Atomic Scale Processing Mini-Symposium
Room A107-109 - Session AP+PS+TF-MoM

Thermal Atomic Layer Etching and Deposition

Moderator: Jean-Francois de Marneffe, IMEC, Belgium

8:20am **AP+PS+TF-MoM-1 Atomic Layer Etching of Aluminum and Aluminum Oxide for Optical Applications**, ***John Hennessy***, *R. Rodríguez, A. Jewell,* Jet Propulsion Laboratory **INVITED**

Thermal atomic layer etching can be utilized for the surface preparation of aluminum in order to improve its optical performance at ultraviolet wavelengths. In this work we report on the use of trimethyaluminum and anhydrous hydrogen flyoride to remove the native oxide of aluminum prior to encapsulation with fluoride dielectric materials. This ALE/ALD process is used for the fabrication of reflective coatings and bandpass filters operating at wavelengths shorter than 200 nm. The etch rate of aluminum oxide is observed to be dependent on chamber conditioning with a significant enhancement in etch rate observed when the cyclic etching is performed in the presence of alkali halide materials. This enhancement can reduce the temperature threshold where etching dominates the reaction cycle over deposition.

The reduction of the overall processing temperature can enhance the compatibility of the full coating process with some temperature-sensitive substrates, and limit the amount of etch damage experienced by aluminum surfaces. Etching into the aluminum surface is generally observed to result in non-conformal etching which greatly increases the surface roughness of films and degrades the optical performance of resulting structures. Reducing the etch temperature can mitigate this effect by increasing the selectivity of the native oxide removal over the underlying metal. Optimization of these processes may provide insight into achieving conformal ALE of aluminum surfaces. The extension of these atomic layer processing methods towards the fabrication of meter-class mirror coatings is also discussed in the context of future large UV space observatories for NASA astrophysics applications.

9:00am **AP+PS+TF-MoM-3 Thermal Etching of First Row Transition Metal Oxides using Acetylacetone and O_3: Pathway for Atomic Layer Etching**, ***Jonathan Partridge***[1], *S. George,* University of Colorado at Boulder

Etching metal oxides with halogen-free methods is important during processing to avoid corrosion.Acetylacetone (Hacac) is an organic hydrocarbon.Hacac can supply acac ligands that can form volatile metal complexes with most transition metals.Consequently, Hacac can spontaneously etch metal oxides to form $M(acac)_x$ and H_2O.One difficulty is that Hacac can also decompose on the metal oxide surface and block the spontaneous etching.However, this surface poisoning also leads to a self-limiting reaction. The O_3 exposure can then remove the carbonaceous decomposition species and produce a pathway for atomic layer etching.

Thermal etching of first row metal oxides was demonstrated using Hacac and O_3 at pressures of 2.5 Torr at 250 °C.A quadrupole mass spectrometer (QMS) reactor with molecular beam expansion and line-of-sight to the ionizer was employed to detect etch species with high sensitivity.Metal oxide nanopowders were used to maximize the surface area and signal intensity of the etch products. The reactant sequence used five sequential Hacac exposures, one O_3 exposure, and one final Hacac exposure to check for etch product enhancement after O_3 exposure.Etching was monitored by the production of $M(acac)_x$ etch products.

$M(acac)_x$ etch products were observed for Sc_2O_3, V_2O_5 and VO_2, Cr_2O_3, Mn_2O_3 and MnO, Fe_2O_3 and Fe_3O_4, Co_3O_4 and CoO, CuO and Cu_2O, and ZnO. No etching was observed for TiO_2, MnO_2, and NiO. The metal oxides that etched either displayed (1) spontaneous etching by Hacac with no self-limiting behavior or (2) etching that limited itself versus Hacac exposure.The metal oxides that were spontaneously etched by Hacac were Mn_2O_3 and MnO, Co_3O_4 and CoO, and ZnO.The metal oxides that displayed self-limiting behavior were Sc_2O_3, V_2O_5 and VO_2, Cr_2O_3, Fe_2O_3 and Fe_3O_4, and CuO and Cu_2O.ALE processes for these metal oxides that displayed self-limiting reactions are possible using Hacac and O_3.

A comparison between the $M(acac)_x$ etch products and the metal oxide also provided information about oxidation state changes during etching.The x in $M(acac)_x$ is both the number of acac ligands and the oxidation state of the M metal center.Sc_2O_3, Cr_2O_3, MnO, Fe_2O_3, CoO, CuO, and ZnO all formed $M(acac)_x$ etch products with the same oxidation state as the metal oxide.In contrast, the other metal oxides all displayed evidence for reduction during etching.This reduction may occur by oxygen loss during the combustion of Hacac.

9:20am **AP+PS+TF-MoM-4 Selectivity between Silicon-Based Materials for Thermal Atomic Layer Etching and Spontaneous Etching**, ***Marcel Junige***, *S. George,* University of Colorado at Boulder

Sub-10-nm technology nodes must overcome the limits of photolithography. This requires selectivity between various Si-based materials for thermal atomic layer etching (ALE) and spontaneous etching. This work examined selectivity between silicon dioxide (SiO_2) and silicon nitride (SiN_x) for thermal ALE using trimethylaluminum (TMA) and hydrogen fluoride (HF), as well as for spontaneous etching using HF alone, at 275℃. Distinct etch rates between SiO_2 and SiN_x achieved inherent selectivity.

Experiments were conducted in a hot-wall, viscous-flow vacuum reactor with good control over the pressure during static reactant dosing to ensure reproducibility. *In situ* spectroscopic ellipsometry (iSE) was utilized to study etch-per-cycle (EPC), synergy, and selectivity characteristics. Sodium bifluoride ($NaHF_2$) was tested as an alternative HF source. $NaHF_2$ is a solid salt with negligible HF vapor pressure at room temperature, making $NaHF_2$ safer to handle than HF-pyridine. $NaHF_2$ delivered HF pressures up to 15 Torr when heated to 150℃ without releasing sodium. During thermal ALE of alumina (Al_2O_3), $NaHF_2$ exhibited diffusion-limited fluorination and EPC characteristics comparable with HF-pyridine.

For thermal ALE of SiO_2 alternating TMA and HF, the EPC and synergy were –0.2 Å and 88%, indicating minor spontaneous etching by HF alone. This moderate synergy for SiO_2 thermal ALE improved to 95% by ensuring water-free conditions during fluorination. On the other hand, the EPC for SiN_x thermal ALE was –1.1 Å. The EPC for SiN_x was expected to be much lower than for SiO_2 because no oxygen reactant was employed to oxidize SiN_x. However, iSE experiments revealed that repeated exposures of HF alone spontaneously etched SiN_x. Anhydrous HF vapor might form F^- species at the surface that have been attributed to dominate SiN_x etching. Spontaneous etching using static exposures of 45 s at 3 Torr HF alone obtained a high selectivity of ~50:1 for SiN_x removal over SiO_2 retention.

For thermal ALE alternating TMA and HF in co-dose with ammonia (NH_3), the selectivity inverted to ~9,000:1 for SiO_2 over SiN_x. HF+NH_3 co-dosing led to rapid spontaneous etching of SiO_2. NH_3, similar to water, might facilitate the dissociation of HF into H^+ and F^-, where the increased F^- concentration immediately produces HF_2^- species. HF_2^- species have been attributed to dominate SiO_2 etching.

In conclusion, this work demonstrated conditions for inherently selective gas-phase etching of either SiO_2 or SiN_x.

9:40am **AP+PS+TF-MoM-5 Thermal Atomic Layer Etching of SnO_2 by Fluorination and Ligand-Exchange Using HF and $Al(CH_3)_3$**, *C. Li,* University of Colorado Boulder, China*; J. Partridge,* ***Steven George,*** University of Colorado Boulder

Thermal atomic layer etching (ALE) can be achieved with sequential, self-limiting surface reactions. One mechanism for thermal ALE is based on fluorination and ligand-exchange reactions. For metal oxide ALE, fluorination converts the metal oxide to a metal fluoride. The ligand-exchange reaction then removes the metal fluoride by forming volatile products. Previous studies have successfully applied this thermal ALE strategy for Al_2O_3, HfO_2, and ZrO_2 ALE. However, no previous investigations have explored the thermal ALE of SnO_2 films.

This study demonstrated the thermal ALE of SnO_2 thin films using sequential, self-limiting thermal reactions with hydrogen fluoride (HF) and trimethylaluminum ($Al(CH_3)_3$, TMA) as the reactants. The initial SnO_2 films were grown by atomic layer deposition (ALD) using tetrakis(dimethylamino) tin and H_2O_2. The thermal SnO_2 ALE process was then studied using various techniques including quartz crystal microbalance (QCM), spectroscopic ellipsometry (SE), and quadrupole mass spectrometry (QMS).

In situ QCM experiments monitored SnO_2 ALE at temperatures from 250 to 300 ℃. The SnO_2 etching was linear versus the number of HF and TMA reaction cycles. The QCM studies also showed that the sequential HF and TMA reactions were self-limiting versus reactant exposures. The SnO_2 etching rates increased at higher temperatures. The QCM analysis measured mass change per cycle (MCPC) values that varied from −44.32 ng/(cm^2 cycle) at 250 °C to −123.5 ng/(cm^2 cycle) at 300 °C. These MCPCs correspond to SnO_2 etch rates from 0.64 Å/cycle at 250 °C to 1.78 Å/cycle at 300 °C.

SE measurements confirmed the linear removal of SnO_2 and the etching rates. QMS analysis also revealed the volatile etching products during the

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[1] **TFD James Harper Award Finalist**

sequential HF and TMA exposures on SnO_2 at 300 °C. These QMS investigations observed $Sn(CH_3)_3^+$, indicating $Sn(CH_3)_4$ as the etch product during TMA exposures. $Al_xF_y(CH_3)_z$ dimer and trimer species were identified as the ligand-exchange products. QMS analysis during multiple sequential TMA doses before HF/TMA cycling also revealed that fluorination was necessary for $Sn(CH_3)_4$ etch product evolution. This observation indicated that TMA does not convert SnO_2 to Al_2O_3. The results indicate that thermal SnO_2 ALE using sequential HF and TMA exposures occurs by fluorination and ligand-exchange reactions.

10:40am **AP+PS+TF-MoM-8 Reactivity and Volatility as Key Metrics for Classifying the Substrate Selectivity of Ligands in Atomic Level Processing,** ***Hadi Abroshan,*** Schrödinger, Inc.*; S. Lim,* Schrödinger, Inc., Republic of Korea*; A. Chandrasekaran,* Schrödinger, Inc.*; S. Elliott,* Schrödinger, Inc., Germany*; H. Kwak, M. Halls,* Schrödinger, Inc.

One of the main challenges in the area-selective deposition or etch for semiconductor processing is finding a single reagent that undergoes different chemistry on different substrates. The reagent may be an organometallic complex containing a particular ligand or may be the protonated version of that ligand. In this work we propose that examining just two properties of the organometallic complex across a series of metal cations is sufficient to give an indication of the area-selectivity that can be achieved with reagents based on the particular ligand chemistry.

The first property is reactivity towards the hydrolysis reaction, which gives information about oxide formation versus surface passivation or etching, and the second property is volatility of the organometallic reagent or etch by-product. Figure 1a shows the four limiting cases of the combination of these two properties. Using quantum chemical and machine learning methods to predict the properties, such reactivity-volatility maps can be plotted quickly for a wide range of ligands and metal-containing substrates. We validate our results on the chloro ligand (Figure 1b), thd, RCp and NR2 against area-selective experiments, including those using HCl as etchant [1], ruthenocene and ferrocene [2] as metal sources and β-diketonates as inhibitors [3]. While approximate, this approach provides a starting point for designing and understanding atomic-level processes that are area-selective with respect to a wide variety of substrates.

[1] M.F.J. Vos et al., Chem. Mater. 31, 3878 (2019).

[2] H. Nadhom et al., J. Phys. Chem. Lett. 12, 4130 (2021).

[3] A. Mameli et al., ACS Nano 11, 9303 (2017).

11:00am **AP+PS+TF-MoM-9 Etching of Silicon Nitride Using Vapor-Phase HF Exposures at Various Temperatures: Role of Ammonium Hexafluorosilicate Salt***,* ***Vahid Ghodsi,*** *S. George,* University of Colorado Boulder

The etching of silicon nitride (SiN_x) was explored using vapor-phase HF exposures at various temperatures. The investigations were performed using *in situ* quadrupole mass spectrometry (QMS) and *ex situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to detect the volatile and non-volatile etch products, respectively. These QMS and ATR-FTIR studies provide valuable understanding of the SiN_x atomic layer etching (ALE) process employing hydrofluorocarbon plasma to form $(NH_4)_2SiF_6$ salt at low temperatures and then thermal annealing at higher temperatures to desorb the salt [N. Miyoshi *et al.*, Jpn. J. Appl. Phys. **56,** 06HB01 (2017)].

At low temperatures, T≤60°C, QMS detected the evolution of SiF_4 from HF exposure at 0.5 Torr on SiN_x. SiF_4 formed concurrently with the formation of a $(NH_4)_2SiF_6$ salt layer on the SiN_x surface according to: $Si_3N_4 + 16HF(g) \longrightarrow 2(NH_4)_2SiF_6 + SiF_4(g)$. To verify the presence of the salt, the temperature could be ramped up to 200°C in the absence of HF exposure. During this temperature ramp, QMS detected SiF_4 at higher temperatures T≥80°C corresponding to the thermal decomposition of the $(NH_4)_2SiF_6$ salt according to: $(NH_4)_2SiF_6 \longrightarrow 2NH_3(g) + 2HF(g) + SiF_4(g)$.

When the HF exposure was performed at higher temperatures T≥120°C, SiF_4 was again observed as an etch product. However, no secondary rise of SiF_4 was detected by QMS during the temperature ramp to 200°C in the absence of HF exposure. This behavior indicated that the $(NH_4)_2SiF_6$ salt did not form on the surface at temperatures T≥120°C. The spontaneous etching of SiN_x with no salt on the SiN_x surface is possible at these higher temperatures. ATR-FTIR studies corroborated the salt formation at lower temperatures and the salt decomposition at higher temperatures.

To demonstrate that HF exposures could achieve high SiN_x etch rates without salt formation, experiments were conducted at T≥140°C with higher HF pressures. A four-fold increase in HF pressure to 2.0 Torr led to a ~five-fold increase in SiF_4 signal intensity measured by QMS. At these higher temperatures T≥140°C, SiN_x etching can proceed with no inhibition from the salt.

11:20am **AP+PS+TF-MoM-10 Crystal Phase Transformations During Thermal Atomic Layer Etching of Hafnium–Zirconium Oxide (HZO) Using Hydrogen Fluoride and Dimethylaluminum Chloride***,* ***Aziz Abdulagatov,*** *J. Partridge,* University of Colorado at Boulder*; M. Surman,* ASM Microchemistry Ltd., Finland*; S. George,* University of Colorado at Boulder

Thermal atomic layer etching (ALE) of $Hf_{0.5}Zr_{0.5}O_2$ (HZO) was previously demonstrated using hydrogen fluoride (HF) and dimethylaluminum chloride (DMAC) [1]. This current work focused on crystallographic transformations of HZO during ALE. Grazing incidence x-ray diffraction (GIXRD) analysis of initial 10 nm thick HZO film on 20 nm thick TiN on Si revealed orthorhombic (o-phase), tetragonal (t-phase), and monoclinic phases (m-phase). *Ex situ* spectroscopic ellipsometry and X-ray reflectivity (XRR) measurements showed that sequential exposures of HF and DMAC at 250 °C resulted in a linear decrease in film thickness with an HZO etch rate of ~0.45 Å/cycle.

GIXRD studies observed that the peaks associated with the o- and t-phases decreased faster in intensity than the m-phase peaks. As the number of ALE cycles increased, only the m-phase remained before the majority of the HZO film was removed by etching. Interestingly, as o- and t-phases were removed, the grain size of the m-phase crystallites increased in size according to the Scherrer equation. XRR investigations also monitored a decrease in the film density with ALE. In addition, atomic force microscopy (AFM) measurements observed that the density decrease was accompanied by an increase in film roughness.

Powder diffraction (PXRD) studies were also conducted to investigate the phase transformation of crystalline ZrO_2 powder at 250 °C. ZrO_2 powder was used as a model system since the chemical properties of HfO_2 and ZrO_2 are very similar. PXRD analysis of as-received ZrO_2 powder showed crystallographic planes of mostly m-phase with some cubic (c-phase) and t-phase. As expected, the etching of ZrO_2 powder resulted in a mass loss. PXRD also observed the loss of c- and t-phases and an increase in grain size of m-phase crystallites. The results for the HZO films and ZrO_2 powder are similar. There are crystal phase transformations that occur with loss of o- and t-phases and growth of m-phase during thermal ALE.

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

11:40am **AP+PS+TF-MoM-11 Novel Conversion Half-Cycle for Thermal ALD of High-Density Hfo_2 and Its Use in HfO_2/Al_2O_3 Nanolaminate Dielectric Barriers***,* ***Dane Lindblad,*** Forge Nano

Hafnium dioxide, HfO_2, is an attractive material for use as a dielectric barrier in high-power SiC and GaN electronics, both MOSFET and HEMT, due to its high dielectric constant and thermal stability. Current techniques for depositing HfO_2 by thermal atomic layer deposition (ALD) tend to produce low density and performing films. While plasma enhanced ALD (PEALD) is employed to improve the performance, the high field and fast switching requirements of the device can make the barriers insufficient. In addition, not all applications can accommodate plasma. As such, a novel conversion process, referred to as the "CRISP" process, for the deposition of HfO_2 via thermal ALD has been explored. Utilizing the tool's unique ability to introduce a small amount of non-metal catalyst during the conversion half-cycle, the CRISP process employs surface catalysis to increase growth per cycle, improve stoichiometry, increase density, and modify crystal morphology compared to HfO_2 films grown with conventional conversion methods, O_3, as shown in Figure 1 and Table 1 below. A comparison of the HfO_2 films grown using the CRISP process and the conventional O_3 process, both deposited at 250°C, will be presented. Furthermore, due to the layer-by-layer growth of ALD, this deposition technique lends itself well to the fabrication of nanolaminate materials. Specifically, HfO_2/Al_2O_3 laminate stacks can be precisely manufactured to alter the bulk material properties and curate device performance, allowing one to choose improvements in leakage current or dielectric breakdown in the nanolaminate film. An initial investigation into the performance of various HfO_2/Al_2O_3 laminate stacks is presented, and this work, coupled with higher quality HfO_2 films, gives insight into the use of these materials for the next generation of high-power electronic devices.

