undoped MoS₂ coatings demonstrate a near bulk density, and maintain an ultra-low initial friction, both before and after aging. Sandia National Laboratories is managed and operated by NTESS under DOE NNSA contract DE-NA0003525. SAND2024-06329A

Plasma Science and Technology

Room Central Exhibit Hall - Session PS-ThP

Plasma Science and Technology Poster Session

PS-ThP-1 Atmospheric Pressure Plasma Pencil as a Sterilization Source, *Abdul Majid*, University of Gujrat, Pakistan; *N. Rehman*, COMSATS, Pakistan
Plasma based sterilization, at atmospheric pressure in Pencil configuration, is a newly developing technique which have several advantages over the conventional techniques. It is environment friendly technique which has low initial and operational costs and requires low temperature processing. UV radiations, heat and reactive species densities are the major players of plasma based sterilization [1].

In the present study He-O₂/Ar mixture plasma was generated in locally made atmospheric pressure plasma pencil. Optical Emission Spectroscopy (OES) is employed to explore the optimum conditions. Explicitly, rotational temperature, integrated/normalized intensity of UV_a, UV_b, and UV_c radiations, [O] atomic density and dissociation fraction are measured as a function of discharge parameters (RF power, different gases concentration and flow rate of gases). The rotational temperature 'T_r' is measured via fitting simulated spectra on the experimental spectra of selected rotational levels of 2nd positive system of nitrogen N₂ (C³ Π_u, v' => B³ Π_g, v'). The results show that the average gas temperature increases (320 - 408 K) with increase in RF power and O₂ concentration in the mixture. Similarly, the normalized UV radiation intensity determined by integrating the regions of UV_a, UV_b, and UV_c (240 - 400 nm). The results show that UV radiation intensity has optimum value at 0.3% oxygen in the mixture. The [O] atomic density and dissociation fraction are evaluated by using 'advanced actinometry technique' in which argon is used as actinometer. Ar-I line (2P₁-1S₂) at 750 nm and O-I line (3P - 3S) at 844 nm are used to determine the atomic oxygen density [O] and dissociation fraction [O]/[O₂]. The results show that both increases with RF power and O₂ concentration in the mixture up to 0.7% in the mixture and beyond 0.7% both starts to decrease by increasing RF power. As UV radiations is the main agent to kill or remove micro-organisms from different surfaces like food and biological instruments [2] therefore 0.3% O₂, 110W RF power and 500 SCCM flow rate is the proposed optimum condition for plasma based sterilization with atmospheric pressure plasma Pencil.

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PS-ThP-2 Effect of In-Situ Heat Treatments on PVDF Film Characteristics Deposited by Using Atmospheric Pressure Plasma Synthesis, *H. Tae*, School of Electronic and Electrical Engineering, College of IT Engineering, Kyungpook National University, Republic of Korea; *Eun Young Jung*, The Institute of Electronic Technology, College of IT Engineering, Kyungpook National University, Republic of Korea; *H. Suleiman*, School of Electronic and Electrical Engineering, College of IT Engineering, Kyungpook National University, Republic of Korea; *C. Park*, Electrical Engineering, Milligan University, USA

In recent, the development trends of energy storage devices, will be stretchable, bendable, and portable device with light weight in the field of flexible devices, including nanogenerator and sensors. Thus, piezoelectric polymers have received attractive attention for their application [1]. Among of these piezoelectric polymers, polyvinylidene fluoride (PVDF) and its copolymers have been mostly studied due to specific properties. The PVDF thin film is usually used by solution-based synthesis, such as a electrospinning and spin casting [2]. However, these methods are unsuitable for applying the field of flexible devices due to their problems, such as complex, dangerous, and heating procedures according to the chemicals. To solve these problems, it is necessary to develop new processes based on low-pressure and atmospheric pressure plasma (APP) processes. Among these plasma processes, the low-pressure plasma have the biggest disadvantages in industrial applications, including the large equipment, high cost, and difficulty in transmitting heat on film owing to the use of a vacuum system. Thus, the APP process appears to be a promising method to deposit the polymer film on the point of view a simple, low cost, and heating-free process. For this reason, many studies has been currently investigated on the APP process for polymer film deposition [3,4]. Accordingly, to enhance the structural phase of PVDF thin

film, this study investigated the effects of in-situ heat treatment on PVDF thin film characteristics during the APP process in terms of different heating temperatures (room temperature, 100, 150, and 200°C) using scanning electron spectroscopy (SEM), Fourier transforms-infrared spectroscopy (FT-IR), X-ray diffraction, and impedance analyzers. The PVDF thin film was deposited by APP process during 1 h using a mixed polymer solution composing of PVDF polymer nano powder and dimethylformamide (DMF) liquid solution. In addition, the in-situ heat treatment was performed through substrate heating on a hot plate while depositing the PVDF thin film by the plasma. Based on the FT-IR and SEM results, after PVDF thin film deposition at 150°C during 1 h, PVDF thin film was smoothly formed with PVDF nanoparticles and the DMF component in the form of bubbles was largely reduced. Moreover, in FT-IR spectra, two phases (α and β phases) were observed in in-situ heated PVDF film, which the peaks at 975 and 1402 cm⁻¹ represent α-phase and the peak at 1072 cm⁻¹ indicates β-phase. The detailed experimental results of PVDF thin films produced by in-situ heat treatment are currently being studied and will be described in detail.

PS-ThP-3 Uniformity Monitoring of Photoresist Etching using Multi-Channel Endpoint Detection in Inductively Coupled Plasma, *Sanghee Han*, Sungkyunkwan University (SKKU), Republic of Korea; *J. Kim*, Sungkyunkwan University, Republic of Korea; *H. Chae*, Sungkyunkwan University (SKKU), Republic of Korea

In this work, the uniformity of photoresist (PR) etch rates was monitored with multi-channel optical emission spectroscopy (OES). Etch rate uniformities were controlled from center-high etch rate to edge-high etch rate by varying gas flow rates, source power, bias power, and CF₄/O₂/Ar plasma pressure in a 300mm cup-type inductively coupled plasma (ICP) descum chamber. Eight fiber optics in an 8-way jig were mounted on a rectangular viewport of the chamber and the eight optical fibers were connected to a switching module that transfers signals to a single spectrometer. We can exclude variations of signals originating from different spectrometers with this configuration. The spatially resolved endpoints were determined with CO (428-431nm) band in all PR etch processes, while other relatively strong peaks such as O (777nm), F (703nm), and CO (481-483nm) show no difference in spatial variation in PR etch rates. The CO (428-431nm) band corresponds to the de-excitation of CO from the state d³Δ with a vibrational number of 14 or 16 to the metastable state a³π. The results indicate that to monitor etch uniformity effectively, it is necessary to observe emissions from select excited states of etch products, which only transition to a metastable state of those products. The etch profiles across the wafer were determined based on the etch endpoints from 8-channel optical emission spectroscopy (OES) under various conditions, and these results aligned with the trends observed in thickness measurements conducted using a reflectometer.

PS-ThP-4 Effect of Mask Pattern on the Tribological Properties of Pattern Plasma Nitrided AISI H13 Tool Steel, *Junji Miyamoto*, *R. Tsuboi*, Daido University, Japan

Plasma nitriding is widely used for mechanical parts, dies and tools as one of the surface modification processes. Plasma nitrided material is improved the surface hardness, wear resistance and fatigue strength etc. while maintaining the core properties. An advantage of plasma nitriding over conventional nitriding is that the former is a clean, nontoxic process that involves a shorter nitriding time than gas nitriding. However, plasma nitrided sample have not be attained low friction coefficient same as samples nitrided by another nitriding method. A mechanical part that contacts two surface requires a reduction in the friction coefficient. Friction accounts for about 23% of all energy consumption worldwide, among which 20% is needed to reduce friction and 3% is required to remanufacture replacements for worn-out parts and equipment. Consequently, studying the characteristics of contact surfaces that reduce friction not only results in energy savings, but also extends the lifetime and dependability of the component. Surface texture technology is crucial for reducing the friction coefficient of contact surface and enhancing friction performance.

There is technology of surface texturing that create a series of regular microstructures on the surface of a sample using process techniques. The textures with suitable size can act as micro-bearing to increase the dynamic pressure between friction pairs, store lubricants, and capture debris produced during the friction process.

In this study, plasma nitriding was performed partially by Electron-Beam Excited Plasma using mask with hole to create surface texturing on the surface of tool steel. The effects of partially plasma nitriding were

investigated, and the tribological properties of surface on the formed partially nitrided layer were clarified.

The results of our experiments show that the hardness of the sample was increased only in the open areas that were not masked. The measured hardness of the nitrided layer of all tool steel work pieces were increased by more than two times that of the core material. Regular micro asperities were formed on the nitrided sample surface.

PS-ThP-5 Effect of Methane Gas on Mechanical Properties of AISI H13 Tool Steel in Open-Air Type Super-Rapid Atmospheric-Pressure Plasma Jet Nitrocarburizing Process, Naoyuki Takahashi, J. Miyamoto, Daido university, Japan

Gas nitrocarburizing is widely used for surface modification of mechanical parts. Nitrocarburized steel is effective improved wear resistance, fatigue strength, seizure resistance, and corrosion resistance. An advantage of gas nitrocarburizing over surface heat treatment is that the treatment temperature is lower than that of carburizing or induction hardening treatments. However, the gas nitrocarburizing treatment method has shortcomings, such as the long treatment time and the use of ammonia gas. Therefore, we are developing a super-rapid atmospheric-pressure plasma jet nitrocarburizing treatment technology with short treatment time and nontoxic process. In our previous studies, the mechanical properties of nitrocarburized tool steel by atmospheric-pressure plasma jet using argon, nitrogen, and methane in open-air atmosphere were clarified.

In this study, the effects of methane gas on mechanical properties of AISI H13 tool steel were clarified. Plasma nitrocarburizing of AISI H13 tool steel was performed by open-air type atmospheric-pressure plasma jet under methane gas ranging from 0.020 to 0.035 slm applied.

The results show that the surface hardness of the nitrocarburized samples were increased by increasing the amount of methane gas.