Biomaterial Interfaces Division
Room B117-119 - Session BI1+PS-MoM

Microbes and Fouling at Surfaces

Moderators: Kenan Fears, U.S. Naval Research Laboratory, **Sally M. McArthur**, Deakin University, Australia

8:20am **BI1+PS-MoM-1 Amphiphilic Coatings for Marine Low-Fouling Applications***, **Axel Rosenhahn**,* Ruhr University Bochum, Germany **INVITED**

Manmade materials in contact with ocean water become rapidly colonized by living matter like bacteria, diatoms, barnacles, or mussels. Increased fuel consumption, failure of devices, and substantial maintenance costs are among the penalties associated with marine biofouling. As the historical paradigm to combat fouling by biocide releasing coatings is increasingly challenged by legal restrictions, environmentally benign low-fouling materials for marine applications are intensively explored [1]. While several hydrophilic and hydrophobic materials show promising properties, their combination into amphiphilic coatings unites the best of the two worlds [2]. As hydrophilic compound, zwitterionic materials with different molecular architectures were developed and their structure-function relationship against different fouling organisms have been studied [3]. Amphiphilic coatings based on zwitterionic polymers have been designed and their anti-polyelectrolyte properties have been characterized by several methods including AFM and SPR. Their antifouling properties against a range of marine fouling species and in short term field exposures have been assessed and the results will be discussed under consideration of the interaction of the organic coatings with inorganic particulate matter in the ocean [4,5,6]. Based on the obtained data, design criteria for optimized zwitterionic building blocks for fouling-release technologies will be discussed.

[1] M. Callow, J. Callow, Nature Communications 2011, 2, 244

[2] S. Krishnan, C. Weiman, C. Ober, J. Materials Chemistry 2008, 18, 3405

[3] A. Laschewsky, A. Rosenhahn, Langmuir 2018, 35, 1056

[4] F. Koschitzki, R. Wanka, L. Sobota, J. Koc, H. Gardner, K.Z. Hunsucker, G.W. Swain, A. Rosenhahn, ACS Applied Materials & Interfaces 2020, 12(30), 134148

[5] J. Koc, E. Schönemann, R. Wanka, N. Aldred, A.S. Clare, H. Gardner, G.W. Swain, K. Hunsucker, A. Laschewsky, A. Rosenhahn, Biofouling 2020, 36(6), 646

[6] L. Schardt, A.M. Guajardo, J. Koc, J.L. Clarke, J.A. Finlay, A.S. Clare, H. Gardner, G.W. Swain, K. Hunsucker, A. Laschewsky, A. Rosenhahn Macromolecular Rapid Communications 2021, 43(12), 2100589

9:00am **BI1+PS-MoM-3 Bio-Informed Interface Design and Synthesis to Manipulate Microbial Behavior***, **Rong Yang**,* Cornell University **INVITED**

Biofilm is often considered detrimental, which needs to be minimized as it can cause infections and fouling in healthcare, food and water manufacturing, and underwater civil and military activities. Nevertheless, we also believe such naturally occurring biofilm can be desirable, upon appropriate programming via precise control over the surface they inhabit, as building blocks for self-actuated and self-repairing "living" coatings. To gain insight into the biointerface, research in the past two decades has unraveled the fundamental thermodynamics and hydrodynamics that have guided the design of numerous antifouling/antimicrobial surfaces. However, the biological effects of insoluble materials remain elusive. Recent advances in vacuum-based synthesis have enabled well-defined material properties at length scales relevant to microbes' biochemical and biophysical activities, enabling a bio-informed materials design approach. Motivated by the unmet needs for antifouling materials and living materials, our recent research has advanced our current understanding of the biointerface in three critical ways: (***i***) leveraging dynamic surface chain reorientation to achieve antifouling at the air-liquid-solid interface, the importance of which has been overlooked in past research; (***ii***) recognizing bacteria to be complex microorganisms with dynamic structure and metabolism and sophisticated chemical communication systems and leveraging the recent breakthroughs in microbiology to guide the design of bio-active polymer coatings; (***iii***) enabling living materials by performing polymerization directly on living organisms, which overcomes the limited tunability of the native microbial extracellular scaffolds and preserves the function and viability of coated organisms by avoiding harmful synthesis conditions. We seek to underscore the importance of understanding detailed microbe-material interactions and provide an outlook on extending the material-bacteria interactions beyond "kill or repel" towards signaling and control.

9:40am **BI1+PS-MoM-5 Using Flow-Cells to Culture Microbial Biofilms for Improved Secondary Ion Mass Spectral Imaging***, **Yuchen Zhang**,* Oak Ridge National Laboratory, USA*; X. Yu,* Oak Ridge National Laboratory

Bacterial biofilms are a main player in organic processing in the environment. Therefore, characterization and understanding of the biofilm interactions with groundwater and soil components is important in deepening our knowledge in the biosphere and rhizosphere. We present two approaches to prepare the bacterial biofilms suitable for time-of-flight secondary ion mass spectrometry (ToF-SIMS). *Shewanella* MR-1 was used as the model bacteria biofilm due to their known traits in subsurface, surface, and soil microbiology. A mixture of silica, alumina, and iron oxide was used as the model soil system. In the static culture, the bacteria were inoculated in a multi-well cell culture dish at their log phase. Then minerals were added to the culturing well. The mixture of the bacteria biofilms and minerals were scratched off carefully and deposited onto the clean silicon (Si) wafers before ToF-SIMS analysis. Second, we used a microfluidic cell to culture biofilms. We made a modification of the system for analysis at the liquid vacuum interface (SALVI) microfluidics for biofilm attachment in the growth and detection chamber. The mineral components were mixed to the growth media at a ratio of 1:1 by volume as nutrients to support the biofilm's growth. During static culturing, a series of Si wafers were used to capture the temporal progression of the biofilms and the soil components over days. In dynamic cultures, effluents were collected onto clean Si substrates. The time intervals were chosen based on the growth curve of the strain. Distinctive fatty acids peaks of *Shewanella* biofilms, such as myristic acid (m/z^- 227, $C_{14}H_{27}O_2^-$), palmitic acid (m/z^- 255, $C_{16}H_{31}O_2^-$), and arachidic acid (m/z^- 311, $C_{20}H_{39}O_2^-$), and the biomarker riboflavin peak (m/z^- 241, $C_{12}H_9N_4O_2^-$) are observed in the dynamic results. In contrast, the static results do not provide as much information. This finding indicates that static culture is not optimal for studying biofilms using ToF-SIMS. Our results demonstrate that sample preparation is quite critical in microanalysis of bacteria biofilms, specifically in surface analysis like ToF-SIMS. The microfluidic growth chamber is more flexible in microbial culture and media tuning, both are important in simulating a variety of conditions to understand microbes and soil interactions at the microscale. Additionally, characteristic signals of biofilms are not buried under the mineral components in the dynamic setup, which is imperative in understanding the role of biofilms in soil aggregation and bioremediation occurring at the microbial interface.

10:00am **BI1+PS-MoM-6 Role of Microbial Biofilms in the Settlement of Macrofoulers on Antifouling Marine Coatings***, **Sara Tuck**, M. Kardish,* US Naval Research Laboratory*; B. Orihuela,* Duke University*; G. Vora,* US Naval Research Laboratory*; D. Rittschof, K. Franz,* Duke University*; K. Fears,* US Naval Research Laboratory

Accumulation of biofouling on submerged surfaces is a foundational problem for maritime transport and human health. Biofouling build-up increases the drag coefficient, fuel consumption, exhaust emissions, and operational costs. Traditionally, biofouling is inhibited by the application of antifouling coatings, the most popular of which, contain copper. Copper-based antifouling coatings can contain up to ~75% CuO, by weight, in attempt to release sufficient levels of copper to deter the settlement of fouling organisms. Despite these high loadings, the efficacy of these antifouling coatings has been declining with the emergence and spread of copper tolerant species. Microbial communities resistant to copper have been found to form mature biofilms on these coatings, which could be altering the interfacial properties to create more favorable conditions for the settlement of a broader biofouling community. To gain an understanding of the mechanisms responsible for the loss in antifouling performance, coated and uncoated polyvinyl chloride panels were submerged at estuarine and marine field test sites and microbial communities were harvested. Collected biofouling communities were cultured and individual species were collected and identified. Copper tolerance was assessed by re-exposing cells to copper-containing coatings and traditional antimicrobial assays to determine susceptibility to an array of biocides. Finally, resistant biofilms were formed on marine coatings to assess the effect of their presence on the settlement of acorn barnacle larvae.

Plasma Science and Technology Division
Room A106 - Session PS+TF-MoM

Plasma Processing for Advanced Emerging Memory Technologies

Moderators: Harutyun Melikyan, Micron Technology, **Jeffrey Shearer**, TEL

8:20am **PS+TF-MoM-1 IBE Patterning and Characterization of High Density STT-MRAM at Pitch 50nm and MTJ CD 20nm***, **Romuald Blanc**, L. Souriau, K. Wostyn, S. Couet, F. Lazzarino,* IMEC, Belgium

Spin Transfer Torque Magnetic Random Access Memory (STT-MRAM) is a promising non-volatile memory technology that offers high-density storage, low power consumption, and fast read/write operations. One potential application of STT-MRAM is as a last level cache (LLC) in computer systems, since it can offer higher performance, lower power consumption, and higher scaling potential than traditional SRAM. However, the patterning of STT-MRAM with Ion Beam Etching (IBE) at CD 20nm and pitch 50nm presents several challenges such as high aspect ratio, damaged magnetic-tunneling junction (MTJ) and sidewall shorts[1,2]. IBE relies on physical ion sputtering which does not allow high selectivity to the hard mask, therefore the choice of the hard mask stack is crucial to avoid excessively high aspect ratio[3]. In this study, we use a hybrid hard mask composed of high-density diamond-like carbon (DLC) to increase etch selectivity and TiN which becomes the STT-RAM top electrode.

In this talk, we present the magnetic and electrical results obtained for STT-MRAM at pitch 50nm using multiple process conditions of IBE main etch, sidewall clean and post-oxidation. We demonstrate that the etch parameters have a significant impact on device yield, with the best condition leading to a wafer-level yield of 95% functional devices with Tunnel Magnetoresistance (TMR) higher than 100%. On the best devices, we measure a TMR of 170% which corresponds to the TMR value before MTJ patterning. Finally, we report a switching current of 20µA with low dependence on pulse width from 5 to 20ns which is consistent with a MTJ CD of 20nm.

References:

[1] Lei Wan et al, *Fabrication and Individual Addressing of STT-MRAM Bit Array With 50 nm Full Pitch*, IEEE TRANSACTIONS ON MAGNETICS, VOL. 58, NO. 5, MAY 2022

[2] Murat Pak et al, *Orthogonal Array Pillar Process Development for High Density 4F2 Memory Cells at 40nm Pitch and Beyond*, SPIE Advanced Lithography 2022, Paper 12051-45

[3] Kuniaki Sugiura et al, *Ion Beam Etching Technology for High-Density Spin Transfer Torque Magnetic Random Access Memory*, Japanese Journal of Applied Physics 48 (2009) 08HD02

8:40am **PS+TF-MoM-2 Cryogenic Etching by Physisorption of Neutrals for High-Aspect-Ratio Contact***, **Masahiko Yokoi**, R. Suda, K. Tanaka, M. Tomura, K. Matsushima, Y. Ohya, M. Honda, Y. Kihara,* Tokyo Electron Miyagi Limited, Japan

The most crucial challenge in High-Aspect-Ratio (HAR) dielectric etching is supplying both ions and etchants [1] at the same rate to the etch front. If a large amount of etchant supplied to bottom of the feature is consumed by sufficient ion bombardment, higher aspect ratio etching with superior etching rate can be achieved. Conventional HAR processes which rely on the formation of radicals utilize fluorocarbon and hydrofluorocarbon gases combined with high-applied bias power. However, the stable chemisorption of radicals on feature sidewalls decreases the radical flux at the etch front, which results in a lack of radical supply and a drastic etch rate attenuation in the high aspect region. A technological breakthrough has long been required to solve this problem.

In this work, we focus on neutral physisorption at cryogenic temperatures. There have been several reports on plasma etching in the cryogenic temperature regime [2, 3], but the mechanism has not yet been well understood nor implemented for HAR dielectric etching. We have evaluated a novel etchant in cryogenic temperature and discovered a synergy between hydrogen fluoride (HF) as the etchant and HAR etching process. The dielectric etch rate strongly correlates with the physisorption of the HF, enhanced in the cryogenic temperature regime. The direct injection of HF as the process gas yields higher partial pressure and increased flux compared to radical flux formed by plasma reaction in vapor phase. Furthermore, we confirmed that the phosphorous-containing gas acts as an effective catalyst in the HF reaction. The phosphorous-containing gas stabilizes the HF or etchant physisorption on the SiO_2 film, which provides an etch rate enhancement at cryogenic temperature. In this conference, we will present a detailed surface reaction model.

Applying this innovative process to HAR etching enables a higher etch rate, higher selectivity, and higher aspect ratio etching capability. This novel process will enable the manufacturing of next-generation 3D NAND flash memory devices.

[1] K. Ishikawa, et al., Jpn. J. Appl. Phys. Vol. 57, No. 6S2, 06JA01, (2018).

[2] T. Ohiwa, et al., Jpn. J. Appl. Phys. Vol. 31, p.405, (1992).

[3] R. Dussart, et al., J. Phys. D: 47123001, (2014).

9:00am **PS+TF-MoM-3 Plasma Etching Processes Challenges in Emerging Non-Volatile Memories***, C. Boixaderas, T. Magis, C. Socquet, A. Roman, B. Martin,* CEA-LETI, France*; B. Fontaine, P. Gouraud,* STMicroelectronics, France*; J. Dubois,* STMicrolectronics, France*; N. Posseme,* STMicroelectronics, France*; L. Grenouillet, C. Jahan, G. Navarro, G. Bourgeois, M. Cyrille, **Thierry Chevolleau**,* CEA-LETI, France **INVITED**

Since the appearance of flash memory in 1980s, the non-volatile memory (NVM) market is in constant evolution. Nowadays the random access memory (RAM) market is divided into two categories: standalone memories and embedded memories that are integrated into the core CMOS.Since the 2010s, new non-volatile embedded memories are emerging to achieve specific performances in terms of storage, speed, endurance and retention. Such advanced memories are based on resistive (RRAM), material phase change (PCRAM), magnetic (MRAM) and ferroelectric (FeRAM) properties. An overview of the main advanced memory technologies will be presented (operation principles, materials and investigated multilayers stacks).

We will address the patterning challenges that we are facing for the integration of the advanced non-volatile memories. We will mainly focus on the etching and stripping development in terms of scaling down, profile control and plasma induced damages on features sidewalls. The etch process optimization to control the profile and potential technological solutions to minimize plasma damages will be also presented and discussed in terms of plasma surface-interaction.

9:40am **PS+TF-MoM-5 Principle and Application of Etching Lag Mitigation in High Aspect Ratio Contact Process***, **Kyoungsoo Chung**, H. Kim, S. Park, J. Min, K. Yoon, B. Kuh,* Samsung Electronics, Republic of Korea

High Aspect Ratio Contact (HARC) etching is associated with various defects, such as random bending, global tilting, hole distortion, and vertical CD reduction. Depth loading, in particular, is significant and is intricately linked to all these issues. The implementation of a cryogenic process with specific gases has been verified to increase the initial etch rate by nearly threefold compared to the high-temperature process. Furthermore, this procedure has also amplified the patterned aspect ratio where etching lag is observable, in addition to increasing the etch rate. We engage in a comprehensive review and investigation of the mechanisms contributing to the improvement of etching lag. Firstly, it is essential to attain a substantial physisorption amount of neutrals, including radicals, while concurrently delivering highly directional ion energy to activate the surface. Additionally, the transport of neutrals within the hole is crucial for the etchant to be effectively adsorbed up to the etch front. We argue that elements such as a cryogenic environment, low-molecular-weight etchants, compounds that facilitate surface reactions, and a distribution of highly energetic ions are vital for overcoming depth loading. Ultimately, we propose advanced strategies for next-generation HARC etching, based on the lag reduction mechanisms.

10:00am **PS+TF-MoM-6 Etching Selectivities of SiO_2 and SiN Against *a*-C Films Using CF_4/H_2 with a Pseudo-Wet Plasma Etching Mechanism***, **Yusuke Imai**, S. Hsiao, M. Sekine, T. Tsutsumi, K. Ishikawa,* Nagoya University, Japan*; M. Iwata, M. Tamura,* Tokyo Electron Ltd., Japan*; Y. Iijima,* tokyo Electron, Japan*; T. Gohira, K. Matsushima, Y. Ohya,* Tokyo Electron Ltd., Japan*; M. Hori,* Nagoya University, Japan

With the advancement of cloud computing and AI technology, there is a growing demand for high-speed processing of large amounts of data and high-capacity storage. To manufacture 3D NAND, it is necessary to etch the layer structure where SiO_2 and SiN layers are alternately stacked, utilizing the amorphous C layer as a mask. A continuous increase of interest using cryogenic etching for high aspect ratio structure can be observed. Recently, etch selectivities among SiO_2, SiN and poly-Si with CHF_3/Ar and an ultra-high speed etch process at cryogenic temperature for 3D NAND have also been reported.[1,2] However, the cryogenic etching on variation of selectivities among SiN and SiO_2 over a-C have not been discussed yet. In this study, the etching selectivity among SiO_2, SiN and a-C was investigated by varying the hydrogen content (20 to 60 %) in CF_4/H_2 plasma at substrate temperature (T_s) of -60 and 20 °C. A capacitively coupled plasma reactor was used in the experiments, The total flow rate of gas mixture of CF_4 and H_2 was set at 150 sccm and the pressure during process was fixed at 4 Pa. As shown in the supplementary file, at T_s = 20 °C, the both ER of SiO_2 and SiN films decreased with increasing the hydrogen content, which is consistent with previous studies. Contrarily, for T_s = -60 °C the ER of SiO_2 reached its maximum at around 30-40% hydrogen additives, while the ER value of SiN decreased by nearly half compared to that at 20 °C. As a consequence, the etching selectivity of SiO_2/SiN at 20 °C was found to be less than 1 for all hydrogen contents, indicating that SiN was preferentially etched. For T_s = -60 °C it exhibited values greater than unity with the same process. This demonstrates that surface reactions and etching mechanism were changed when substrate was cooled. On the other hand, for *a*-C films increasing the hydrogen content in the CF_4/H_2 plasma results in a transition from etching to deposition. The transition point was found to be H_2 additive of around 50% at 20 °C and around 30% at -60 °C, indicating a wider process window with infinite etching selectivities of SiO_2/SiN over *a*-C mask at low T_s. The etching characteristics at low temperature is correlated to the surface reactions between the films and neutral HF, based on the results of HF molecular density during plasma discharge using FTIR. A pseudo-wet etching mechanism was proposed to explain the obtained results. The bias power was also varied to investigate the etching behavior further at cryogenic temperature.