PS-ThP-6 High-Voltage Custom Waveform Bias for Ion Energy Distribution Control, James Prager, T. Ziemba, P. Melnik, J. Perry, C. Bowman, EHT Semi

As the market demands solid-state non-volatile memory storage, plasma etching high-aspect-ratio (HAR) features is becoming increasingly important. To minimize feature defects like bowing and twisting defects, precision control of the ion energy distribution (IED) is required. Eagle Harbor Technologies (EHT), Inc. has developed a unipolar wafer bias power system that can operate up to 15 kV at 400 kHz. In this work, EHT is using a retarding field energy analyzer (RFEA) to investigate IEDs with these high-voltage custom waveforms. A 60 MHz capacitively coupled plasma source with a pedestal that can be biased is being used to experimentally test IED control using these high voltage custom waveforms. EHT will present RFEA measurements of the IED with energies above 2.5 kV. Future plans will also be discussed.

PS-ThP-7 High-Voltage Bipolar Tailored Waveforms with Droop Compensation for Ion Energy Control, Timothy Ziemba, J. Prager, P. Melnik, J. Perry, C. Bowman, EHT Semi

In plasma processing applications, like etching, the ion energy and flux can be independently controlled with the use of multiple power systems. Typically, a high-frequency RF generator is used for plasma production, and a low-frequency RF generator is used to bias the wafer. Using RF for the wafer bias power system produces a very broad ion energy distribution (IED) at the wafer surface. Eagle Harbor Technologies (EHT), Inc. has developed a high-voltage bipolar waveform generator that can be used to provide precision control of the ion energy distribution at the wafer surface. This power system is being tested in an experimental plasma chamber with a 60 MHz capacitively coupled plasma source and a pedestal that can be biased. EHT will present IED measurements collected using a retarding field energy analyzer (RFEA) with energies up to 2.5 kV. Additionally, we will show IED calculations from bias waveforms for ions over 5 kV when the voltage exceeds the limits of the RFEA.

PS-ThP-8 Electron-Assisted Etching of Poly-Si and SiO₂ in An Inductively Coupled CF₄ Plasma, Jiwon Jung, C. Chung, hanyang university, Republic of Korea

Low-energy electron beam is generated to assist the Poly-Si and SiO₂ etching via grid system in an inductively coupled CF₄ plasma. The etch rate of Poly-Si and SiO₂ increases with electron beam energy, which is regarded that the electron assist the surface etching process. To verify this, Poly-Si and SiO₂ etching is performed in several plasma conditions, which leads different etch rate depending on the presence or absence of radicals and electron beams. Poly-Si and SiO₂ are not etched without radicals of CF₄ plasma, while they are etched with radicals. When the electron beam and

radicals of CF₄ plasma exist simultaneously, etch rate increases dramatically than the case of CF₄ plasma without electron beam. This is because electrons assist the etching process. Furthermore, F radical density variation as increasing electron beam energy is measured by OES measurement to demonstrate that the reason of etch rate increase is not F radical density variation. The surface roughness is measured after low-energy electron beam etching and compared with that after the ion-assisted etching.

PS-ThP-9 Laser-Induced Fluorescence Transitions Relevant for the Microelectronics Industry, V S Santosh K Kondeti, S. Yatom, I. Romadanov, Y. Raitzes, Princeton Plasma Physics Laboratory; L. Dorf, A. Khomenko, Applied Materials Inc.

A diverse combination of feed gases is utilized in creating low-temperature plasmas for applications in the microelectronics industry. These plasmas generate a wide combination of reactive and non-reactive species, with a spatial and temporal fluctuation in the density, the temperature, and the energy. Precise understanding of these parameters and their variations is crucial the advancement of microelectronics through validated modeling and designing relevant devices. Laser-induced fluorescence (LIF) offers spatially and temporally resolved information of the plasma-produced radicals, ions, and metastables. However, implementing this diagnostic tool requires the knowledge of the optical transitions, including the excitation and the fluorescence wavelengths. This information is often scattered across extensive literature from widely different fields. This study analyzes and compiles the available transitions for laser-induced fluorescence of more than 160 chemical species pertinent to the microelectronics industry. The plasma generated by the feed gas mixture and its interaction with the chamber walls and materials generates a complex combination of reactive species. Our analysis will show the overlapping LIF transitions that need to be considered when selecting and implementing LIF in plasmas with a complex combination of feed gases, such as those employed in the processing of microelectronics.

Acknowledgement: This work was supported by the U.S. Department of Energy through contract DE-AC02-09CH11466.

PS-ThP-10 A Dry Process of Iodine Chemistry for Euv Sensitizer/Underlayer, Phong Nguyen, N. Stafford, Air Liquide

As extreme ultraviolet lithography progresses towards achieving finer details, challenges like stochastics and sensitivity emerge for polymeric photoresists. To meet the demands of high-volume manufacturing and overcome the limitations of EUV source power, enhancing resist sensitivity is crucial for achieving high-resolution patterning while ensuring pattern fidelity and uniformity. One promising approach involves incorporating atoms with high photoemission cross-sections, such as iodine, into the resist composition to significantly enhance material absorbance. Exploring the incorporation of iodine into carbon-containing layers presents an intriguing avenue for advancement.

In recent years, Air Liquide has spearheaded the development of a series of low global warming potential chemistries, facilitating the formation of atomically smooth iodine-containing layers with adjustable thickness and iodine concentration through a low-pressure plasma process. These film properties are studied using scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS).

PS-ThP-11 2D Particle-in-Cell Modeling of an Inductively Coupled Plasma for the Semiconductor Industry, Willca Villafana, Princeton University Plasma Physics Lab; D. Sydorenko, University of Alberta Edmonton, Canada; I. Kaganovich, Princeton University Plasma Physics Lab

The state-of-the-art EDIPIC-2D code [1] now includes self-induced electromagnetic effects using the Darwin Direct Implicit algorithm [2]. The cell size can be greater than the Debye length and the time step may exceed the period of Langmuir oscillations, which are acute constraints to the standard explicit Particle-In-Cell code [3]. Therefore, the code can now model Inductively Coupled Plasma (ICP) Reactors of a realistic size using a modest amount of computational resources. In this work, we showcase the example of an ICP reactor operating in the sub-mTorr range, that could be typically used for etching in the semiconductor industry. We emphasize our analysis of key parameters essential for atomic precision processing such as the ion energy flux and the ion angle distribution function as measured at the wafer.

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PS-ThP-12 On the Compensation Method of the Attenuation of the Light Intensities in Fluorocarbon Plasmas, *C. Chung*, Hanyang University, Republic of Korea; *Hyeon ho Nahm*, Hanyang University, Republic of Korea; *J. Lee*, Hanyang University, Republic of Korea

We investigated the attenuation of light intensity due to fluorocarbon film on the view port (quartz window) in a C_4F_8 plasma reactor. For the compensation of the light intensity, fluorocarbon film thickness is measured by using an electrical method. The electrical method is based on the difference of the film impedance when triple AC voltages are applied to the film. Transmittivity of the fluorocarbon film at various conditions are measured. The transmittivity varies depending on wavelengths and the thickness of the film. For accurate plasma parameter measurement by the line ratio technique, it is crucial to account for the attenuation in light intensity caused by the films during plasma processes. Based on the transmittivity data and the real time thickness of the film on the view port, we successfully compensate the attenuation of light intensity. As a results, plasma parameters from the compensated line ratios are consistent with other measurement those from Langmuir probes.

PS-ThP-13 GaN and NiO Metal-Semiconductor-Metal Photodetectors Fabricated via Hollow-Cathode Plasma-Assisted Atomic Layer Deposition, *S. Allaby*, *H. Mousa*, *M. Silverman*, *H. Saleh*, *S. Choe*, *L. Antoine*, *J. Goosen*, *Fatih Bayansal*, *I. Sifat*, *A. Agrios*, *N. Biyikli*, University of Connecticut

Metal-semiconductor-metal (MSM) photodetectors (PDs) have gained significant interest in optoelectronic applications in industrial, environmental, and even biological fields. MSM PDs benefit from simplicity in design, large active area, fast response, and low dark current. PDs fabricated from materials such as GaN, NiO, AlGaIn, ZnO, Nb₂O₅, and TiO₂ have attracted attention from researchers owing to their wide energy band gaps. Among these materials, both GaN and NiO semiconductors stand out as promising candidates for ultraviolet/visible photonic devices due to their wide bandgap energies.

Herein, we report on MSM PDs based on GaN and NiO films which were deposited on sapphire and glass substrates respectively, using hollow-cathode plasma-assisted atomic layer deposition (HCP-ALD). GaN was deposited at 200°C using triethylgallium (TEG) as the metalorganic precursor and N₂/H₂ plasma as the co-reactant. NiO was deposited at 100°C using nickelocene (NiCp₂) as the metalorganic precursor and O₂ plasma as the co-reactant. The rf-plasma power was maintained at 100W for both films. Aluminum interdigitated electrodes, with widths and spacing of 500 microns, were deposited onto the films using e-beam evaporation.

The deposited films were characterized for their optical and structural properties. Both films deposited showed strong absorption in the UV region ($\lambda=190-380$ nm) yet demonstrated lower absorption in the visible and near-IR regions. As a result of the analysis using the Tauc relation, the band gaps of GaN and NiO films were found to be 3.32 and 2.95 eV, respectively. XRD analysis revealed a preferred orientation along (002) direction for both films. I-V characteristics of the fabricated MSM PDs were conducted under dark and light conditions. An incandescent light source at a distance of ~10 cm from the sample was applied to generate the photocurrent. Bias-dependent photocurrent signals were observed for both GaN and NiO MSM PD samples. On the other hand, NiO photoresponse showed a significantly slower temporal response indicating a notable persistent photoconductivity.

PS-ThP-14 Dual Capability PEALD/PAALE Reactor Design, *Biolol Kuyel*, *A. Alphonse*, *J. Alex*, NANO-MASTER, Inc.

Nano-Master has developed a hybrid PECVD/PEALD tool capable of depositing ALD and PECVD layers on silicon wafers within the same chamber with no hardware modifications. In this paper, we will propose a novel reactor design capable of performing PEALD and PAALE in the same chamber without breaking the vacuum. Removing native oxides from a Si wafer using other means, such as reactive ion etching or wet etching, results in substrate damage and defects to the wafer. Here, we will discuss the means of removing the native oxide from the Si wafer surface using plasma-assisted atomic layer etching (PAALE) before depositing AlN in the same chamber and without or low substrate damage. The PEALE of native

oxide on the silicon wafer will occur in the same PEALD chamber, which prevents re-oxidation between the steps. The objective of the study is to develop a tool that can perform precise atomic layer etching and damage-free atomic layer deposition of high quality AlN in the same chamber.