[1] R. Dussart *et.al.*, J. Appl. Phys. **133**, 113306 (2023).

[2] Y. Kihara *etal*., VLSI symposium T3-2 (2023)

10:40am **PS+TF-MoM-8 Enhancing Etching Processes at Lower Wafer Temperatures: New Insights into Chemical and Physical Mechanisms*, Thorsten Lill,*** Clarycon Nanotechnology Research, Inc. **INVITED**

Lower temperatures hold significant importance for etching advanced memory devices. In this presentation, we provide a comprehensive overview of the chemical and physical processes involved in etching at lower wafer temperatures. Traditionally, plasma etching techniques heavily rely on the generation of radicals that readily chemisorb onto the surface. However, at low temperatures, molecules tend to adsorb through physisorption, lacking the necessary energy to overcome the energy barrier required for a chemical reaction. However, the concentration of neutrals in typical plasma used for semiconductor manufacturing is notably higher (by one to two orders of magnitude) than that of radicals. At lower temperatures, the physisorption of neutrals becomes significant, increasing their concentration on the surface and contributing to the etching process once chemically activated by energy from the plasma [1].

Etching of high aspect ratio structures utilizes ions and neutral reactive species that must effectively traverse through high aspect ratio features to reach the etch front. We present computational results on neutral transport within such features, exploring the influence of aspect ratio, profile shape, and surface processes including adsorption, desorption, and diffusion of neutral species. Our findings indicate a substantial increase in the steady-state transmission probability with the introduction of surface diffusion [2]. While spontaneous and collision-induced desorption of adsorbed neutrals alone do not alter the steady-state transmission probability, they do impact the time required to reach it. However, in the presence of surface diffusion, spontaneous desorption enhances the transmission probability, whereas desorption resulting from collisions with co-flowing nonreactive gas reduces it. These results unveil the potential for enhancing neutral transport at low surface temperatures, facilitated by physisorption and surface diffusion mechanisms.

By shedding light on the intricate interplay between chemical and physical phenomena during etching processes at lower temperatures, this presentation provides insights into the optimization of etching techniques for advanced memory devices.

[1] T. Lill, I. L. Berry, M. Shen, J. Hoang, A. Fischer, T. Panagopoulos, J. P. Chang, and V. Vahedi, J. Vac. Sci. Technol. A 41, 023005 (2023).

[2] T. Panagopoulos, T. Lill, J. Vac. Sci. Technol. A 41, 033006 (2023)

11:20am **PS+TF-MoM-10 High Selectivity Etching via Pulsed Selective Deposition*, André Amend,*** *M. Yakushiji, K. Kuwahara,* Hitachi High-Tech, Japan

Semiconductor device structures are shrinking and increasing in verticality, thus requiring novel plasma dry-etching processes to manufacture high Aspect-Ratio (AR) profiles on nanometer scales. Fabrication of such devices requires hard masks (HM) with high etching resistance that have small Critical Dimension (CD) and large height, corresponding to the needs of the device dimensions. As a result, creating the HMs themselves becomes more expensive and requires costly multi-layer processes to deal with the relatively low etching resistance of the C-rich photomask, which transfers the device pattern via photolithography. HM fabrication could be significantly simplified by an etching process that selectively etches hard materials, such as SiO_2, even under soft C-rich masks.

Here, a Phase Mask Reconstruction Process (P-MRP) is introduced, that drastically increases the SiO_2 etching selectivity and is compatible with small CD structures. P-MRP allows control of the C-based mask shape while etching SiO_2 via a time-modulated bias voltage, that tunes separate selective mask deposition and sample etching phases with a frequency up to above 1000 Hz. While a high voltage is applied to the sample, high-energy ions promote etching, whereas deposition occurs during the low voltage phase. Preferential deposition on the mask is achieved via chemical selectivity and radical shading due to the mask AR.

By precise control of the time-modulated sample bias voltage to adjust etching and deposition phases, the etching selectivity, as well as the mask shape and stability, can be controlled, which is critical to processing small patterns. To achieve high selectivity, the net etching rate on top of the mask can be decreased by reducing average ion energy, while controlling the mask side-deposition rate via the maximum ion energy and duration of the deposition phase. Since P-MRP rapidly alternates mask etching and mask passivation (during the deposition phases) low pattern roughness is achieved as well. For Line/Space and Hole patterns with CD 16-26 nm, etching selectivity as high as 10 was demonstrated while etching a depth of up to 200 nm of SiO_2, with AR of up to about 10.

This result indicates that P-MRP could be used to simplify and accelerate HM fabrication. Furthermore, since deposition selectivity is also achieved through AR shading, it can be adopted to process materials other than C-masks and SiO_2 etching targets, as well.

Atomic Scale Processing Mini-Symposium
Room A107-109 - Session AP+PS-MoA

Plasma Enhanced Atomic Layer Etching

Moderators: Robert Bruce, IBM Research, T. J. Watson Research Center, **Scott Walton**, Naval Research Laboratory

1:40pm **AP+PS-MoA-1 Chemical Contrast by Nitridation for Improving Atomic Layer Etching Selectivity in Interconnect and EUV Absorber Applications***, **Taylor G. Smith**[1],* University of California, Los Angeles*; J. de Marneffe, V. Philipsen,* IMEC, Belgium*; J. Chang,* University of California, Los Angeles

As extreme ultraviolet lithography (EUVL) dominates the fabrication of future integrated circuits, advanced EUV photomask absorber materials such as Ni and Ni-Al alloys are needed. As Ru emerges as the capping layer for EUV absorber and a potential supplementary material for backend interconnects, the fact that Ru etches rapidly in oxygen requires a different approach (e.g., nitridation) to create the needed chemical contrast for atomic layer etching. In this work, we present a plasma-thermal atomic layer etching (ALE) approach to etch Ni that relies on nitriding the metal surface using nitrogen plasma, then removing the surface metal nitride with formic acid (FA) vapor. Previous work relied on oxygen plasma as the modification step to form a surface NiO [1]. However, oxygen plasma is known to etch Ru, the standard capping material in EUVL masks. Here we explore a nitrogen plasma-based ALE process to increase the selectivity of the Ni etch to the Ru capping layer. An additional motivation for exploring nitridation-based ALE is that metal nitrides, unlike metal oxides, do not form spontaneously in air, making it possible to ascertain that all surface metal nitride formation must be a result of the plasma processing.

The composition of the metal nitride layer is measured by X-ray photoelectron spectroscopy (XPS) and is controlled by varying the plasma power, pressure, and exposure time. Ni films nitridized in a 500 W, 35 mTorr nitrogen plasma for 5 min have a surface composition of $Ni_{2.8}N$, close to the stoichiometric Ni_3N composition. XPS also confirmed the removal of the surface Ni_xN after exposure to FA vapor at 80°C as manifested by the disappearance of the metal nitride N 1s peak at 397.6 eV. The thickness of the Ni films as a function of ALE cycles is measured by scanning electron microscopy (SEM) and spectroscopic ellipsometry (SE), with the etch rate measured by SE being 0.49 ± 0.20 nm/cycle. We also determine the selectivity of the plasma nitridation ALE process to common hardmasks and to Ru. Finally, we extend this plasma nitridation ALE chemistry to Ni-Al alloys, determining both the etch rate and the stoichiometry changes in the film as a function of ALE cycles.

1. X. Sang and J. P. Chang, J. Vac. Sci. Technol. A **38** (4), 042603 (2020).

2:00pm **AP+PS-MoA-2 Anisotropic and Selective Atomic Layer Etching of Ruthenium***, **Owen Watkins**,* University of California at Los Angeles*; H. Simka,* Samsung*; J. Chang,* University of California at Los Angeles

Ruthenium has been proposed as a replacement for copper in sub-10 nm interconnects, where it has a lower resistivity and does not need as thick of a diffusion or adhesion layer. Ruthenium is known to be etched aggressively in an oxygen plasma by the formation of RuO_4. A reactive ion etching process using plasma with both O_2 and Cl_2 is a direct, high etch rate method, but there is a need to achieve better control and selectivity in order for Ru to be a viable interconnect material. In this work, a thermodynamic approach was first taken to determine viable chemistries. It confirmed that Ru and RuO_2 react with atomic O spontaneously to form RuO_4, and with atomic N to form a metastable RuN layer.RuN reacts with atomic O, but the reaction is less favorable, and can be reduced by H and H_2 into metallic Ru. The thermodynamic assessment led to a novel three-step process to control the etching of ruthenium where a nitrogen plasma forms RuN on the surface of the ruthenium thin film, a hydrogen plasma reduces some of the RuN, creating a surface layer of Ru, then an oxygen plasma etches this topmost layer of Ru but is unable to etch into the RuN.Experimental validation was first realized by exposing blanket Ru film to the sequential process. Compared to a baseline of continuous O_2 plasma with equal conditions and total exposure time as the O_2 plasma step, the three-step process shows an increase in RMS surface roughness of 0.05 nm/cycle and a post-etching resistivity of 30 µΩ-cm, whereas continuous O_2 plasma shows an increase of 0.2 nm/30s of exposure and a post-etching resistivity of 280 µΩ-cm. Finally, using a SiO_2-patterned Ru structure, a highly anisotropic etch profile was obtained:the nitrogen plasma exposure forms RuN on the exposed surface and sidewalls. Hydrogen plasma with an applied bias anisotropically reduces RuN. Then, an oxygen plasma selectively etches Ru while leaving RuN on the sidewall intact. By creating the anisotropy in the previous steps, a gentler O_2 plasma exposure can be used, which results in anetch rate of 4 nm per cycle and a selectivity of Ru vs. SiO_2/Si_3N_4 of 15, compared to conventional O_2 + Cl_2 RIE plasma etching in literature that reports etch rates in excess of 40 nm per minutes and selectivities around 6.

2:20pm **AP+PS-MoA-3 Mechanisms and Benefits of Cryogenic Processes in Silicon Based Material Atomic Layer Etching***, **Remi Dussart**, R. Ettouri, J. Nos, G. Antoun, P. Lefaucheux, T. Tillocher,* GREMI CNRS/Université d'Orléans, France **INVITED**

Since its introduction in 1988, plasma cryogenic processing has been applied to deep etching of silicon for microelectronics and MEMS devices. High aspect ratio structures can be obtained at very low temperature (typically -100°C) of the substrate in SF_6/O_2 plasma. The mechanism is based on a passivation SiO_xF_y layer, which forms at low temperature only. The formation of this passivation layer has been characterized by in-situ diagnostics such as ellipsometry, mass spectrometry and XPS. SiF_4 molecules which correspond to the main by products of silicon etching by fluorine can also participate in the passivation layer formation and reinforce it. The composition of the SiO_xF_y layer formed in SiF_4/O_2 plasma strongly depends on temperature. In particular, the fluorine content significantly increases below a temperature threshold between -60°C and -100°C. However, this threshold is reached at higher temperature if we process a Si_3N_4 surface instead of a Si surface.

We can take advantage from these interesting properties at cryogenic temperature to develop new cryo-ALE processes. In this presentation, two different types of cryo-ALE will be introduced. The first one is based on the physisorption of C_4F_8 molecules without plasma followed by an argon plasma step to etch SiO_2 at the atomic scale. The second one consists in alternating SiF_4/O_2 plasma interacting with a cooled substrate with argon plasma. During the SiF_4/O_2 plasma, the passivation layer composition can be tuned depending on temperature and substrate material surface. In particular, we will show that a very good etch selectivity between Si_3N_4 and Si can be obtained at a temperature of -65°C for which a very low etch rate is obtained for Si while Si_3N_4 surface is etched at a higher rate. This property can be explained by the chemical analysis of the two surfaces at low temperature. Finally, some experiments of cryoetching in CHF_3/Ar plasma will be presented showing some interesting trends at low temperature on different silicon based materials.

3:00pm **AP+PS-MoA-5 Damage Formation Analyses of Steady Plasma-Enhanced Atomic Layer Etching for Silicon Nitride with Molecular Dynamics Simulations***, **Jomar U. Tercero**[2],* Osaka University, Japan*; A. Hirata,* Sony Semiconductor Solutions Corporation, Japan*; M. Isobe, K. Karahashi,* Osaka University, Japan*; M. Fukasawa,* Sony Semiconductor Solutions Corporation, Japan*; S. Hamaguchi,* Osaka University, Japan

Molecular dynamics (MD) simulations were performed to study the etching mechanisms and surface damage formations during the plasma-enhanced atomic layer etching (PEALE) of silicon nitride (SiN). PEALE is a thin-layer etching technique to achieve a uniform and precisely etched material surface. The typical ALE process consists of alternating self-limiting adsorption and desorption steps. In the adsorption step, the material is exposed to reactive species, which modifies the surface layer. In contrast, in the desorption step, the modified surface is bombarded with low-energy inert ions, resulting in the removal of the modified layer. A recent report on SiN PEALE processes with hydrofluorocarbon (HFC) radical adsorption and Ar ion impacts has shown that C tends to accumulate on the surface, which causes an etch stop [1]. Our simulations of an ideal PE-ALE system with CH_2F radical adsorption and Ar ion bombardment have revealed that the remaining C atoms from the initial ALE cycle can trigger the C accumulation. The surface damage was also observed due to the ion bombardment. Due to the formation of a C layer, high-density Si-C bonds were found to remain on the surface after several ALE cycles, causing further accumulation of C atoms. Therefore, we introduced a short O_2 plasma irradiation process after the desorption step to help remove the problematic C atoms [2]. Our simulations agree with the experimental observations that the additional O_2 plasma irradiation step can prevent the etching from stopping. The Si-C bonds were minimized since O atoms reacted with the C atoms, forming CO

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[1] **PSTD Coburn & Winters Student Award Finalist**

[2] **PSTD Coburn & Winters Student Award Finalist**

and CO_2 species. Regardless, Ar ions with sufficient incident energy are still needed for the etching to proceed, which can cause damage to the etched surface. To understand the effect of the energetic ions in the desorption step, we also performed SiN PEALE with heavier inert gas ions such as Kr. It has been observed that, while Kr ions have shallow penetration depths than Ar ions and therefore cause less surface damage, Ar ions remove C atoms from the surface more efficiently than Kr ions.

References

[1] A. Hirata, M. Fukasawa, K. Kugimiya, K. Nagaoka, K. Karahashi, S. Hamaguchi, and H. Iwamoto, *JVST A*, **38**, 062601 (2020).

[2] A. Hirata, M. Fukasawa, J.U. Tercero, K. Kugimiya, Y. Hagimoto, K. Karahashi, S. Hamaguchi, and H. Iwamoto, *JJAP* (2022).

3:20pm **AP+PS-MoA-6 Orientation Dependent Etching of Silicon: A Computational Chemistry Study*, Yuri Barsukov*,** *O. Dwivedi, S. Jubin, J. Vella, I. Kaganovich,* Princeton University Plasma Physics Lab

Orientation dependent etching of silicon is a phenomenon, when etch rate of silicon surface depends on the surface orientation. It was experimentally established that Si(111) surface is slower etched than Si(100) and Si(110). In this case the etch profile becomes anisotropic (without plasma and ions) and the surface is textured with micro- and nano-scale pits. In other words, anisotropy of the etching determines surface roughness. Plasma-less atmospheric dry etching is one of the applications of this processing in technology of black silicon production for photovoltaic solar cell manufacturing, where F_2 gas makes silicon surface rougher. On the other hand, rough surface is unwanted during manufacturing of integrated circuits, because it leads to degradation of device characteristics. Thus, basic understanding of this phenomenon is needed to better control surface structure during the etching.

We performed modeling of Si(100), Si(110) and Si(111) etching by F_2 molecule combined with DFT (density functional theory), TST (transition state theory) and MD (molecular dynamics) approaches like it was done in [1,2]. The combination of DFT and TST enables us to calculate probabilities of gas-surface reactions and perform kinetic modeling of the etching, while under MD approach evolution of the surface at different temperatures at ns time-scale is considered.

We assumed that F_2 dissociative chemisorption leading to Si-Si bond breaking is rate-determining step of whole etching process and reproduce the experimental measurements that the barrier of F_2 dissociation on Si(111) is significantly higher than on Si(100) and Si(110). We established that the value of the barrier is determined by the charge distribution on the surface, and the charge distribution in turn is determined by the number of F atoms incorporated into the surfaces.

Our modeling was validated and well reproduced experimental data such as values of activation barrier and etch rate as a function of temperature.

Based on our mechanism of the etching we will perform similar modeling aimed to design new etchants for Si etching to better control roughness and surface texturing.

References:

1. S Jubin et al, *Frontiers in Physics* 10, (2022) DOI: 10.3389/fphy.2022.908694.
2. Y Barsukov et al, *Nanotechnology* 32, 475604 (2021) DOI: 10.1088/1361-6528/ac1c20.

4:20pm **AP+PS-MoA-9 Process Drift of SiO_2 Atomic Layer Etching in HFC and FC/Ar Chemistries by Optical Spectroscopy and Surface Chemistry Analysis*, Antoine Ronco*[1]**, *F. Boulard, N. Posseme,* Univ. Grenoble Alpes, CEA, Leti, France

Manufacturing new semiconductor devices requires atomic scale control of etching processes in order to decrease their dimensions. Atomic Layer Etching (ALE) allows such thin control of the processes [1][2]. One of the challenges is tuning the durations of the deposition and activation steps to obtain a process with a stable amount of material etched per cycle. If not tuned correctly the fluorocarbon (FC) film can accumulate on the sample's surface causing a drift in the amount of material etched per cycle (EPC)[3]. In this paper, we investigate the use of Optical Emission Spectroscopy (OES) to monitor the drift of a quasi-ALE process. Then, we study the impact of the gas chemistry on the appearance of the drift. Finally, we optimize contact hole etching and especially the landing on the etch stop layer.

The samples studied consist of 100 nm SiO_2 on Si blanket wafers. The experiments are carried out in a 300 mm capacitively coupled plasma reactor. The wafers are etched using C_4F_8, C_4F_6, or CH_3F/Ar based chemistry in a two steps approach, namely deposition and activation. The reactor is cleaned using an O_2 plasma before and after etching each wafer.

We observe a decrease in EPC of a quasi-ALE process when increasing the number of cycles. The examination of the evolution of the intensities of OES spectra through deposition and activation steps reveals that the line at 251 nm, which could correspond to CF/CF_2 radicals, is an indicator of the drift of the process [4]. The decreasing intensity observed during the activation step suggests the accumulation of a carbon film on the sample's surface. This is confirmed through XPS analysis showing an increase in carbon content on the sample's surface when increasing the number of cycles. The correlation between XPS analysis, OES observation, and EPC evolution with the number of cycle shows that the EPC drift can be monitored in real time using OES.

We use this method to study the impact of gas chemistry on the drift of our etching process for SiO_2 and SiN etching. The effect of the FC gas used on the selectivity and uniformity of our process is also reported.