PS-ThP-15 Radio Frequency Plasma Reactor for the Surface Modification of Powder Materials, *Michael Denchy*, *J. Kintzer*, *G. Troop*, *D. Jensen*, Advanced Cooling Technologies, Inc.

Chemically active plasmas afford a highly reactive environment through which a wide range of materials can be selectively modified with nanoscale control and precision. Advanced Cooling Technologies, Inc. (ACT) and its team of research and development and engineers have recently developed a newly commissioned research-scale radio frequency (RF) plasma reactor for surface treatment of powder materials. Reported here is the initial characterization of this system and its application to the nanoscale modification of metal surfaces, including surface oxide reduction and the deposition of a functional fluorocarbon coating. Surface oxide reduction and coating deposition were accomplished via processes employing a reducing argon/hydrogen (Ar/H₂) plasma and plasma enhanced chemical vapor deposition (PECVD), respectively. Reduction of the native oxide layer of Al metal powder was measured via inert gas fusion (IGF), a bulk oxide measurement technique for solid materials. The deposited fluorocarbon coating was investigated via atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS) measurements of a coated ultra-flat Al thin film substrate. The plasma environments of both processes were probed via optical emission spectroscopy (OES) measurements and the presence of long-lived gas phase species from each process were detected using downstream mass spectrometry (MS) analysis.

PS-ThP-16 SF₆- and CF-based Plasmas Interaction with Si and SiO₂ at Room and Cryogenic Temperature: Insights from Molecular Dynamics Simulation, *J. ROMERO CEDILLO*, *G. CUNGE*, *Emilie DESPIAU-PUJO*, LTM, CNRS/Universite Grenoble Alpes, France

Introduced in the early 90s to perform deep etching of silicon, plasma cryoetching involves using highly reactive plasmas, such as SF₆- or CF- based plasmas, to etch materials cooled down to temperatures below -100°C with high anisotropy. During cryoetching of silicon in SF₆ plasmas, the addition of small amounts of oxygen allows to form a temperature sensitive SiO_xF_y passivation layer on the sidewalls of the trench, which prevents spontaneous lateral etching and desorbs completely when the substrate is returned to room temperature. Cryogenic processes have the advantage of being polymer-free and clean, which prevents process drift and makes them suitable for new applications where smooth sidewalls or reduced plasma-induced damage are required. These features are attractive for etching porous low-K materials in the back-end-of-line of advanced CMOS technology; applications to atomic layer etching of conventional materials (Si, Ge, GaN, InP) or emerging 2D materials (graphene, MoS₂) are also envisaged. Although the understanding and control of plasma cryoetching has improved over the years, the fundamental mechanisms of the formation and desorption of passivation layers are not well understood. And differences between elementary plasma-surface interactions at cryogenic and room temperature remain unclear. In this paper, Molecular Dynamics (MD) simulations are performed to study the interaction between F- and CF- based plasmas with Si and SiO₂ materials. The objective is to understand the impact of ion and radical plasma species (nature, dose, energy, etc.) on the structural and chemical modification of exposed materials, both at room and cryogenic temperatures. Quantitative information on surface reaction probabilities (sticking, thermal desorption, surface diffusion, sputtering yields) will be compared and discussed, to better understand the key mechanisms behind cryoetching and cryo-ALE processes.

This work was supported by ANR, under the project name PSICRYO (No. ANR-20-CE24-0014).

PS-ThP-17 Ion Energy Distributions in a Kaufman-type Ion Beam Source Operated with Ar and O₂, *Raymond Smith*, Department of Electrical and Computer Engineering, University of Nebraska-Lincoln; *E. Rohkamm*, *P. Birtel*, *D. Kalanov*, *F. Frost*, Leibniz Institute of Surface Engineering (IOM), Germany; *U. Kilic*, *E. Schubert*, Department of Electrical and Computer Engineering, University of Nebraska-Lincoln

An energy-selective mass spectrometer has been used to measure ion energy distributions (IEDs) from a broad beam double-grid Kaufman ion source as a function of the grid 1 voltage. Two cases, Ar and mixed Ar/O₂ process gases were studied, and IEDs were measured with and without the presence of a neutralizer current for both cases. A linear, one-to-one relationship between grid one voltage and the energy of single charged and

double charged ions produced inside the ion source was observed. For Ar/O₂, a broad triangular peak is observed for atomic oxygen due to the dissociation of O₂. Additional ionization processes were detected for collision events which occurred in the ion beam outside of the source, and charge transitions caused the formation of fast single charged ions and slow double charged ions. The relationship between the presence of a neutralizer current and the ion energy peak positions are discussed for ionization processes inside and outside of the ion source. Knowledge of ion beam energy distributions will guide ion beam-assisted techniques for applications which require precision such as nanofabrication, sputtering, and ion-beam etching.

PS-ThP-18 Unraveling the Dynamics of Platinum Plasma-Enhanced Atomic Layer Deposition: Real-time Monitoring, Nonlinear Growth, and ALD Recipe Optimization using in-Situ Spectroscopic Ellipsometry, Youssa Traouli, University of Nebraska-Lincoln, USA; *U. Kilic*, University of Nebraska - Lincoln; *E. Schubert, M. Schubert*, University of Nebraska-Lincoln, USA

In this work, we study the time evolution of platinum (Pt) thin film growth by Plasma-Enhanced Atomic Layer Deposition (PE-ALD) using *in-situ* spectroscopic ellipsometry (SE) data in real time. We aim to understand the nonlinear growth regime that occurs during the initial stage of the deposition process. We employ a (MeCp)PtMe₃ organometallic precursor as the primary reactant and a remote oxygen plasma as the co-reactant. With *in-situ* SE, we explore the cyclic surface modifications and unravel the growth mechanisms during the Pt thin films deposition for different number of cycles. The complex dielectric function of platinum thin films is also extracted from the analysis of the *in-situ* ellipsometry data. Additionally, scanning electron microscope and atomic force microscopy are employed to investigate the change in the film surface morphology. We also present crystallographic and chemical analysis using X-ray diffraction and X-ray photoelectron spectroscopy. The insights gained from this study contribute to a deeper understanding of the ALD process for Pt and offer valuable guidelines for the optimization of a robust ALD recipe.

PS-ThP-19 Spatiotemporal Analysis of Electron Heating in Single Frequency and Pulsed-Rf Capacitively Coupled Plasma Using a Parallelized Particle-in-Cell Simulation, H. Lee, Sun Jeong Hwang, J. Mun, Pusan National University, Republic of Korea

In recent semiconductor etching processes, pulse-driven capacitively coupled plasma (CCP) is widely used to achieve high etching selectivity. As technology advances, the equipment structures used in these processes become increasingly complex, requiring various conditions. Consequently, diverse issues are emerging within the CCP equipment, and understanding the various plasma phenomena occurring inside the process equipment is essential for solving these problems. To investigate the nonlinear and transient particle dynamics of CCPs, particle-in-cell (PIC) simulations are required [1,2]. This study uses a parallelized PIC simulation called K-PIC to investigate the onset of arcs in the gap between the wafer edge and the focus ring, which occurs in actual CCP equipment. We report the electron heating concentrated in the gap [3] through spatiotemporal data analysis, examining the effects of driving waveforms and the gap length [4] between the wafer edge and the focus ring.

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Plasma Science and Technology Room 124 - Session PS+TF-FrM

Plasma Processes for Coatings and Thin Films

Moderators: François Reniers, Université Libre de Bruxelles, Belgium, Scott Walton, Naval Research Laboratory

8:15am **PS+TF-FrM-1 Interaction of Polycrystalline Aluminum Oxide and Sapphire Surfaces with Halogen-Containing Plasmas and Gases, Takuya Ishihara, H. Tochigi**, Azbil corporation, Japan; **H. Kang**, Osaka University, Japan, Republic of Korea; **T. Ito, K. Karahashi, S. Hamaguchi**, Osaka University, 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 $\alpha\text{-Al}_2\text{O}_3$) 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 [2-6]. In this study, ion beam experiments were performed, aiming to understand the surface modification mechanisms of Ni-based alloys and polycrystalline Al_2O_3 film by fluorine-containing plasmas. With the irradiation of energetic F^+ and Cl^+ ions, it was found that the typical etching rates of Al_2O_3 are about one-half of those of Ni-based alloys. It was also found that the fluorinated layers of Al_2O_3 were thinner than those of Ni-based alloys. In addition, surfaces of sapphire samples were exposed to xenon difluoride (XeF_2) gases for 3 and 6 months. The sapphire surface was fluorinated over the first 3 months, but the depth of the fluorinated layer did not increase much after 6 months. It indicates that a diaphragm made of pre-fluorinated sapphire may be able to prevent the signal shift of the manometer used under highly corrosive conditions in semiconductor manufacturing.

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8:30am **PS+TF-FrM-2 Development of Corrosion-Resistant, Low-ICR aC and TiN Coatings Using HIPIMS for Bipolar Plate Manufacturing for Hydrogen Fuel Cells, Nicholas Connolly**, University of Illinois at Urbana-Champaign; **Z. Jeckell**, University of Illinois Urbana-Champaign; **R. Paul, M. Hysick**, Starfire Industries; **M. Hossain, B. Jurczyk, D. Ruzic**, University of Illinois Urbana-Champaign

Bipolar plates (BPPs) are a critical component in proton exchange membrane fuel cells (PEMFCs) that provide conducting paths for electrons between cells, distribute and provide a barrier for reactant gases, remove waste heat, and provide stack structural integrity. Stainless steel, specifically 316L, BPPs possess high electrical and thermal conductivity, good gas impermeability, and superior mechanical properties and formability. However, stainless steel has relatively low corrosion resistance and high contact resistance in the hydrogen fuel cell stack. Additionally, to meet the Department of Energy (DOE) cost/kW target for hydrogen fuel cells, recycling of the BPPs is practically a necessity.

In order to address these challenges, we will present work on two complementary studies. The first study is deposition of conformal

amorphous carbon (aC) and titanium nitride (TiN) thin films using HIPIMPS with positive cathode reversal. The interfacial contact resistance (ICR), corrosion current, and corrosion potential are reported for various aC and TiN thin films to characterize the contact resistance and corrosion resistance. The second study is etching of the previously deposited aC and TiN films in a HIPIMS system with a high-voltage cathode reversal, testing the possibility of recycling the BPP. The contact resistance and corrosion resistance are compared after the initial film deposition and then after etching of the initial film and redeposition on the same substrate.