Finally, the impact of gas chemistry and number of cycles on pattern etching is characterized using a Scanning Electron Microscope (SEM). Particular interest is paid to the conformality of the FC film deposited on patterns and etching at the bottom of the contact.

[1] K. J. Kanarik et al., JVSTA **33**, no 2, 020802, 2015

[2] G. S. Oehrlein, et al., ECS J. Solid State Sci. Technol. **4**, no 6, N5041–N5053, 2015

[3] C. M. Huard, et al., JVSTA **36**, no 6, 06B101, 2018

[4] R. W. B. Pearse, et al., The identification of molecular spectra, 4th ed. London: Chapman & Hall, 1976.

4:40pm **AP+PS-MoA-10 Atomic Layer Etching of Superconducting Titanium Nitride Thin Films Using Molecular Oxygen and H_2/SF_6 Plasma*, Azmain Hossain*,** *A. Minnich,* California Institute of Technology

Microwave loss in superconducting titanium nitride (TiN) films is attributed to two-level systems in various interfaces arising in part from oxidation and microfabrication-induced damage. Atomic layer etching (ALE) is an emerging subtractive fabrication method which is capable of etching with Angstrom-scale etch depth control and potentially less damage. However, while ALE processes for TiN have been reported, they either employ HF vapor, incurring practical complications; or the etch rate lacks the desired control. Further, the superconducting characteristics of the etched films have not been characterized. Here, we report an isotropic plasma-thermal TiN ALE process consisting of sequential exposures to molecular oxygen and an SF_6/H_2 plasma. For certain ratios of SF_6:H_2 flow rates, we observe selective etching of TiO_2 over TiN, enabling self-limiting etching within a cycle. Etch rates were measured to vary from 1.1 Å/cycle at 150 °C to 3.2 Å/cycle at 350 °C using ex-situ ellipsometry. We demonstrate that the superconducting critical temperature of the etched film does not decrease beyond that expected from the decrease in film thickness, highlighting the low-damage nature of the process. The ALE-treated films were also studied using XPS and AFM. These findings have relevance for applications of TiN in microwave kinetic inductance detectors and superconducting qubits. (arXiv:2307.02821)

5:00pm **AP+PS-MoA-11 Quasi-Atomic Layer Etching of X-Cut MgO-Doped Lithium Niobate Using Sequential Exposures of H_2 and SF_6 Plasma*, Ivy Chen*,** *J. Solgaard, R. Sekine, A. Hossain, A. Ardizzi, D. Catherall, A. Marandi,* California Institute of Technology*; F. Greer,* Jet Propulsion Laboratory (NASA/JPL), California Institute of Technology*; A. Minnich,* California Institute of Technology

Lithium niobate ($LiNbO_3$, LN) is an emerging platform for integrated photonics. Recent demonstrations of record on-chip quantum states, >100 GHz electro-optic modulators with CMOS compatible voltages, and multi-octave frequency combs with ~100 fJ pump pulse energies highlight the potential of this platform to enable novel on-chip photonic functionalities. However, thin-film lithium niobate (TFLN) devices suffer from large scattering losses resulting from the surface roughness left by Ar^+ milling, the standard technique used for nanophotonic LN waveguide fabrication, negatively impacting device performance. Atomic layer etching (ALE) can potentially mitigate scattering losses due to its ability to smooth surfaces to sub-nanometer length scales, but no ALE process has been reported for TFLN. Here, we report an anisotropic quasi-ALE process for X-cut MgO-doped LN using sequential exposures of H_2 and SF_6 plasma. We observe etch rates up to 2.1 nm/cycle with a synergy of ~97% and characterize the

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[1] **PSTD Coburn & Winters Student Award Finalist**

etched surfaces using X-ray photoelectron spectroscopy, secondary ion mass spectrometry, and atomic force microscopy. This process has the potential to serve as a post-processing step to smooth patterned TFLN surfaces which may both increase the performance of existing TFLN devices and enable novel devices not attainable in other integrated photonic platforms.

Plasma Science and Technology Division
Room A106 - Session PS+SE-MoA

Plasma Sources, Diagnostics, Sensors and Control

Moderators: Michael Gordon, University of California at Santa Barbara, **Yohei Ishii**, Hitachi High Technologies America Inc.

1:40pm **PS+SE-MoA-1 On the Influence of the Target Material on the Discharge Properties of the High Power Impulse Magnetron Sputtering Discharge***, **Jon Tomas Gudmundsson**, K. Barynova,* University of Iceland*; M. Rudolph,* Leibniz Institute of Surface Engineering (IOM), Germany*; J. Fischer,* Linköping University, Sweden*; S. Suresh Babu,* University of Iceland*; M. Raadu, N. Brenning,* KTH Royal Institute of Technology, Sweden*; D. Lundin,* Linköping University, Sweden

High power impulse magnetron sputtering (HiPIMS) operation results in increased ionization of the sputtered species and lower deposition rate than the dc magnetron sputtering discharge, when operated at the same average power. We have applied the ionization region model (IRM) [1] to model HiPIMS discharges in argon with a number of different targets [2,3], to study various processes, such as working gas rarefaction and refill processes, the electron heating mechanisms, ionization probability and back-attraction of the sputtered species, and recycling mechanisms. The HiPIMS discharge can contain a large fraction of ionized sputtered material and often a significant fraction, of the ions involved in the sputter process are ions of the target material. This also implies that a large fraction of the ions of the sputtered species can be attracted back to the target and are not deposited on the substrate to form a film or coating. Self-sputtering and the self-sputter yield are therefore expected to play a significant role in HiPIMS operation, and have a decisive impact on the film deposition rate, at least for metal targets. We explore the relationship between the self-sputter yield and deposition rate as well as the ionization and back attraction probabilities. The back-attraction probability appears to decrease with increased self-sputter yield. The various contributions to working gas rarefaction including electron impact ionization, kick-out by the sputtered species, and diffusion, are evaluated and compared for the different target materials, over a range of discharge current densities. For all cases the working gas rarefaction is found to be significant, and to be caused by several processes, and that their relative importance varies between different target materials. In the case of a graphite target, electron impact ionization is the dominating contributor to the working gas rarefaction, with 55 - 64 % contribution, while the kick-out, or sputter wind, has negligible influence, whereas in the case of tungsten target, the kick-out dominates, with 39 - 48 % contribution. The relative role of kick-out by the sputtered species increases and the relative role of electron impact ionization decreases with increased mass of the target atoms.

[1] Huo et al., Journal of Physics D: Applied Physics 50, 354003 (2017)

[2] Gudmundsson et al., Surface and Coatings Technology 442, 128189 (2022).

[3] Babu et al., Plasma Sources Science and Technology 31, 065009 (2022)

2:00pm **PS+SE-MoA-2 Numerical Analysis of Curling Probe Designing for an Effective Electron Density Measurement in Plasma***, **Daisuke Ogawa**, S. Kato, H. Sugai, K. Nakamura,* Chubu University, Japan

Electrons make a main contribution to generating reactive species in a low-temperature plasma. Optical emission is often utilized to monitor plasma, but it should be noted that the ultimate origin of the emission is due to collisions with the electrons in the plasma. This means that electron monitoring could be the primary information of the plasma. A curling probe is one of the probes that enable an electron density measurement in the plasma. The probe measures the density derived from a shift of the fundamental resonant frequency that the probe holds. Therefore, the probe measures the density even in an environment where the plasma makes a dielectric film deposition. The probe utilizes a slot antenna to make the electromagnetic resonance, which is equipped on the top surface of the probe. This antenna structure gives an advantage in directional electron density measurement. This directionality is useful, particularly when the probe desires to be embedded into a wall and/or an electrode. Recently, we have also developed a technique with the curling probe that enables one to make in-situ measurements of electron density in plasma and the film thickness deposited on the probe surface. The technique requires two different-sized curling probes, so we named it the double curling probe method. This technique is potentially powerful in a plasma-processing reactor with electron density monitoring. However, we noticed that the technique requires further improvement in their measurement resolution; the frequency shift is not always noticeable, especially when the deposited film thickness is small. The frequency resolution depends on the quality factor of an inverted peak in the reflectance spectrum. According to the circuit theory, the factor depends on antenna configuration, such as the antenna's resistance, inductance and capacitance. These parameters depend on the antenna design, so we have researched how curling probe design affects the factor with an electromagnetic wave simulator, CST microwave studio. Our recent result showed that the factor depends on the antenna material, the antenna length, and the antenna thickness. In particular, the long antenna helps stabilize the factor even when increasing electron density in plasma. In this presentation, we will show our recent analysis to suggest what antenna design a curling probe ought to have to improve electron density measurement with a curling probe.

2:20pm **PS+SE-MoA-3 Annular Beam Confocal Laser-Induced Fluorescence Diagnostic for Measurements of Ion Velocity Distribution Function in Industrial Plasmas***, **Ivan Romadanov**, Y. Raitses,* Princeton Plasma Physics Laboratory

Laser-Induced Fluorescence (LIF) is a powerful diagnostic tool for analyzing ion velocity distribution functions (VDFs) in plasma [1]. However, the requirement for two-sided access to plasma for beam injection and fluorescence collection in conventional LIF configuration is not always practical. Confocal LIF configurations, which are widely used in various fields such as biology and medicine, have been developed for several plasma diagnostic applications [2]. The primary advantage of confocal LIF configurations is the coincidence of the laser beam injection and fluorescence collection branches, enabling measurements in systems with limited optical access or complex geometries. This study introduces a novel variation of confocal LIF - Annular Beam Confocal Laser-Induced Fluorescence (ABC-LIF) configuration [3]. The proposed LIF configuration utilizes a structured Laguerre-Gaussian laser beam with an annular intensity profile, generated by diffractive axicons. This approach facilitates LIF signal collection along the main optical axis within the ring region while controlling spatial resolution through laser beam parameters, such as annulus thickness and beam diameter. Consequently, all enclosed fluorescence light is collected, maximizing the signal-to-noise ratio (SNR). This method achieves a spatial resolution of approximately 5 mm at a 300 mm focal distance, with the potential for 1 mm resolution, comparable to conventional LIF. The ABC-LIF configuration benefits from a small depth of field (DOF), typically achieved by Gaussian beams of large diameter, while the Laguerre-Gaussian beam allows for maintaining spatial separation between fluorescence and laser lights at comparable DOF values. Additionally, the configuration circumvents issues with beam back reflection. The ABC-LIF configuration was experimentally verified in industrial DC plasma source measurements of argon ion VDFs. Comparisons between confocal and conventional LIF revealed good agreement in determining plasma parameters, such as ion temperature, flow velocities, and ion density profiles. Applicable to various plasma processing equipment and sources, including hollow cathodes, microplasmas, and electric propulsion, the ABC-LIF configuration presents a promising diagnostic tool for industrial plasmas.

References

[1] Bachet G et al 1998 Phys. Rev. Lett. 80 3260

[2] Thompson D et al 2017 Rev. Sci. Instrum. 88 103506

[3] I. Romadanov, Y. Raitses, arXiv preprint arXiv:2303.12580. (2023)

Funding Acknowledgement: This work was performed under the U.S. Department of Energy through contract DE-AC02-09CH11466.

2:40pm **PS+SE-MoA-4 Control of Electron Energy Distribution Function in Electron Beam Generated ExB Plasma***, **Nirbhav Chopra**, Y. Raitses,* Princeton Plasma Physics Laboratory

Electron beam (e-beam) generated plasmas are promising for low pressure, low damage threshold material processing applications requiring efficient generation of ions and radical species [1,2]. The production of reactive species generated by electron impact is controlled by the electron energy distribution function (EEDF). In this work, we investigate the EEDF and plasma parameters of a partially magnetized plasma generated by e-beam in low pressure (0.1-10 mTorr) argon and nitrogen. The e-beam (energy < 100 eV) is extracted from a negatively biased thermionic filament and injected into a cylindrical vacuum chamber with applied axial magnetic field. The EEDF is measured using electrostatic probes. Results show the presence of e-beam electrons with energies comparable with the applied cathode voltage and a group of warm electrons (10-30 eV). Mechanisms of the formation of this intermediate group of electrons will be discussed. In addition, we will present and discuss the effect of the addition of nitrogen gas to the argon plasma on the EEDF.

[1] Zhao F et al C G 2021 *Carbon* **177** 244–51

[2] Walton S G et al 2015 *ECS J. Solid State Sci. Technol.* **4** N5033–40

3:00pm **PS+SE-MoA-5 Expanding the Capabilities of Microwave Hairpin Resonator Probes***, **Steven Shannon**,* North Carolina State University **INVITED**

Microwave hairpin resonator probes are a common diagnostic for measuring electron density in plasmas. They are particularly effective in low temperature plasmas, RF driven plasmas, reactive (particularly depositing) plasma chemistries, and other plasma environments that can challenge the effective use of comparable probe diagnostics such as Langmuir probes or emissive probes. Efforts to increase the utility of these probes through both innovative probe design (such as biasing and curling probe design) and combination of the hairpin probe with other diagnostic techniques (such as laser photodetachment studies in electronegative discharges) have increased the utility of hairpin probes in the field of experimental plasma science. This work presents efforts to expand on the measurement capabilities of these probes in two ways. First, the analysis of resonance data is expanded to account for plasma contributions to the Q-factor of the loaded resonance circuit. From this, additional plasma parameters such as electron neutral collision frequency can be estimated. Second, the time resolution of these probes are expanded to provide insight into the time modulation of plasma discharges including pulsed RF discharges, and can be extended to time resolved measurements within the period of an RF driven system, complimenting the growing area of phase resolved plasma characterization. The methods for expanding the capabilities of these probes are presented in this talk as well as examples of where this extension of probe capability has provided insight into basic plasma phenomena including moderate pressure operation of RF discharges, sheath heating, probe perturbation effects on density measurement, electronegative plasma instabilities, and the role of plasma edge uniformity on power coupling in inductively coupled plasma reactors. This work has been supported by the National Science Foundation, U.S. Department of Energy, Samsung Electronics, Applied Materials Inc. MKS Instruments and the state of North Carolina.

4:00pm **PS+SE-MoA-8 Time-Resolved Electron Energy Distribution in a Multi-Frequency Capacitively Coupled Plasma Reactor***, C. Kelly, **Md. Amzad Hossain**, D. Kapelyan, D. Ruzic,* University of Illinois at Urbana-Champaign

This work uses a time-resolved Langmuir probe to measure the electron energy distribution function (EEDF) in a capacitively-coupled parallel-plate (CCP) plasma reactor. The EEDF completely determines the plasma chemistry in a low-temperature plasma, and that is why it is so important to obtain. By seeing how the EEDF changes throughout an RF cycle, both as a function of time and position, one then knows the extent by which altering the RF waveform can affect the energy of the electrons. Often industry mixes RF frequencies to alter the plasma -- particularly the ion energy distribution at the substrate. Here we add a second frequency in a systematic manner and examine the changes in the instantaneous EEDF. We also examine the turn on and turn off times of the RF generator itself.

Specialized circuits were designed for this work to ensure high frequency fidelity so digitization at 1.5 GHz is possible and accurate. A set of experiments were conducted to show how only altering circuit parameters affect the results, and steps were taken to eliminate those effects. Spatial variations of the resulting EEDFs were investigated, especially near the edge of the CCP reactor, to see which aspects change the most with radius.

4:20pm **PS+SE-MoA-9 Mass Spectral Characterization and Control of Plasma Etch Processes***, L. Shoer, P. Heil, S. Pursel,* Intel Corporation*; N. Salovich,* Edwards Vacuum*; **David Shykind**,* Intel Corporation

As semiconductor critical dimensions have reached the single-digit nanometer scale, reproducible control of etch processes has become critically dependent on consistent wafer-to-wafer processing. Nanometer feature sizes and atomically thin layers have led to a regime where traditional bulk plasma characterization techniques no longer give insight into the chemical processes occurring on the wafer. Furthermore, the number of moles of reactants on the walls of an etch chamber are greater than or equal to the quantity of reactants intended to be etched on a wafer itself. Uncontrolled, this situation complicates etch processes, introducing hysteretic behavior even assuming an ideal input stream of identical wafers, and exacerbates actual wafer-to-wafer variation effects. We show how high-speed (subsecond time resolution), non-invasive mass spectrometry of plasma cleaning, seasoning and actual etch steps themselves leads to improved performance and enhanced mechanistic understanding of plasma etch processes.

4:40pm **PS+SE-MoA-10 Development of a Catalytic Probe for the Detection of Fluorine Radicals with Applications to Semiconductor Manufacturing***, **Nicholas Connolly**, J. Mettler, R. Garza, R. Sankaran, D. Ruzic,* University of Illinois Urbana-Champaign

Plasma processing is an essential part of integrated circuit manufacturing, with plasma etching, plasma strip, and chamber cleaning being three critical steps. All of these steps rely on radicals, highly reactive neutral species created in the plasma, to drive the desired etching reactions. Because of the importance of radical species in etching reactions and rates, quantification of the densities of these species is important for understanding plasma etching dynamics. Additionally, spatial resolution of radical densities allows specific knowledge of etch dynamics at a substrate or a chamber component of interest.

One technique that has been developed to detect and quantify radical species is a catalytic probe, which consists of two thermocouples each coated with a different metal. The different metals catalyze the recombination of radical species at different rates, leading to a temperature difference between the thermocouples. This temperature difference is proportional to the density of radical species, and so a radical density can be determined. The catalytic probe technique provides in-situ, spatially resolved radical densities. This has advantages over techniques which gather a line-averaged signal, such as optical emission spectroscopy (OES), and measurement methods that require ex-situ analysis, such as coupon etch rates.

Previous studies have applied catalytic probes to the detection of hydrogen (H), oxygen (O), and nitrogen (N) radicals.[1] To our knowledge, a catalytic probe for fluorine (F) has yet to be reported. Here, we present a thermocouple-based catalytic probe to determine spatially resolved fluorine radical densities in SF_6/Ar plasmas. The catalytic activity of zinc, copper, and gold is reported. The radical densities determined from the radical probes are compared to those determined via actinometry and coupon etch rates. These methods also provide verification of the recombination coefficient of the probe material and thereby confirm the quantitative results of the radical probe.

[1] D. Qerimi, I. Shchelkanov, G. Panici, A. Jain, J. Wagner, and D.N. Ruzic. J. Vac. Sci. Technol. A 39, 023003 (2021).

5:00pm **PS+SE-MoA-11 Multi-Diagnostic Investigation of Etching Plasma Species in an Industry-Grade Inductively-Coupled Plasma Etcher***, **Jeremy Mettler**[1], N. Connolly, S. Dubowsky, D. Ruzic,* University of Illinois at Urbana-Champaign

Plasma etching kinetics and reaction mechanisms often involve complex interactions between radical, neutral, and charged species. Optimization of etch rate and selectivity for a given process can be tedious without a detailed mechanistic understanding of the etching mechanisms, which in turn can be difficult to determine without accurate measurements of all relevant plasma species. Many diagnostics exist which are able to measure some of these species, but each has their own tradeoffs, and none are able to measure all species under all conditions.

In this work we discuss the development of a suite of plasma diagnostics for measuring the environment in an etching system, including neutral, charged, and radical species. To accurately measure each component of the

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[1] **PSTD Coburn & Winters Student Award Finalist**

etch process, results from appearance energy mass spectroscopy, optical emission spectroscopy, fluorine radical probe analysis, and Langmuir probe analysis are combined, with overlap in the sensing capabilities of each diagnostic used for cross-validation. The use of multiple independent diagnostics with different spatial resolutions and species sensitivities provides flexibility and increased confidence in quantitative results. This work will present a comparison of results obtained by the individual diagnostics across several CF_4 based etching conditions in an industry-grade inductively-coupled plasma etching tool. Further comparison will be made between experimental etching results and 0-D plasma modeling of the etching system.

Atomic Scale Processing Mini-Symposium
Room A107-109 - Session AP+EM+PS+TF-TuM

Area Selective Processing and Patterning

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

8:00am **AP+EM+PS+TF-TuM-1 Area-Selective Deposition in Nanoscale Patterns***, **Annelies Delabie,*** Imec Belgium, and KU Leuven Belgium*; J. Clerix,* IMEC Belgium*; K. Van Dongen,* IMEC, Belgium*; J. Sinha,* IMEC Belgium*; L. Nyns,* IMEC, Belgium*; R. Nye,* LAM Research*; G. Parsons,* North Carolina State University*; J. Swerts,* IMEC Belgium **INVITED**

Manufacturing nano-electronic devices becomes more and more complex as the device dimensions reach the nanoscale and a wide range of new materials is being implemented to achieve high device performance. Additional complexity comes from the use of three dimensional (3D) structures to reduce the active footprint. Area-Selective Deposition (ASD) provides a promising avenue to assist and/or even simplify device manufacturing processes. ASD is a technique to deposit material only on a pre-defined area of a patterned surface (the growth area), while no deposition is intended on other areas of the same surface (the non-growth area). As such, ASD can be used to replicate patterns on 3D substrates and to (partly) fill narrow trenches or holes from the bottom up. ASD can be achieved by tuning the adsorption and diffusion kinetics in atomic layer deposition (ALD) and chemical vapor deposition (CVD) processes. Insight in the chemical and physical processes is essential to enable rational design of new ASD processes for nano-electronic device manufacturing for advanced technology nodes.

This presentation will discuss the growth mechanisms during ASD on substrates that contain nanoscale patterns, where the geometry of the nanopatterns can affect the growth behavior, selectivity and uniformity. An aminosilane small molecule inhibitor can enable ASD on a wide range of materials with SiO_2 as the non-growth surface [1]. The selectivity of TiO_2 ALD relies mainly on adsorption. Selectivity loss during TiO_2ALD occurs via a nucleation site generation mechanism: small TiO_2 nanoparticles are continuously generated during ALD by slow, unintentional adsorption on the passivated non-growth surface area [2]. ASD super cycles consisting of inhibitor adsorption, TiO_2 ALD and etch effectively improve the selectivity, but may compromise the height uniformity in nanoscale patterns. The selectivity of Ru and $Ge_2Sb_2Te_5$ ALD relies on a complex interplay of adsorption, diffusion and aggregation. We reveal a pattern-dependent selectivity for Ru ALD, which is explained by aggregation of Ru adspecies at the pattern edges [3]. We conclude that the selectivity and uniformity of ALD processes can change when pattern dimensions reach the nanoscale.

[1] K. Van Dongen et al, *J. Vac. Sci. Technol. A* 2023, 41, 032404.

[2] R. A. Nye et al, *Appl. Phys. Lett.* 2022, 121, 082102.

[3] J.-W. J. Clerix et al, *Appl. Surf. Sci.* 2023,626, 157222.

8:40am **AP+EM+PS+TF-TuM-3 N-Heterocyclic Carbenes as Small Molecule Inhibitors in AS-ALD***, **Cathleen Crudden,*** Queen's University, Canada **INVITED**

A unique carbon-based SMI, called an N-heterocyclic carbene (NHC), has been developed as a small molecule inhibitor using carbon as the heteroatom. NHCs have been used in organometallic and catalysis chemistry for decades, where they are renowned for their ability to form strong bonds to metal surfaces. We have developed a suite of organic SMIs with high volatility and thermal stability enabling deposition in an ALD tool. We demonstrated strong binding of the SMI to Ru, Co, Mo and Cu and selectivity for binding to metal surfaces in the presence of insulators. These results are informed by surface science studies including microscopy and spectroscopy.

9:20am **AP+EM+PS+TF-TuM-5 Unraveling Precursor Blocking Mechanisms in Area-Selective Atomic Layer Deposition Using Small Molecule Inhibitors***, **Olaf Bolkenbaas,** M. Merkx,* Eindhoven University of Technology, Netherlands*; P. Yu,* eindhoven University of Technology, Netherlands*; T. Sandoval,* Universidad Tecnica Federico Santa Maria, Chile*; E. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands

Area-selective atomic layer deposition (ALD) has garnered significant attention as a potential technique for enabling the further miniaturization of semiconductor devices. One method for achieving area-selective ALD is through the use of small molecule inhibitors (SMIs) that selectively block deposition on certain materials. Previous research has indicated that precursor blocking by SMIs involves two components: the chemical removal of reactive surface sites and the physical blocking of the surface, also referred to as chemical passivation and steric shielding respectively [1]. However, it is difficult to differentiate between these two factors as they occur simultaneously. In this work we attempt to unravel the steric shielding and the chemical passivation contributions by the SMI acetylacetone (Hacac) with the use of reflection adsorption infra-red spectroscopy (RAIRS) on dehydroxylated Al_2O_3 surfaces obtained through annealing.

When comparing Hacac adsorption on an as-prepared and an annealed Al_2O_3 surface using RAIRS, a lower amount of Hacac adsorbates was observed on the annealed surface. Furthermore, a higher fraction of the Hacac adsorbates was present in the more strongly bonded chelate configuration. This difference in the distribution of the binding configurations demonstrates that the density of surface sites affects the SMI adsorption behavior. We expect that this different adsorption behavior is caused by a lower amount of steric hindrance between the SMIs on the annealed Al_2O_3 surface. Furthermore, the increase in the amount of adsorbates in the chelate configuration will result in a higher contribution of chemical passivation on the dehydroxylated surface, since only the adsorbates in the chelate configuration chemically passivate the surface [2]. From this we can conclude that the removal of surface sites can be used to obtain a better understanding of the two precursor blocking mechanisms. This better understanding will create opportunities for the development of new area-selective ALD strategies involving the removal of reactive surface sites before the functionalization with SMIs to improve selectivity.

[1] Merkx, et al., Chem. Mater. **32**, 3335–3345 (2020).

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

9:40am **AP+EM+PS+TF-TuM-6 Topographically-Selective Deposition Using Amorphous Carbon as Inhibition Layer***, **Thijs Janssen,** M. Merkx, W. Kessels, A. Mackus,* Eindhoven University of Technology, The Netherlands

To accommodate the increasing complexity of device architectures in nanoelectronics, new nanoscale processing techniques are required. Selective deposition techniques have been developed in recent years to enable bottom-up and self-aligned processing[12]. While traditional area-selective deposition distinguishes between areas depending on their chemical character, topographically-selective deposition (TSD) distinguishes between areas based on their orientation within a 3D structure[2,3]. Such TSD approaches offer new fabrication opportunities, for example when the growth and non-growth areas possess similar material properties, or when too many different materials are present within the device structure. Previously reported TSD methods have been demonstrated only for specific materials.

In our work, we develop a versatile TSD strategy that is potentially suitable for a broad range of materials. Our approach utilizes a pulsed Ar/CH_4 plasma to selectively apply an amorphous carbon (aC) inhibition layer on horizontally-oriented surfaces by relying on the directional ions from the plasma. The vapor-phase selective deposition of aC is integrated together with existing ALD processes and plasma treatments into a TSD supercycle recipe.

The highly inert surface of aC lacks suitable absorption sites for ALD precursors and co-reactants, making it an effective inhibition layer. It was found that only the horizontally-oriented surfaces are covered by the aC layer, thus subsequent ALD of target materials proceeds exclusively on vertically-oriented surfaces.

Successful ALD inhibition on the aC surface is established for several different target materials such as TiO_2 using TDMAT and H_2O, Nb_2O_5 using TBTDEN and H_2O, and NiO_x using $Ni(BuAMD)_2$ and H_2O. In particular 90% selectivity was maintained for 35 cycles TiO_2 deposition (1.09 ± 0.01 nm selective growth), 70 cycles Nb_2O_5 deposition (4.38 ± 0.02 nm) and 40 cycles of NiO_x deposition (1.28 ± 0.01 nm). It is demonstrated for NiO_x that the supercycle can be repeated, which effectively resets the nucleation delay, such that a thicker film (nominally ~5 nm after 4 supercycles) can be deposited selectively.

1. Mackus, A. J. M., Merkx, M. J. M. & Kessels, W. M. M. From the Bottom-Up: Toward Area-Selective Atomic Layer Deposition with High Selectivity. *Chem. Mater.***31**, 2–12 (2019).
2. Parsons, G. N. & Clark, R. D. Area-Selective Deposition: Fundamentals, Applications, and Future Outlook. *Chem. Mater.***32**, 4920–4953 (2020).

3. Chaker, A. *et al.* Topographically selective deposition. *Appl. Phys. Lett.* **114**, (2019).

11:00am **AP+EM+PS+TF-TuM-10 A ReaxFF Study for Hacac Interaction on Al_2O_3 Surface in Area-Selective ALD***, **Naoya Uene,*** Tohoku University, Japan*; I. Tezsevin, W. Kessels, A. Mackus,* Eindhoven University of Technology, Netherlands*; A. van Duin,* Pennsylvania State University*; T. Tokumasu,* Tohoku University, Japan

An area-selective ALD process of SiO_2 was developed comprising acetylacetone inhibitor (Hacac), bis(diethylamino)silane precursor (BDEAS), and O_2 plasma reactant pulses. Hacac inhibitors lead to delayed SiO_2 growth on the Al_2O_3 surface for about 15 ALD cycles, after which the selectivity is lost. Two chemisorption configurations of Hacac inhibitors on Al_2O_3 surfaces have been reported: monodentate and chelate configurations. (Merkx et al. 2020) Density functional theory (DFT) calculations have shown that the monodentate configuration is relatively reactive with incoming BDEAS, causing the loss of selectivity due to precursor-inhibitor reactions. Therefore, exploration of the relative densities of the chelate/monodentate configurations on the surface is crucial for the understanding of the selectivity loss mechanism. We aim to understand the reaction mechanisms of Hacac inhibitor adsorption on Al_2O_3 surfaces at the atomic scale.

Up to now, the investigation of the adsorption of inhibitor molecules has been studied via DFT calculations. Thereactive force-field molecular dynamics (ReaxFF MD), which can simulate chemical reactions and physical dynamics at the atomic scale, has been used for gas-surface systems. (van Duin et al. 2001) We performed ReaxFF MD simulations to consider the chemical reactions of Hacac inhibitor molecules with dislocation effects on the surface. An initial force field has been developed for the Hacac interaction on Al_2O_3 surface based on the two existing force fields: Li/Si/Al/O force field for Al_2O_3 structure and protein force field for carbohydrate interactions. (Kim et al. 2016; Monti et al. 2013) The initial force field is trained for Hacac geometry, and their reaction on an OH-terminated Al_2O_3 surface is also modeled.

We performed ReaxFF MD simulations using the developed force field. The simulation consists of three steps. First, the Al_2O_3 surface is pre-thermally relaxed. Then, the Hacac inhibitor is supplied on the relaxed surface, followed by post-thermal relaxation of the Hacac-adsorbed surface. We first confirmed the temperature stability of the Al_2O_3 surface with different temperatures. Our force field can control the temperature of the Al_2O_3 surface ranging from 300 K to 1500 K. Next, sequential adsorption of 20 Hacac inhibitor molecules was simulated on the temperature-controlled Al_2O_3 surface, as shown in the supplemental document. The findings from our ReaxFF simulations provide in-depth insights into the mechanisms of Hacac adsorption and saturation on the surface. These insights will be used for the investigation of precursor blocking and blocking selectivity loss in our future work.

11:20am **AP+EM+PS+TF-TuM-11 Enhancement of TMSDMA Passivation on SiO2 by Surface Fluorination***, **Anthony Valenti,*** SUNY College of Nanoscale Science and Engineering*; C. Vallée,* SUNY College of Nanoscale Science and Engineering, France*; C. Ventrice,* SUNY College of Nanoscale Science and Engineering*; K. Tapily, K. Yu, S. Consiglio, C. Wajda, R. Clark, G. Leusink,* TEL Technology Center, America, LLC, USA

With the ever-shrinking scale of semiconductor devices, area-selective atomic layer deposition (AS-ALD), a bottom-up and self-aligned patterning process with atomic-scale control has been in development in order to meet the demands of industry. This technique is typically conducted by promoting growth on specific surface termination types, while inhibiting growth on the other surface types of the substrate via selective chemisorption of molecules that are inert to the deposition process. With its affinity for chemisorbing to hydroxylated oxide surfaces, specifically SiO2, but not on Si or non-oxidized metal surfaces, N-(trimethylsilyl)dimethylamine (TMSDMA) has been of recent interest for its use as a small molecule inhibitor (SMI) for area selective deposition (ASD). Upon interaction with a surface hydroxyl group, the TMSDMA molecule dissociates, resulting in a trimethylsilyl group bonded to the chemisorbed oxygen atom of the hydroxyl group. Although TMSDMA-passivated SiO2 typically remains inert over several ALD cycles, nucleation of the growth precursor can eventually occur. This may be due to hydroxyl groups on the surface that did not interact with TMSDMA molecules and/or non-hydroxylated sites that were not passivated by trimethylsilyl groups. For instance, surface siloxane bridges do not dissociate TMSDMA and can act as nucleation sites for the ALD growth precursor. In order to enhance the passivation of SiO2 surfaces, the use of co-passivants has been explored. In particular, a remote NF3 plasma has been studied as a means for forming a co-inhibitor. Dosing before or after TMSDMA treatment has been investigated. The deposition of the small molecules were carried out on 10 Å SiO2/Si(100) substrates. Water contact angle measurements were taken to determine relative surface passivation of each sample. Angle-resolved X-ray photoelectron spectroscopy and attenuated total reflection/Fourier transform infrared spectroscopy were performed in order to characterize the chemical state of each surface. Our results indicate that exposure of the substrate to the NF3 plasma after passivation with TMSDMA, results in damage to the passivating layer. However, exposure of the surface to the NF3 plasma before TMSDMA exposure maintains the passivation of the SiO2 surface. In addition, temperature programmed desorption (TPD) measurements are being conducted to assess the relative coverage of the inhibiting film on each sample and its thermal stability.

11:40am **AP+EM+PS+TF-TuM-12 A Study of Elucidation and Improvement of TiO_2 Selectivity by First-Principles Based Thermodynamic Simulation***, **Yukio Kaneda**,* Sony Semiconductor Solutions Corporation, Japan*; E. Marques, S. Armini, A. Delabie, M. van Setten, G. Pourtois,* IMEC, Belgium **INVITED**

Area-selective deposition (ASD) enables the deposition of materials in a targeted area, typically a pre-patterned surface, while preventing the growth on adjacent surfaces.[1] The technique is appealing for both academia and industry as it offers a vehicle to simplify material developments in nanoelectronics. Consequently, numerous efforts have been dedicated to investigate the factors driving the selectivity mechanisms and to identify optimal process deposition conditions, including surface treatments, that enable highly selective processes.

The "selectivity" dimension results from the identification of the right combination of precursors (including co-agents), surface treatments, and reactor operating conditions. This is typically a complex and laborious process that requires many systematic and tightly controlled experiments. As a result, the development of highly selective ASD processes is often a slow and challenging task where any form of guidance provided by modeling insights can be precious.

In this context, we studied, by combining thermodynamic considerations and first principle simulations, the reactivities of complex surface chemical reaction networks and the factors impacting on selectivity. In this talk, we will discuss the case of the ASD of TiO_2 on SiO_2 substrates terminated with either "reactive" (-OH) or "passivated" alkyl-silyl groups. First, we will first briefly discuss the validation of our approach by comparing our model prediction with experimental measurements for the case of the ALD of TiO_2 using the precursors $TiCl_4$ and $Ti(OMe)_4$ and then report the insights gained for the identification of optimum Ti precursor and inhibitor for the ASD of TiO_2. We will then extend the discussion to the case of the ASD supercycles of TiO_2, where the interaction of some Ti precursors (or of their ligands) leads to the degradation of the surface "passivation" and then requires restoring the surface by injecting of alkyl-silyl functional groups. We will review the strategies that worked with their drawbacks.

[1] Gregory N. Parsons and Robert D. Clark, Chem. Mater. **2020**, 32, 12, 4920–4953

[2] Job Soethoudt, *et al.,The Journal of Physical Chemistry C***2020***124* (13), 7163-7173

[3] Janne-Petteri Niemelä *et al.,Semicond. Sci. Technol.***2017** 9 (32), 093005

Biomaterial Interfaces Division
Room B117-119 - Session BI+AS+PS-TuM

Biomolecules and Biophysics at Interfaces

Moderators: Christopher So, Naval Research Laboratory, **Markus Valtiner**, Vienna University of Technology, Austria

8:00am **BI+AS+PS-TuM-1 Probing Protein Structure on Nanoplastic Surface by Sum Frequency Scattering***, **Akriti Mishra,** T. Weidner,* Aarhus University, Denmark

The safe use of nanoparticle protein conjugates in biomedical applications like disease diagnosis, drug delivery, biosensing, etc. depends on the efficacy and stability of these conjugates in body fluids. To date, several analytical techniques like UV-Vis, dynamic light scattering, Fourier transform infrared spectroscopy, circular dichroism, nuclear magnetic resonance, etc. have been used to study the interaction of proteins on nanoparticle surface. Since most of the techniques can not differentiate between the surface bound and the free proteins in solution, it becomes impossible to gather any information about the interfacial proteins. The confirmation of a protein after adsorption on nanoparticle surface can be drastically different from that in solution, which may hamper or amend the activity and function of proteins. Surface sensitive sum frequency scattering (SFS) stands out best in this case since it selectively probes the vibrational modes of the adsorbed analytes on any interface. Sum frequency generation from flat interfaces has been successfully shown to provide rich information about the structure, order, and composition of molecules at the interface. Recently, our group has shown that SFS can effectively probe the structure and orientation of model peptides at nanoscopic oil particle surfaces.1 We will here discuss how also complex human corona proteins can be probed on particle surfaces. We focus on alpha synuclein (aS) interactions with nanoparticles relevant for medical applications and environmental nanoplastics. aS is a 14 kDa intrinsically disordered protein known to form amyloids called Lewy bodies, which can propagate across the neurons to induce Parkinson's disease (PD). Using SFS we follow how aS binds and folds on polymer nanoparticle surfaces. SFS spectra in the amide I region strongly suggest that aS folds into beta sheet and fibrillated structures at the nanointerfaces This is in contrast with flat surfaces, where monomers and helical folds dominate based on reflection SFG experiments.2 We believe, aS binding to the nanoparticles leads to close packing of aS monomers, which leads to the formation of beta sheet and fibrillar type structures.