8:45am **PS+TF-FrM-3 Evolution of Graphene Nanoflake Size and Morphology in Atmospheric Pressure Microwave Plasma, Parker Hays, D. Patel, D. Qerimi**, University of Illinois at Urbana-Champaign; **M. Stowell, LytEn; D. Ruzic**, University of Illinois at Urbana-Champaign

Graphene was synthesized using an atmospheric pressure microwave plasma system, employing argon/nitrogen mixtures as carrier gases and methane as the carbon precursor. This study investigates the effects of varying methane flow rates and plasma power on graphene growth, including the role of gas temperature. The process involves the decomposition and subsequent reorganization of carbon radicals into graphene sheets. To collect the synthesized graphene, tungsten carbide rods were strategically positioned at three distinct points along the plasma column.

The variations in particle diameter were systematically analyzed using Dispersive Light Scattering (DLS) and Scanning Electron Microscopy (SEM). Results indicate that particle diameter generally decreases along the plasma column until reaching a critical power threshold. Beyond this threshold, the diameter increases, particularly at the middle collection port, suggesting the presence of an optimal "Goldilocks zone" for graphene growth. This zone, located at the juncture between the bulk plasma and its afterglow, exhibits a significant temperature gradient, potentially ideal for graphene formation.

Further, an increase in methane flow rate correspondingly reduced the particle diameter across all ports, attributed to enhanced plasma quenching effects. Conversely, an escalation in plasma power led to an increase in particle diameter, likely due to the extension of the plasma field.

These findings demonstrate that manipulating methane flow rates and plasma power can significantly influence graphene particle size, optimizing growth conditions within the identified Goldilocks zone. This study provides a deeper understanding of the thermodynamic and chemical mechanisms governing graphene synthesis in microwave plasma systems, offering a pathway to tailored graphene production for advanced material applications.

9:00am **PS+TF-FrM-4 Gentle Processing of Graphene and Diamond in a Low Temperature Magnetized Plasma, Yevgeny Raitses**, Princeton Plasma Physics Laboratory; **F. Zhao**, Fermi Lab; **C. Pederson, K. Fu**, University of Washington; **A. Dogariu**, Princeton University

In this work, we present results of the use of a low temperature plasma in applied magnetic field for graphene hydrogenation and hydrogen passivation of diamond. The chemical functionalization of two-dimensional materials is an effective method for tailoring their electronic and chemical properties with encouraging applications in energy, catalysis and electronics. Experiments on graphene hydrogenation [1] revealed that with the applied magnetic field of 10-50 Gauss, a plasma generated by a DC-RF source of non-thermal electrons at a hydrogen pressure of about 10 mtorr is capable to achieve a high (~ 36%) hydrogen coverage without damage on monolayer graphene. Plasma measurements utilizing electrostatic probes for measurements of plasma properties, optical emission spectroscopy for characterization of plasma chemical composition and two-photon absorption laser-induced fluorescence (TALIF) for measurements of absolute hydrogen density revealed that with the applied magnetic field, the plasma density and the density of hydrogen atoms are much larger than without the magnetic field. The latter explains a high converge observed in the treated 2D material [1]. In more recent experiments, the same plasma source was applied for hydrogen passivation of diamond for quantum defect charge state control [2]. Measurements indicate that in this novel plasma treatment hydrogen terminates the surface with no observable damage to diamond.

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9:15am **PS+TF-FrM-5 A Plasma-Based Anodization Process for the Production of AlF₃ Layers**, *Scott Walton, J. Murphy*, US Naval Research Laboratory; *L. Rodriguez de Marcos, J. Del Hoyo, M. Quijada*, NASA; *V. Wheeler, M. Sales, M. Meyer, D. Boris*, US Naval Research Laboratory

Efficient ultraviolet (UV) mirrors are essential components in space observatories for UV astronomy. Aluminum mirrors with fluoride-based protective layers are commonly the baseline UV coating technology; these mirrors have been proven to be stable, reliable, and with a long flight heritage. However, despite their acceptable optical performance, it is still insufficient for future large telescopes in which several reflections are required. Recently, a readily scalable, plasma-based passivation process was developed to produce a thin AlF₃ layer on the surface of aluminum. The passivation process uses an electron beam generated plasma produced in a fluorine-containing background (SF₆ or NF₃), to simultaneously remove the native oxide layer while promoting the formation of an AlF₃ layer with a tunable thickness. Interestingly, this process has the characteristics of classic aluminum anodization – either electrochemical or plasma – where oxygen is replaced by fluorine. The process takes advantage of the ability for electron beam driven plasmas produced in electronegative gas backgrounds to generate substantial densities of negative ions, which are utilized to grow the fluoride layer. In this presentation, we will discuss the process using operating parameter studies, plasma diagnostics, and materials characterization, with an eye on understanding the growth mechanisms and the potential for better process control. This work partially supported by the Naval Research Laboratory base program.