Fig 1. Schematic of the SFS experiments to follow the binding of aS to polymer nanoparticles particles and the corresponding SFS spectrum

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1.) Thaddeus W. Golbeck, Kris Strunge, Adam S. Chatterly, and Tobias Weidner* J. Phys. Chem. Lett. 2022, 13, 10858-62.

2.) Kris Strunge, Tucker Burgin, Thaddeus W. Golbek, Steven J. Roeters, Jim Pfaendtner and Tobias Weidner* Umbrella-like helical structure of alpha-synuclein at the air-water interface observed with experimental and theoretical sum frequency generation spectroscopy, in preprint.

8:20am **BI+AS+PS-TuM-2 The Structure of Alpha-Synuclein at Lipid Interfaces Determined by Experimental and Theoretical Sum Frequency Generation Spectroscopy***, K. Strunge, K. Pedersen, T. Golbek, M. Brgenhøj, D. Otzen, B. Schiøtt,* ***Tobias Weidner,*** Aarhus University, Denmark

The aberrant folding of α-synuclein (αS) into amyloid aggregates is associated with Parkinson's disease. It has been shown that the refolding into oliogomers and harmful fibrils can be catalyzed by lipid-membrane surfaces. Despite the importance of lipid interactions, the 3D-structure of lipid-membrane bound αS, and thereby, the mechanism of the catalysis process, is still not known at the molecular level. Here, we report interface-specific sum-frequency generation (SFG) experiments revealing how monomeric αS binds, folds and orients at anionic lipid membranes. Since SFG is inherently surface specific and unbond proteins are not detected, the experiments can be performed at high αS concentrations, far beyond previous structural studies. To interpret the experimental SFG data and develop a high fidelity structural model of the aS binding motif, we developed an analysis method in which out-of-equilibrium molecular-dynamics (MD) simulations are linked to excitonic amide-I SFG spectra calculations. 10s of thousands of theoretical spectra calculated for frames of extensive MD simulations are evaluated pooled for their experimental fitness to determine the structure of aS binding at low, physiological and pathological aS concentrations. We find that at low and physiological αS concentrations, the protein binds in a flat geometry, while at elevated, pathological concentrations, a transition to an upright αS binding pose occurs. This upright conformation promotes lateral interactions and likely explains how protein concentrations can catalyze the formation of αS amyloids.

8:40am **BI+AS+PS-TuM-3 Lubricant Viscosity Affects the Antifouling Activity of PFPE Based SLIPS Coatings***,* ***Onur Özcan****, J. Karthäuser, R. Kopecz, A. Gelhar, A. Rosenhahn,* Ruhr-Universitat Bochum, Germany

Settlement of organisms on submerged surfaces can enhance the spread of life-threatening infections.[1] Therefore it is desired to identify methods for the prevention of biofilm formation. The omniphobic properties of slippery liquid infused porous surfaces (SLIPS) have been shown to provide outstanding protection against biofouling, icing, corrosion and to be repellent against complex liquids like blood.[2] In this study, we examine the fouling behavior of E. coli, P. fluorescence, and B. subtilis on seven different superhydrophobic perfluoropolyether (PFPE) urethane methacrylate-based SLIPS with varying lubricant viscosities. The polymers were fabricated following our previously published grafting-through protocolby which superhydrophobic micro-structured porous PFPE matrices could be obtained by adding cychlohexanol as pore forming agent to the monomer mixture.[3,4] The coatings were incubated in an excess of seven different lubricants of varying viscosities to obtain SLIPS. In dynamic attachment assays we were able to show the antifouling capabilities of these SLIPS with organism reductions of up to 90% compared to the dry, smooth, and hydrophobic butyl methacrylate references. Our results further revealed critical species-specific settlement on the coatings that depended on the viscosity of the incorporated liquid, highlighting the relevance of the choice of the lubricant in the design of low-fouling SLIPS.

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9:00am **BI+AS+PS-TuM-4 Orientation of the Dysferlin C2A Domain is Responsive to the Composition of Lipid Membranes***, A. Carpenter,* Oregon State University*; S. Roeters, T. Weidner,* Aarhus University, Denmark*;* ***Joe Baio,*** Oregon State University

Dysferlin is a 230 kD protein that plays a critical function in the active resealing of micron-sized injuries to the muscle sarcolemma by recruiting vesicles to patch the injured site via vesicle fusion. Muscular dystrophy is observed in humans when mutations disrupt this repair process or dysferlin is absent. While lipid binding by dysferlin's C2A domain (dysC2A) is considered fundamental to the membrane resealing process, the molecular mechanism of this interaction is not fully understood. By applying nonlinear surface-specific vibrational spectroscopy, we have successfully demonstrated that dysferlin's N-terminal C2A domain (dysC2A) alters its binding orientation in response to a membrane's lipid composition. These experiments reveal that dysC2A utilizes a generic electrostatic binding interaction to bind to most anionic lipid surfaces, inserting its calcium binding loops into the lipid surface while orienting its β-sheets 30–40° from surface normal. However, at lipid surfaces, where PI(4,5)P2 is present, dysC2A tilts its β-sheets more than 60° from surface normal to expose a polybasic face, while it binds to the PI(4,5)P2 surface. Both lipid binding mechanisms are shown to occur alongside dysC2A-induced lipid clustering. These different binding mechanisms suggest that dysC2A could provide a molecular cue to the larger dysferlin protein as to signal whether it is bound to the sarcolemma or another lipid surface.

9:20am **BI+AS+PS-TuM-5 Probing the Interfacial Action of *Thermomyces Lanuginosus* Lipase at Lipid Surfaces with Vibrational Sum Frequency Spectroscopy – from Monolayers to Emulsions***,* ***Khezar Saeed,*** *K. Strunge, T. Golbek, T. Weidner,* Aarhus University, Denmark

Lipases are a diverse class of biologically important enzymes with a key role in the digestion of dietary fats. The general ability to catalyse triacyl glyceride hydrolysis also enables their application to a wide variety of systems outside of the digestive tract, including transesterification, enantioselective synthesis and as an additive to laundry detergents. Key to their efficacy is the phenomenon of interfacial activation. For lipases this almost universally involves the "opening" of a lid domain upon interaction with a lipid surface, revealing a hydrophobic region containing the active site. The lipase derived from the *Thermomyces lanuginosus* fungus (TLL) is used extensively on an industrial scale as an additive to laundry detergents. As such significant effort has been expended to genetically engineer improvements to the lipase function, with particular attention paid to this lid region. Gaining a deeper understanding of the interfacial activation mechanisms of such lipases could inform the design of improved enzymes in the future.

The inherent surface sensitivity of vibrational sum frequency generation (VSFG) spectroscopy can provide the required molecular level information to further our understanding of the interfacial activation of TLL. VSFG spectroscopy relies on the selection rules associated with frequency mixing of high power visible and infrared laser beams, resulting in a vibrational spectrum of solely the interfacial region. Three key results are presented here:

(i)The TLL-catalysed reaction at the air/triglyceride/water interface can be monitored by reflection VSFG spectroscopy, showing loss of ester carbonyl modes and appearance of carboxylate stretching modes of the fatty acid products.

(ii)Comparison of experimental and predicted VSFG spectra of the amide I band are used to interpret structural changes in the lid domain of TLL upon interaction with a hydrophobic surface.

(iii)Specially formulated emulsions allow further analysis using our new angle-resolved sum frequency scattering spectrometer, showing the first example of reaction dynamics at a particle surface probed by vibrational sum frequency scattering spectroscopy.

This work highlights the utility of VSFG spectroscopy for studying interfacial reactions. Not only does it offer a label-free method of following surface reactions, but it also provides structural and orientational information on interfacial species when combined with appropriate simulations. Furthermore, the results from the sum frequency scattering spectrometer open the door to studying a whole new class of chemical systems at particle surfaces with as yet unseen levels of molecular detail for such systems.

11:00am **BI+AS+PS-TuM-10 An *in Situ* Look at Interfacial Controls on Nucleation, Self-Assembly, and Crystal Growth in Biomolecular and Biomimetic Systems***, **Jim De Yoreo**,* Pacific Northwest National Laboratory **INVITED**

From harvesting solar energy to capturing CO_2 to purifying water, living organisms have solved some of the most vexing challenges now faced by humanity. They have done so by creating a vast library of proteins and other macromolecules that can assemble into complex architectures and direct the mineralization of inorganic components to produce materials characterized by a hierarchy of structure. While the high information content contained within the intricate sequences of the proteins is crucial for accomplishing these tasks, self-assembly and mineralization are nonetheless constrained to proceed according to the physical laws that govern all such processes, even in synthetic systems. An understanding of the mechanisms by which biological systems successfully manipulate those laws to create hierarchical materials would usher in an era of materials design to address our most pressing technological challenges. In this talk, I will present the results of recent research using in situ atomic force microscopy and in situ transmission electron microscopy to directly observe interfacial structure, protein self-assembly, and nanocrystal formation in biomolecular and biomimetic systems, including protein-directed nucleation of calcium carbonate and calcium phosphate and mineral-directed nucleation of two-dimensional protein assemblies. The results elucidate the mechanisms by which the interface between biomolecules and materials directs nucleation, self-assembly and crystal growth, leading to unique materials and morphologies. The results reveal the importance of surface charge, facet-specific binding, solvent organization near interfaces, and, more generally, the balance of protein-substrate-solvent interactions in determining how ordered materials emerge in these systems.

11:40am **BI+AS+PS-TuM-12 the Surface Chemistry of Gecko Toe Pads***, **Mette Heidemann Rasmussen**, K. Holler,* Department of Chemistry, Aarhus University, Denmark*; J. Baio,* School of Chemical, Biological and Environmental Engineering, Oregon State University*; C. Jaye, D. Fischer,* National Institute of Standards and Technology, Gaithersburg*; S. Gorb,* Functional Morphology and Biomechanics, Zoological Institute, Kiel University, Germany*; T. Weidner,* Department of Chemistry, Aarhus University, Denmark

Geckos can climb nearly all surface and are able to cling to walls and ceilings using their toe pads. The gecko adhesion mechanism has been debated over the past years. Current models include van der Walls, hydrophobic and acid-base interactions. Even though the adhesion mechanism of the spatulas has been studied in detail, the surface chemistry involved in the gecko adhesion mechanism is unclear. What is the structure of the supporting proteins within the spatula at the very tips of the setae within the gecko toe pad? What is the role of lipids in the adhesion process? Understanding the surface chemistry of the adhesion of the gecko toe pads gives insight into this highly specialized biological interface, and give clues for materials scientists aiming at mimicking the gecko adhesion mechanisms. Using near edge X-ray absorption fine structure (NEXAFS) imaging and spectroscopy we have studied the structure and order of the molecules at the outermost surface layer of gecko toe pads. We show that the keratin molecules within the spatulas are highly organized and adopt a flat, strand-like geometry, which may support the stability and adaptability of gecko setae (1). We will also discuss evidence showing that a nanometer-thin ordered lipid layer is covering the beta proteins (2).

1. Structure of Keratins in Adhesive Gecko Setae Determined by Near-Edge X-ray Absorption Fine Structure Spectromicroscopy. J Phys Chem Lett. 2022 Mar 10;13(9):2193–6.

1. Evidence that gecko setae are coated with an ordered nanometre-thin lipid film. Biology Letters. 18(7):20220093.

12:00pm **BI+AS+PS-TuM-13 All-Atom Simulations of Peptide Aggregation: Understanding and Predicting Biopolymeric Morphologies***, A. Kwansa, A. Cannon,* North Carolina State University*; **Yaroslava Yingling**,* 911 Partners Way, Engineering Building I, Campus Box 7907

The self-assembly and aggregation of partly or completely disordered peptides have emerged as crucial areas of research with broad implications in therapeutics, supramolecular assembly, and functional biomaterials. Understanding the intricate processes underlying the self-assembly and aggregation of these proteins is essential for harnessing their functional properties and expanding their applications. Simulations can be used to isolate the importance of the interplay between aggregate morphology and secondary structure formation. However, most of the simulation's studies investigate either single peptide in solution or several short peptide analogues. We used large-scale all-atom MD simulations to investigate the structure of hydrated peptide aggregates in detail. Two example systems were investigated, reflectin and elastin-like peptides (ELP). Reflectin proteins, found in cephalopods, play a pivotal role in dynamic coloration for camouflage and communication. On the other hand, ELP proteins possess unique thermoresponsive properties, making them attractive for drug delivery systems, tissue engineering, and biomaterial design. We found significant differences between the structure of a single polypeptide in water and the structure of peptide within the aggregate. Overall, the aggregation process is driven by the formation of peptide–peptide interactions whereas the average hydration of peptides remains almost the same between dissolved and aggregated states. Even though the aggregation is driven by hydrophobic interactions, aggregate has no hydrophobic core and contains many water molecules. Overall, our findings provide an insight into the sequence-dependent structure of aggregates and molecular behavior of individual peptides during aggregation.

Plasma Science and Technology Division
Room A106 - Session PS-TuM

Plasma Processing for Advanced Logic Device Fabrications

Moderators: John Arnold, IBM Research Division, Albany, NY, **Tetsuya Tatsumi**, Sony Semiconductor Solutions Corporation

8:00am **PS-TuM-1 Chemical Role of a Small Amount of Cl--$_2$ in O_2/Cl_2 Plasma for Ru Etching Reaction***, **Masaya Imai**, M. Matsui, R. Sugano,* Hitachi, Ltd., Japan*; T. Shiota, K. Takasaki,* Hitachi High Technologies, Japan*; Y. Ishii,* Hitachi High Technologies America Inc.*; M. Miura, K. Kuwahara,* Hitachi High Technologies, Japan

Ruthenium (Ru) is an attractive candidate as an interconnect metal for future semiconductor devices which can replace conventional copper (Cu). This is because the Ru interconnect below 20-nm-pitch shows a lower resistivity and a higher electromigration reliability than Cu one. Especially, direct patterning of Ru is expected to maximize those advantages. In the patterning process of Ru, the dry etching with oxygen-based plasma is applied because Ru tetraoxides (RuO_4) are volatile. Several reports using reactive ion etching (RIE) showed that the etch rate of Ru is the highest using a O_2/Cl_2 plasma with a 10–20% amount of Cl_2, while it is lower when using pure O_2. The etch rate is also lower when Cl-rich plasma is applied due to the formation of non-volatile Ru chlorides. However, it has not been clarified why a small amount of Cl_2 in the plasma promotes the etching reaction and why the Ru is not etched by pure O_2 plasma.

In this work, the etching reaction mechanism on the Ru surface using a O_2/Cl_2 plasma was investigated by experiments and simulations. Our electron cyclotron resonance (ECR) etcher is unique in that only radicals in the plasma reach the wafer by removing reactive ions using an ion shield plate. Applying this etching technique, we found that Ru can be etched by only radicals in O_2/Cl_2 plasma and that the etch rate was the highest with a ~10% amount of Cl_2. Therefore, a small amount of Cl-based radicals in the plasma explicitly contributes to the chemical reactions to form volatile Ru products, such as RuO_4 and $RuCl_xO_y$.

Using density functional theory (DFT) simulation, we modeled the atomic configuration on Ru surfaces where O and Cl radicals react. In our unit cell, there are nine chemisorption sites for O and Cl. We prepared three surface models where (1) all nine chemisorption sites were covered by O, (2) one chemisorption site was covered by Cl atom and the other eight were covered by O atoms, and (3) two adjacent chemisorption sites were covered by two Cl atoms and the other seven were covered by O atoms. Subsequently, we assumed that the volatile Ru products are formed by the oxidation reactions of the surface Ru atoms. Using nudged elastic band (NEB) method, we calculated the activation energies to desorb the volatile Ru products depending on the surface coverage of chemisorbed O and Cl. Comparing the activation energy among the three surface models, we revealed that it decreases as the number of chemisorbed Cl increases. We concluded that a small amount of Cl_2 in the O_2/Cl_2 plasma contributes to decreasing the activation energy to form volatile Ru products on the surface, resulting in increasing the etching rate of Ru.

8:20am **PS-TuM-2 Coupling of Deposition and Etching to Achieve Selective Removal of TaN with Respect to Ultra Low-*k* Dielectric***, **Ivo Otto IV**,* SUNY Polytechnic Institute*; C. Vallée,* SUNY Polytechnic Institute, France

The transition from silicon oxide and aluminum in the back-end-of-the-line (BEOL) to ultra low-*k* dielectric (ULK) and copper improved RC delay, but came with key challenges, one of which was copper diffusion into the ULK. Diffusion barriers are required in current integration schemes in order to mitigate copper diffusion, and TaN is a key diffusion barrier candidate because of strong dielectric adhesion and low in-plane resistivity properties at sub-5 nm thicknesses. Creation of the BEOL interconnect superstructure is completed in a cyclical fashion, requiring the repeated selective removal of not only copper, but the TaN diffusion barrier selective to the ULK. The TaN diffusion barrier directly contacts the ULK, making selectivity to the ULK of primary importance for this step. ULK films are susceptible to radical-dominated, fluorine-based etching because of the weak bond strength of methyl groups, high porosity allowing high accessibility, and high volatility of SiF_2, SiF_4, and CF_x etch byproducts. The inherent fluorine-based etching pathways make selective fluorine etching of TaN with respect to ULK challenging but may be overcome by coupling of etching and deposition regimes. Plasma-assisted chemical vapor deposition of Si, SiO_2, and SiOF films have been previously explored with Si-containing precursors such as SiF_4 and $SiCl_4$, with additives such as O_2 and H_2 used to manipulate deposited film stoichiometry and film properties. In this work, we explore the use of aforementioned Si-precursors and additives injected directly into an inductively-coupled discharge to perform a protective deposition on the ULK film, while etching the TaN film. The discharge is maintained without applied biasing and at a pressure to remove ion bombardment and allow deposition and etching mechanisms to be radical dominated and isotropic in nature. The focus is mainly the modulation of SiF_4 regimes by exploration of the addition of O_2 or H_2 with modulation of electrostatic chuck temperature, plasma discharge power, and injected species concentration. Ex-situ spectroscopic ellipsometry is utilized with support of scanning electron microscopic imaging to characterize film thickness changes. In-situ optical emission spectroscopy is utilized to better understand the plasma discharge species concentrations and the relevance to observed film thickness modulation. Ex-situ X-ray photoelectron spectroscopy is additionally used to probe the sample surface environment to characterize surface film properties. Though this investigation the possibility of selective deposition on ULK while simultaneously etching TaN is found to be possible by modulation of the aforementioned regimes.

8:40am **PS-TuM-3 Using Metal-Based Photoresists and Hard Masks for Patterning Process Window Expansion***, **Joe Lee**, Y. Mignot, S. Sieg, C. Penny, K. Motoyama, K. Petrillo,* IBM Research Division, Albany, NY*; E. Liu, S. Thibaut, C. Cole,* Tokyo Electron Ltd.

Scaling of critical dimensions calls for greater control of processing conditions for smaller nodes. As such, materials with greater etch selectivity are required to successfully pattern with a healthy process window. Plasma etch tuning can only stretch so far as current schemes face an increasingly heavy burden of walking a tightrope to balance the conservation of photoresist or masking layers while ensuring good clearance of underlying materials. The introduction of metal-containing masking layers, including metalorgano resists (MOR) and metal hard masks, greatly alleviate the burden of traditional soft-mask layers that are more easily deformed during etching. We show schemes that implement its usage, yielding a vast array of benefits, such as reduction of defectivity and roughness in lines, increased flexibility of processing conditions, and a larger process window for structures with aggressive aspect ratios that would otherwise be extremely challenging to produce. Such metal-containing masking layers provide a great benefit to the integrity of multipatterned mandrel structures where pitch doubling is required. As dimensions grow more aggressive, any techniques to alleviate patterning challenges and reduce cycles of learning would be greatly welcome.

9:00am **PS-TuM-4 Understanding Etching of Nanoscale Structures Using Molecular Dynamics and Plasma Modeling***, **Xingyi Shi**, S. Rauf, J. Wang, J. Kenney,* Applied Materials*; J. Booth,* LPP-CNRS, France*; Y. Azamoum,* Helmholtz Institute Jena, Germany*; M. Foucher,* LPP-CNRS, France

Pulsed plasmas are widely used in the semiconductor industry because of the flexibility they offer in controlling etch and deposition processes. Pulsed plasmas allow one to modulate the flux of energetic ions and neutral radicals to the substrate on a millisecond or faster timescale. As the semiconductor industry transitions to sub-5 nm technology nodes, pulsed plasma processes are becoming exceedingly complex due to the need to control surface processes with atomic precision. In this paper, we examine a pulsed chlorine plasma and its interaction with silicon substrates though a combination of fluid plasma simulations, molecular dynamics modeling, and feature scale flux calculations. First, we model the inductively coupled Cl_2 plasma for a range of pressures and powers. The plasma modeling results are compared to experimental measurements of electron density (by microwave hairpin resonator probe) and Cl density (by TALIF with absolute calibration [1]). The validated plasma model is also used to compute the ion angular and energy distribution with pulsed DC bias at low frequency.

From the plasma simulations, we obtain the fluxes and ion angular and energy distributions for the dominant etch species at different pulsing conditions. Cl radicals and Cl_2^+ ions are the primary species in inductive coupled Cl_2 plasma. We then compute the flux distributions for these species inside trench shaped features with aspect ratios ranging from 1 to 100. Due to the directionality of the charged ion species, the ion flux at the bottom of the feature is nearly the same as that at the top of the feature. In contrast, with increasing aspect ratio, fewer radicals can reach the bottom of the feature, resulting in a decrease in the radical to ion flux ratio.

The impact of the change in the flux ratio is examined through molecular dynamics simulations. Based on the flux ratios from the previous analysis, different combinations of chlorine radicals and Cl_2^+ ions at 100eV bombard a bare silicon surface. We observe that the silicon etch yield increases at low Cl/Cl_2^+ flux ratio and plateaus at large flux ratios.

[1] Booth, J. P., Azamoum, Y., Sirse, N., & Chabert, P. (2012). Absolute atomic chlorine densities in a Cl2 inductively coupled plasma determined by two-photon laser-induced fluorescence with a new calibration method. *Journal of Physics D: Applied Physics*, 45(19), 195201.

9:20am **PS-TuM-5 Technology Options to Enable Logic Scaling in Advanced BEOL from Patterning to Metal Interconnect Formation***, **Eric Liu**, A. Ko, N. Joy, S. Rogalskyj, S. Grzeskowiak, A. Krawicz, K. Kanzo, L. Huli, P. Biolsi,* TEL Technology Center, America, LLC **INVITED**

The Back-End-Of-Line (BEOL) process is a crucial step in manufacturing advanced semiconductor logic devices. Recent advancements in EUV lithography, self-aligned multi-patterning, and ruthenium subtractive interconnect formation have led to the developing of more powerful and efficient devices.

EUV lithography employs shorter wavelengths of light to create finer and more complex circuit patterns, enabling the fabrication of smaller interconnects and vias with reduced edge-placement-error and line roughness. This technology has significantly contributed to extending the roadmap of device scaling and reducing the process/design complexity. Self-aligned multi-patterning is another key technique that uses several steps to create a single layer of patterned material with multiple, smaller patterns. This approach enables the self-alignment technique to fabricate more precise and complex circuits with manageable pattern placement and overlay accuracy. Finally, ruthenium subtractive interconnect formation is a novel process that has created interconnects with lower resistance, improved reliability, and overcome the fundamental challenge of RC delay from the conventional damascene approach with copper.

In this presentation, we examine several technology options and innovations to realize the formation of metal interconnects in a critical layer. These innovations include:

1. Advancements in EUV lithography and self-aligned multi-patterning.
2. Patterning consideration between CAR (chemically amplified resist) and MOR (metalorganic resist).
3. Plasma etch interaction to the interconnect material and pattern fidelity.

Meeting the physical and electrical requirements is essential to continuous scaling in advanced BEOL.

11:00am **PS-TuM-10 Direct Ru Etching Mechanism for Advanced Interconnect***, **Miyako Matsui,*** Hitachi, Ltd., Japan*; Y. Ishii, L. Kovatch, K. Maier,* Hitachi High Tech America Inc.*; M. Miura, K. Kuwahara,* Hitachi High Tech, Japan

Logic devices are being continuously scaled by fabricating three-dimensional structures. The recent scaling has been achieved by both pitch scaling and various boosting technologies, such as design technology co-optimization. With the device scaling, alternative metal integrations are also required that enable shrinkage of metal pitch at the back end of the line. Ru is a candidate for interconnect material with metal pitches of 20 nm and beyond, because the Ru interconnect is expected to have lower effective resistance than the Cu interconnect at such small pitches. In addition, Ru is expected to be etched directly, which leads to new scaling boosters, such as semi-damascene patterning. To realize such patterning technology, Ru patterns need to be vertically etched with high selectivity for hard masks. In addition, roughness or other damage should be suppressed to reduce interconnect resistance. In this study, we investigated a Ru etching mechanism using a microwave-ECR etching system. The composition of the etched surface was analyzed by using X-ray photoelectron spectroscopy (XPS), and roughness was measured by using atomic force spectroscopy (AFM).

Ru was etched with high selectivity using Cl_2/O_2 plasma in regard to various materials used for hard masks, which were TiN, Poly-Si, SiO_2, and Si_3N_4. The Ru etch rate was the highest when 20% of Cl_2 gas was added to the Cl_2/O_2 plasma. In that condition, Ru surface was etched by forming volatile RuO_4 or $RuCl_xO_y$, and a smooth surface was obtained after etching. However, when using O_2-rich plasma, nonvolatile RuO_2 was formed, which seems to cause the surface roughness. When using Cl_2-rich plasma, formation of nonvolatile $RuCl_x$ reduced the Ru etch rate and generated the surface roughness by forming micro masks.

We also evaluated a line-and-space Ru pattern with 32-nm-pitch using Cl_2/O_2-based plasma. Selectivity over the Si_3N_4 mask and the Ru sidewall roughness were changed by ion flux, which was adjusted by the duty cycle of wafer bias power using Cl_2/O_2 plasma. When the wafer bias was applied continuously, the Si_3N_4 hard mask widened due to the Si containing by-product. When the ion flux was decreased by reducing a duty cycle of wafer bias, the Ru pattern was vertically etched, but larger sidewall roughness was formed. The roughness was thought to be formed because the sidewalls, on which non-volatile RuO_x and $RuCl_y$ were formed, were etched by O and Cl radicals during the off period of the wafer bias power. We suggested adding a passivation gas to the Cl_2/O_2 plasma to reduce sidewall roughness. Sidewall roughness was thought to be reduced because the sidewalls were uniformly protected from the etching.

11:20am **PS-TuM-11 Study and Characterization of Thick Beol Dual Damascene Self- Aligned via Indenting Etch for Bcd Smart Power Technology Node***, **Pietro Petruzza,*** ST Microelectronics, Italy

Development and characterization of plasma etching processes of manufacturing dielectric self-aligned dual damascene etch for thick Cu BEOL metallization. DD process is carried out by a new reactive ion etching (RIE) employing with RF capacitive-coupled parallel plate plasma (CCP) for BCD smart power 110 nm technology node. The method is accomplished by providing a first inter-level dielectric, SiN via etch (indenting), depositing a second inter-level dielectric layer on the silicon nitride layer; finally selective patterning of line on second inter-level dielectric layer and vias on first inter-level dielectric. These applications require fine patterning of dielectric films by reactive ion etching (RIE) process. Precise control of critical dimensions (CD), etch profile and higher aspect ratio of DD etch are essential factors. Via first DD self-aligned approach increasingly require etching the trench without a stop layer. This place exacting demands on etch uniformity, etch front control and sidewall profile, angle control, micro-trenching effect and it becomes difficult to satisfy high selectivity with minimal small micro-loading at same time. The impact of these issues is crucial when the aspect ratio is very high and on the device are present several patterning structures, typical of smart power technology: ISO and dense with different wide and space. The results show that the loading can be improved and kept at same level when the recess depth increasing.We investigated the DD etching in terms of etching process parameters such as pressure, gas: polymerization gas /O2 mixed, C to F ratio, gas flux directionality, increasing the upper frequency, power. At the same time also the multilayer stack of DD was modulated to meet the requirements of dry etching in terms of robustness and reliability. Using the obtained result, we have provided an etching process with suitable process parameters in order to realize high performance and low-cost semiconductor devices.

11:40am **PS-TuM-12 Process Development of Selective ICP Etching of Si_3N_4 over SiO_2 and of SiO_2 over Si_3N_4 to Produce Dense Arrays of 50 nm Patterns***, **Andréa Fassion**, A. Sarrazin, T. Chevolleau,* Univ. Grenoble Alpes, CEA, Leti, France

The transition of silicon spin qubits from 1D (Dimension) devices to 2D ones demands to produce new architectures and develop dedicated patterning processes **[1]**. To produce the 2D silicon spin qubits devices developed at CEA-Leti, dense and low dimension arrays of patterns are required. 50 nm-wide square-based holes have to be obtained on a thin layer of Silicon On Insulator (SOI) using a crossbar Litho-Etch-Litho-Etch (LELE) scheme. It combines two thin (i.e. 10-40 nm thick) hard mask layers consisting of SiO_2 on Si_3N_4. This patterning scheme requires the anisotropic etching of Si_3N_4 with a high selectivity over SiO_2 and vice-versa.

A previous study showed that a CH_3F/O_2 based plasma allows the etching of Si_3N_4 with a high selectivity over SiO_2 **[2]**. Regarding the selective etching of SiO_2 over Si_3N_4, a recent work presents a process using a BCl_3/Ar based plasma reaching a selectivity of about 4:1 **[3]**. The work presented here aims to further characterize the selectivity mechanisms of both CH_3F/O_2 and BCl_3/Ar based processes.

Etching is performed in an industrial ICP (Inductively Coupled Plasma) reactor. The etching mechanisms are discussed in terms of plasma-surface interactions. These interactions are characterised using in-situ Optical Emission Spectroscopy (OES) and interferometry, ex-situ Spectroscopic Ellipsometry (SE), X-Ray Reflectometry (XRR), Atomic Force Microscope (AFM) and quasi in-situ X-Ray Photoelectron Spectrometry (XPS).

Our study shows that CH_3F/O_2 based processes reach an etching selectivity higher than 15:1 and that it strongly relies on the use of F-poor fluorinated gas, high amount of O_2 and high-pressure conditions (figures enclosed). Our work also reveals that BCl_3/Ar based processes selectivity relies on both bias voltage and the operating pressure (figures enclosed). It also shows that BCl_3/Ar based process enable a SiO_2 etching ranging from 2 to 15 $nm.min^{-1}$ with a selectivity over Si_3N_4 of 7:1 and 3:1, respectively.

According to these selective and low etch rate processes, alternative integration strategies are proposed and applications to patterns will be presented.

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12:00pm **PS-TuM-13 Plasma etch study of $Nb_xTi_{(1-x)}N$ metal lines for Superconducting Digital Logic***, **Yann Canvel**, L. Souriau, V. Renaud, A. Pokhrel, A. Gupta, M. Kim, J. Soulie, S. Sarkar,* IMEC, Belgium*; A. Herr, Q. Herr,* IMEC*; F. Lazzarino, Z. Tokei,* IMEC, Belgium

In the development of next-generation logic devices, an attractive complement to CMOS technology would be to leverage the superconducting technology which operates 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 backend fabrication of superconducting metal lines using direct metal etch (DME) approach at relatively small CD/pitch dimension.

In this communication, an in-depth plasma etch investigation is reported to demonstrate the patterning of $Nb_xTi_{(1-x)}N$ wires. Using the Reactive Ion Etching (RIE) technique, the study has firstly consisted of screening the plasma chemistry and the tool-related parameters. It has provided some solid learnings to roll out a process optimization, leading to the successful fabrication of $Nb_xTi_{(1-x)}N$ metal lines at CD of 50 nm and pitch of 200 nm. Finally, some electrical measurements at room and cryogenic temperatures will complete the investigation validating the fabrication of the smallest superconducting interconnects ever produced.

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).

Atomic Scale Processing Mini-Symposium
Room A107-109 - Session AP1+2D+EM+PS+TF-TuA

Atomic Layer Processing: Integration of Deposition and Etching

Moderator: John F. Conley, Jr., Oregon State University

2:20pm **AP1+2D+EM+PS+TF-TuA-1 Combination of Plasma-Based Atomic-Scale Deposition and Etching Processes for Advanced Patterning***, Marceline Bonvalot,* LTM - MINATEC - CEA/LETI, France*; C. Vallée,* SUNY College of Nanoscale Science and Engineering*; r. gassilloud, T. Chevolleau,* CEA/LETI-University Grenoble Alpes, France*; N. Possémé,* STmicroelectronics, France **INVITED**

Selective Deposition processes have gained increased research interest in recent years, because they enable the accurate placement of a thin film on a specific substrate surface (in the case of area selective deposition ASD) or on specifically oriented surfaces (in the case of topographical selective deposition TSD). Such processes require atomic-scale precision, and usually involve Atomic Layer Deposition techniques, with possibly plasma assistance. Several pathways have been proposed in the literature for ASD, most commonly implying surface inhibition treatments with dedicated chemical treatments (self-assembled molecules or small molecule inhibitors for instance) to increase the nucleation delay during the subsequent ALD growth. However, the dedicated inhibition behavior eventually deteriorates when exposed to a few ALD cycles, which requires that on the one hand, nuclei formed on non-growth surfaces be removed and on the other hand, the inhibitor be systematically regenerated.

In this presentation, we will show how the insertion of an *in situ* etching step in the overall ALD process can serve as an effective corrective treatment for this purpose. The etching periodicity in conventional deposition/etching duty cycles will be investigated in details. We will show that the etching step should preferentially be carried out before the transition from the Volmer-Weber 1D island growth mode to the 2D layer by layer growth mode on non-growth surfaces, to limit plasma-induced surface defects. Moreover, the 1D island growth mode seems to coincide with the onset of degradation for the surface inhibition treatment. In this context, it will be shown that the etching periodicity is a determining parameter for the successful development of a selective bottom-up growth strategy.

3:00pm **AP1+2D+EM+PS+TF-TuA-3 Application of Etching Reaction Models to Deposition Processes***, **Nobuyuki Kuboi,*** Sony Semiconductor Solutions Corporation, Japan **INVITED**

Advanced CMOS devices require highly intricate 3D stacked structures with varying aspect ratios such as FinFETs and GAAs [1]. Understanding the process properties of plasma etching [2] and deposition [3] processes based on their mechanism and combinations has become increasingly important in addressing this challenge. Additionally, microfabrication properties should be stably suppressed within a specific range during mass production. However, the monitoring system equipped in the process chamber is limited for mass production. Therefore, we propose predictive models for plasma etching and deposition that consider the physical and chemical aspects of the plasma and surface.

First, we briefly introduce simulations for fluctuations in the SiN etching rate influenced by the chamber wall condition, critical dimensions during Si gate etching caused by $SiBr_x$ by-products dependent on open area ratios on wafer/chip/local-pattern levels, damage distribution affected by local-pattern structure, ion energy, and hydrogen concentration in the SiO_2 and SiN films, and selectivity during SiO_2-ALE [4][5][6].

We then present a modeling and simulation of the deposition process as a motif of the SiN-PECVD process using a 3D voxel method that can be associated with the previous process, such as plasma etching [7]. The model can predict film properties as well as the coverage on a large-scale pattern. Reactions among voxels are considered pseudo treatments for atomistic interactions on the surface. A statistical ensemble method involving probabilities is used to express physical and chemical phenomena such as sticking, migration, and bond formation on the deposited surface. The sticking and bond probabilities are affected by surface damage and IEADFs, respectively. Our model can successfully reproduce the experimental characteristic relationship between the morphology and film density dependent on the SiH_4 flow rate during the low temperature (120 ºC) SiN-PECVD process considering different gas residence times that affect surface reactions. Furthermore, we discuss the issue of modeling the ALD process.

These simulation technologies can aid in optimizing the chamber wall condition, pattern design, and etching/deposition combination process.

[1] N. Singh *et al*., IEEE Electron Device Lett. **27**, 383 (2006).

[2] T. Tatsumi *et al*., Jpn. J. Appl. Phys. 61, SA0804 (2022).

[3] H. C. M. Knoops *et al*., J. Vac. Sci. Technol. A **37**, (2019) 030902.

[4] N. Kuboi *et al*., Appl. Phys. Express **5**, (2012) 126201.

[5] N. Kuboi *et al*., J. Vac. Sci. Technol. A **35**, (2015) 061306.

[6] N. Kuboi *et al*., J. Vac. Sci. Technol. A **37**, (2019) 051004.