9:30am **PS+TF-FrM-6 One-Step Synthesis of Spatially Differentiated Crystalline Vanadium Oxide Coatings Using Atmospheric Pressure Dielectric Barrier Discharge**, *Marie Brabant, A. Demaude, D. Petitjean, F. Reniers*, Université libre de Bruxelles, Belgium

Initially perceived as a limitation, the presence of inconsistencies in DBDs presented obstacles to achieving uniform plasma treatments and coatings. However, recent breakthroughs in immobilizing filaments within DBDs have demonstrated effective control over these irregularities.^{1,2} This development has now enabled the deposition of innovative patterned inorganic coatings that were previously unexplored. Vanadium oxide coatings, in particular, hold promise for diverse applications, including catalysis,³ memory compounds,⁴ or as practical solutions for smart windows.⁵

This study introduces a pioneering method for locally depositing dense crystalline inorganic coatings (V₂O₅) without requiring annealing and utilizing atmospheric pressure DBDs, marking a significant advancement in the field. Vanadium oxide coatings with spatial variation were successfully deposited in a single step using an atmospheric pressure dielectric barrier discharge featuring immobilized filaments. Initial findings indicate fast deposition rates beneath the filament regions and low deposition rates between them. Moreover, differences in the oxidation states of vanadium beneath the filaments and between them were also observed, suggesting different reactivities.⁶

Through the incorporation of a patented inductive heating device into the reactor,^{7,8} coupled with a pulsed signal, crystalline coatings were obtained by heating the substrate at 473 K, occasionally resulting in crystal needles measuring up to 50 μm in length. This crystallinity was confirmed by XRD analysis.

While further optimization is necessary to refine gas and reactive species distribution, this feasibility study demonstrates the potential for locally depositing crystalline coatings using a DBD with immobilized filaments and an appropriate substrate heating system, paving the way for new applications.

Acknowledgements

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9:45am **PS+TF-FrM-7 Biofilm Decontamination in an Endoscope-Like Setup Using a Cold Atmospheric Plasma**, *Juliette Zveny*, Université libre de Bruxelles, Belgium; *F. Reniers, A. Remy*, Université Libre de Bruxelles, Belgium; *T. Serra*, université libre de Bruxelles, Belgium; *A. Bourgeois*, Erasme Hospital, Belgium; *A. Nonclercq, D. Lakhroufi, A. Botteaux*, université libre de Bruxelles, Belgium; *A. Delchambre*, Université Libre de Bruxelles, Belgium; *J. Deviere*, Erasme Hospital, Belgium

Endoscopes are essential medical devices used to detect, prevent and cure many diseases. Well-established cleaning and decontamination procedures allow them to be used safely on multiple patients every day. However, cases of cross-contamination still occur, demonstrating that the decontamination process is flawed.^[1] Here, we propose a novel decontamination method using an Ar/H₂O Cold Atmospheric Plasma (CAP).

In this research, we investigate the effect of CAP not only on bacteria, but also on biofilm. Biofilm is a matrix made by bacteria to increase their resistance to external stress.^[2] *Pseudomonas aeruginosa* biofilms were grown during 24 hours in a PTFE tube mimicking the operating channel of an endoscope before being subjected to plasma treatment. The plasma was generated in a DBD setup with the high voltage applied between a metal wire passing through the contaminated tube and a metal mesh surrounding the tube.

The decontamination process consisted of a 30 min plasma in a water-saturated argon atmosphere. The chemical activity of the discharge was optimized by the presence of water, which allowed the production of hydroxyl radicals (OH) and hydrogen peroxide (H₂O₂), powerful oxidant species. Other parameters, such as the voltage, made it possible to increase the concentration of these species without increasing the power.

Plasma treatments showed effective decontamination capacities, with no bacteria found in the tube after regrowth for various treatment times (5 to 30min). It also shows promising results in terms of biofilm destruction, with up to 79% of the original biofilm destroyed. The biofilm destruction is dependent on the position inside the tube as well as on its own humidity. OES measurements also highlight the voltage dependency on OH radical formation and biofilm destruction.

Acknowledgements:

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10:00am **PS+TF-FrM-8 Nonthermal Plasma Jet Integrated Aerosol-Based 3D Printing with Machine Learning Optimization**, *Jinyu Yang, Y. Du, K. Song, Q. Jiang, Y. Zhang, D. Go*, University of Notre Dame

Aerosol-based printing has emerged as a versatile technique to fabricate functional devices with complex structures, offering high throughput and microscale resolution, along with capabilities unattainable with traditional approaches. Despite these promises, the printing of conductive films often requires post-printing sintering to remove surfactants from the nanoparticle-containing inks and promote the sintering and densification to form a continuous film with desired electrical conductivity, which conventionally demands thermal processing at elevated temperatures. Herein, we report a novel aerosol jet printing method that integrates a nonthermal, atmospheric pressure plasma jet to enable *in-situ* sintering during aerosol deposition. The impacts of various processing parameters on printing quality and *in-situ* sintering efficiency are investigated. A machine learning algorithm is incorporated to provide online, real-time defect detection and parameter control, enhancing the yield of high-quality films via automatic *in-situ* compensation whenever a region-specific anomaly is detected. Our method achieves low temperature sintering of silver nanoparticles with electrical conductivities comparable with those sintered through other plasma treatment approaches. Because the films require no post processing, the overall manufacturing time can be reduced by more than tenfold. This method holds significant potential for technological advances in printed electronics, wearable devices, and biomanufacturing.

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