[7] N. Kuboi *et al*., Jpn. J. Appl. Phys. **62**, (2023) SI1006.

4:20pm **AP1+2D+EM+PS+TF-TuA-7 Recent Advancements for Atomic Layer Advanced Manufacturing Processes: Microreactor Direct Atomic Layer Processing (µDALP™)***, **Maksym Plakhotnyuk,** A. Varga, I. Kundrata,* ATLANT 3D Nanosystems, Denmark*; J. Bachmann,* ATLANT 3D Nanosystems; Friedrich-Alexander Universität Erlangen-Nürnberg, Denmark **INVITED**

As the demand for miniaturized and complex devices continues to grow across various industries, the need for innovative and precise atomic layer advanced manufacturing (ALAM) technologies becomes increasingly apparent[1]. Our company, utilizing proprietary Microreactor Direct Atomic Layer Processing (µDALP™), is at the forefront of pushing sALD's capabilities and broadening its application horizons. The µDALP^{TM} process undergoes the same cyclic ALD process but only in a spatially localized area.[2] The microreactor or micronozzle confines the flows of gases used for ALD within a defined µm-scale centric area on the substrate to deposit the desired material.[3]

ATLANT 3D's recent advancements in our novel µDALP™ technology have enabled innovation within the thin film deposition field ranging from ALD material development to rapid prototyping and manufacturing. The µDALP™ process enables multiple depositions e.g., depositions with varying film thicknesses, to be deposited onto a single wafer used to calculate a given processes growth rate within only a few hours, compared to days for a traditional ALD process. In Addition, innovation of applications including optics and photonics, quantum devices, MEMS, RF electronics, emerging memory technologies, advanced packaging, and energy storage are possible and have been demonstrated using µDALP™ technology.

Discussing the improvements to the µDALP™ process, we have decreased the process resolution, increased material compatibility, and accessible morphologies. Giving one example of the recent development in morphologies, films deposited with µDALP™ have conformal coverage of gratings, microchannels, and trenches up to a depth of 25 µm using a Platinum deposition process. **Fig. 1** demonstrates how a given ALD material process (in this case, Pt) can be used with ATLANT 3D technology to deposit localized area conformal coatings of complex surfaces with an aspect ratio of 1:25. Hence demonstrating the versatility and potential of our technology for achieving inherently selective ALD for processing on complex surface morphologies.

This talk aims to shed light on how our breakthroughs in spatial ALD and µDALP™ technology contribute to the advancement of ALAM and scale-up. Fostering a deeper understanding of our technology's capabilities and exploring the possibilities it opens up for various industries.

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[2] Kundrata I., et al., *Small Methods.*, **2022**, *6 (**5**)*, 2101546

[3] Plakhotnyuk M, et al., *ALD/ALE 2022 [Int. Conf.],***2022**

Atomic Scale Processing Mini-Symposium
Room A107-109 - Session AP2+PS+TF-TuA

Energy Enhanced ALD

Moderator: John F. Conley, Jr., Oregon State University

5:00pm **AP2+PS+TF-TuA-9 Atomic Layer Annealing with Radio Frequency Substrate Bias for Control of Grain Morphology in Gallium Nitride Thin Films***, A. Mcleod, P. Lee,* University of California, San Diego*; S. Yun, S. Ueda,* University of California, San Diego, USA*; Z. Devereaux, C. Winter,* Wayne State University*; J. Spiegelman,* RASIRC*; R. Kanjolia, M. Moinpour,* EMD Electronics, USA*; **Andrew Kummel**,* University of California, San Diego **INVITED**

Low temperature GaN deposition is critical for passivation layers on nitride power FET as low as templating and capping layers on sputtered AlN films for heat spreader. A method of performing atomic layer annealing with RF substrate bias on insulating and amorphous substrates is demonstrated for GaN deposition at 275 ℃. GaN is typically deposited by MOCVD or MBE at >600 ℃, resulting in strain upon cooling; this makes low temperature process alternatives desirable. Tris(dimethylamido) gallium (III) and hydrazine served as precursors while Ar and Kr were used for ion bombardment. Optimization of substrate bias potential is demonstrated by GI-XRD and XRR. Reference films were deposited by thermal ALD and non-substrate biased ALA processes. XPS surface and depth-profiling studies show that applied RF bias decreases film oxygen and carbon content relative to the reference films; these films also show crystallites broadening with increasing film thickness by TEM in contrast to the reference films. In summary, ALA with RF substrate bias is demonstrated as an effective method to deposit GaN thin films at a low deposition temperature on insulators.This technique has recently been expended to growth of InGaN films which applications in microLEDs.

5:40pm **AP2+PS+TF-TuA-11 Atomic Layer Annealing for sub-10 nm, Wake-up Free Ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ Thin Films***, **Yu-Sen Jiang**,* National Taiwan University, Taiwan*; T. Chang, S. Yi,* Taiwan Semiconductor Manufacturing Company, Taiwan*; M. Chen,* National Taiwan University, Taiwan

Conventional annealing techniques pose significant challenges in nanoscale fabrication. One prominent issue involves the heating depth, which typically exceeds the critical dimension of nanoscale devices. Consequently, conventional annealing methods introduce excessive thermal budget, resulting in performance degradation of the devices. Atomic layer annealing (ALA) is capable of adjusting the film quality at the atomic level during low-temperature (300℃) deposition without the need for any post-annealing process, which tremendously lowers the thermal budget and can tailor the film properties as required. In this report, the ALA technique was used to realize sub-10 nm wake-up free ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ (HZO) thin films with high remnant polarization and low thermal budget. The HZO thin films have also been used as gate dielectrics in junctionless transistors, demonstrating steep subthreshold swing (< 60 mV/decade) in nanoscale devices. The outcome manifests the remarkable capabilities of ALA in enabling precise engineering and fabrication of nanoscale materials and devices.

6:00pm **AP2+PS+TF-TuA-12 A System for Predicting the Area Selective Deposition of Titanium: Plasma State Diagnostics Using Electrical Simulation***, **Kyoungmi Choi**, T. Hong, H. Kim, Y. Oh,* Samsung Electronics Co., Inc., Republic of Korea

The selective deposition of thin films in specific areas is crucial for achieving the desired size and lowresistance of semiconductors. Due to differences in chemistry between molecule/surface and molecule/vapor interactions, thin films are selectively deposited on pre-patterned substrates. Although simulations have been used to predict Ti film thickness using plasma simulation and surface reaction models, the effect of selective deposition on the pattern was not studied. In this study, an electrical simulation was used to predict the selectivity of the area selective deposition process on the patterned wafer.

To identify the main factors affecting selectivity, we reviewed the plasma temperature and density. Plasma density can be indirectly inferred from the output current of the matcher. Another factor that influences selectivity is plasma temperature, specifically the electron temperature [eV]. The sheath voltage is proportional to the electron temperature. Therefore, we established an electric simulation system (Fig. 1) to estimate the sheath voltage. The CCP consists of an RF generator, a matcher, and a chamber. We identified the matcher parameters (C_{tune}/C_{load}/L) using the maximum power transmission theory, assuming that the chamber was $Z_{chamber}$(Fig 2). The model was verified using MATLAB and the sheath voltage was derived using the matcher and bottom currents. The simulations and evaluations of pressure/RF power/impedance were performed. The validity of the electrical model was confirmed by comparing the simulation and the experimental current.

To verify the simulation, Ti deposition experiments were conducted on Si/SiO wafers under 7 conditions (Table1). The simulation results for sheath voltage and the experimental results for deposition rate showed a correlation of 0.77, and the Si/SiO selectivity showed a correlation of 0.92(Fig 3).

Through the correlation result,itwasderivedasthefollowingconclusion.The correlation results between sheath voltage and the area selective deposition explains the difference in the activation energy of the Si/SiO surfaces: The Si-Si bonding energy is 3.39 eV and the Si-O bonding energy is 8.29eV (Fig 4). Since there are regions where the plasma temperature is active on Si and inert on SiO, they are selectively deposited. Therefore, a sheath voltage simulation can be used to predict the selectivity. With further development, this simulation can be applied to other deposition equipment that uses plasma, and trends in process results for other process parameters that are sensitive to plasma temperature can be inferred.

Plasma Science and Technology Division
Room A106 - Session PS+MS-TuA

Modelling of Plasmas and Plasma Driven Processes

Moderators: Mingmei Wang, Lam Research Corporation, **Jinyu Yang**, University of Notre Dame

2:20pm **PS+MS-TuA-1 Towards Completing Chemistry Sets for Plasma Simulations***, **Sebastian Mohr**, G. Armstrong, K. Lemishko,* Quantemol Ltd., UK*; A. Owens, W. Wu, J. Tennyson,* University College London, UK

Plasma simulations are widely used in both academic and industrial settings to gain insights into fundamental plasma physics and optimise plasmas processes. Their success not only hinges on a robust physical model but also on the availability of data describing the chemical processes in a discharge. These data can be in the form of

Collision cross-sections, mostly for electron processes

Rate coefficients, mostly for heavy particle processes

Lifetimes and de-excitation channels of excited states

Probabilities for surface reactions

Species properties such as the enthalpy of formation

For rather simple or common gas mixtures such as argon or oxygen, sufficient data can usually be found in existing publications or databases; however, for more complex gas mixtures, especially ones including gases which have not been extensively studied yet, these data are usually not available for all species and reactions of interest. Furthermore, even in quite well known gas mixtures so far unknown or neglected phenomena can become important under specific process conditions. Hence, it is of vital importance to generate new data in a timely fashion.

We have developed a series of software tools to address the issue of missing data for plasma simulation purposes and to give easy access to existing data. These include:

The calculation of missing electron – molecule collision cross sections [1].

An online database QDB [2] of existing plasma chemistry data including both cross-sections and rate coefficients as well as some surface chemistry data

Machine learning algorithms for the quick estimation of species and reaction data [3]

A database of radiative lifetimes for excited states tailored to the needs of plasma modellers [4].

A global plasma model with additional tools such as a chemistry set reduction [5] to tailor a chemistry set to specific process conditions.

A collisional-radiative model to calculate the emission spectrum of a plasma discharge based on the densities of the excited states and the neutral gas temperature.

We will present the latest additions to these tools and examples to showcase their use and their impact on plasma simulations such as adding reactions with formerly unknown cross-sections or rate coefficients to chemistry sets or the impact of adding the radiative decay of vibrational states to a plasma model.

[1] B Cooper at al 2019 *Atoms***7** 97

[2] J Tennyson et al 2022 *Plasma Sources Sci. Technol.***31** 095020

[3] M Hanicinec at al 2023 *J Phys D*, in press, doi:10.1088/1361-6463/acd390

[4] A Owens et al 2023 *Plasma Sources Sci. Technol.*, submitted

[5] M Hanicinec et al 2020 *Plasma Sources Sci. Technol.***29** 125024

2:40pm **PS+MS-TuA-2 Particle-in-Cell Monte Carlo Collision Modeling of Low-Pressure Plasma Discharges***, **Ken Hara**, Y. Yamashita,* Stanford University

Predictive modeling of partially ionized gases plays a critical role for applications such as semiconductor manufacturing, plasma processing, spacecraft propulsion, hypersonic flows, and high-energy density plasmas. However, plasma modeling remains challenging due to the nonlinear coupling of different physical and chemical processes. In particular, when operating the plasma sources at low pressure, the plasma constituents are not in equilibrium and their velocity distribution functions may become a non-Maxwellian due to the lack of collisions. Conventional fluid approaches cannot capture such rarefied flow physics and thus kinetic methods are needed. In this talk, we will present the development of particle-in-cell (PIC) Monte Carlo collision (MCC) models for low-pressure plasma discharges. The in-house PIC/MCC models are applied to various phenomena, including DC/RF breakdown, cylindrical sheath, capacitively coupled plasmas, and plasma instabilities. In particular, the effects of macroparticle (MP) weights on the plasma behavior are studied using a cylindrical (axisymmetric) PIC/MCC model. As the cell center volume is small near the symmetry line compared to the periphery, the numerical noise due to the lack of MPs can artificially generate plasmas near the centerline, leading to numerical plasma nonuniformity. The numerical heating is mitigated by modifying the MP weight. Acceleration of the PIC/MCC simulations and applications to DC/RF breakdown will be discussed in the talk.

3:00pm **PS+MS-TuA-3 Radio-frequency Hollow Cathode Discharge Characterization using Plasma and Machine Learning Models***, **Kallol Bera**, A. Verma, S. Ganta, S. Rauf,* Applied Materials, Inc. **INVITED**

Low to moderate pressure radio-frequency (RF) hollow cathode discharges (HCDs) have gained significance for advanced plasma processing in the semiconductor industry. HCDs form in cylindrical cavities in the cathode. One can use an array of such HCDs to create uniformly dense large-area plasma. In the HCD, RF sheath heating as well as secondary electron acceleration play an important role. For modeling low-pressure RF HCDs, where kinetic effects are important, particle-in-cell Monte Carlo collision (PIC-MCC) modeling scheme has been used. In this PIC-MCC model, using charge density of particles, Poisson equation is solved for electric potential, which yields the electric field. Using this electric field, all charged particles are moved. The code considers particle collisions with each other and with neutral fluid using a Monte Carlo model. The single HCD behavior is studied over a range of pressure, RF voltage, frequency, and secondary electron emission coefficient. A strong positive power deposition region is observed within the hollow-cathode hole. The plasma penetrates inside the hollow-cathode hole with an increase in pressure and frequency, leading to plasma density enhancement. Higher secondary electron emission coefficient has a stronger impact on the plasma penetration into the hole at higher frequency. However, the effect of increasing RF voltage on plasma penetration into the hole is limited. Large area plasma using an array of HCDs is coupled to electromagnetic fields in the process chamber. Multiphysics modeling of an array of RF HCDs is difficult due to the geometrical complexity, which makes the simulations computationally prohibitive. This precludes development and utilization of these models in scenarios where the computations need to be performed rapidly and repeatedly. To overcome these challenges, we developed a deep learning based non-linear model order reduction method for plasma process in HCDs. A space-filling method is used to design computational experiments at different voltages at the fundamental frequency and at the second harmonic along with their phase difference. The temporal voltage-current characteristics of the HCD are used to train the reduced order model based on modified recurrent neural network. Our model predictions match well with the plasma simulation results within and outside the training range at a significantly smaller computational time. Further, an electromagnetic model is developed with coupled non-linear voltage-current characteristics from the neural network model. The coupling of electromagnetic field to non-linear discrete discharges characterizing an array of HCDs for large area plasma is in progress.

4:20pm **PS+MS-TuA-7 Experimental Characterization and Modeling of the Spatial Afterglow of Plasmas***, **Nabiel Hilmy Abuyazid**,* University of Illinois at Urbana Champaign*; N. Uner,* Middle East Technical University, Turkey*; S. Peyres, R. Sankaran,* University of Illinois at Urbana Champaign

There has been recent interest in the spatial afterglow of plasmas because of its potential role in charging and agglomeration of aerosol particles as well as neutralization and dosing of surfaces. In general, the spatial afterglow is analogous to a temporal afterglow, characterized by a decay of charge resulting from a change in the applied power, except that the charge decay occurs in space rather than in time. However, the nature of the charge decay has been much less studied than temporal afterglows, perhaps because of the challenge of performing experiments at higher pressures and in smaller dimensions.

Here, we performed double Langmuir probe (DLP) measurements, which enable spatial measurements of the plasma density, and developed a one-dimensional advection-diffusion-recombination model that describes the charge decay in the spatial afterglow. Our results show excellent agreement between experimental measurements and model outputs over different pressures. Experimental measurements were limited to a pressure of 300 Torr at which point the DLP traces no longer exhibited known shapes and could not be analyzed to extract plasma parameters. By validating the model at the lower pressures, we were then able to extend the model to predict behavior at higher pressures, up to atmospheric. At pressures above ~75 Torr, the rate of charged species decay is primarily influenced by pressure, as three-body recombination becomes increasingly dominant over diffusional losses, and is secondarily influenced by gas flow velocity and temperature. Importantly, our findings reveal a transition from ambipolar diffusion to free diffusion at some distance from the bulk plasma within the spatial afterglow. First studied in temporal afterglows, apparent diffusivities of charged species vary as the plasma decays, eventually reaching a critical point where the ambipolar field becomes too weak and charged species begin to diffuse freely. The shift to free diffusion could lead to negatively-charged electrons being lost and positively-charged ions remaining, which has been previously reported to explain how aerosol particles that leave a bulk plasma negatively charged become neutralized or even positively charged after their transit through the spatial afterglow.

4:40pm **PS+MS-TuA-8 Circuit-based Reduced Order Model for Fluid Plasma Simulation of Capacitively Coupled Plasma Reactors***, **Sathya Ganta**, A. Verma, K. Bera, S. Rauf,* Applied Materials, Inc.

Fluid plasma simulations are essential for the design of radio frequency (RF) driven capacitively coupled plasma (CCP) reactors used for plasma-based deposition/etching processes. One can assess on-wafer performance using the computed ion/neutral fluxes, sheath potentials, and ion energies. These plasma parameters are directly related to process parameters like deposited film thickness, film stress, wet etch rate, uniformity etc. Hence, the fluid plasma simulations are vital to the semiconductor industry. To predict the ideal process parameters required to meet the on-wafer specifications, one needs to run a large number of simulations in the multi-dimensional process space, which requires enormous computational resources. A key aid in such scenarios would be fast and reliable reduced-order surrogates to the computationally cumbersome plasma fluid simulations. This paper explores one such reduced-order surrogate model based on a circuit-based estimation of the RF sheath. Here, the RF sheath is estimated to be a circuit consisting of a constant current source predicting ion current, a diode predicting electron current and a capacitor predicting the displacement current where these three circuit elements are in parallel to each other. First, a small set of 1D plasma fluid simulations are run corresponding to a set of process parameters that span the entire process space. The results from these plasma simulations, specifically the sheath voltage and current characteristics, are used to fit the parameters of the current source, diode and capacitor that form the RF sheath using a non-linear regression model. Once the circuit parameters are fitted, the resulting RF sheath circuit is coupled to an electromagnetic finite difference time-domain (FDTD) simulation making it a reduced-order surrogate of the plasma fluid simulation. The reduced order model is finally run corresponding to a new set of process parameters within the process space and its performance is compared to that of fluid plasma simulations and analyzed.

5:00pm **PS+MS-TuA-9 Fully Kinetic Modeling of Wafer Processing Chambers in CCP and coupled ICP/CCP Systems Using VSim***, Daniel Main, E. Lanham, J. Cary, T. Jenkins, J. Leddy, S. Kruger,* Tech-X Corporation

Inductively Coupled Plasmas (ICPs) are extensively used for materials processing in the semiconductor industry, typically with the addition of an RF bias [1]. For these reactors, it is assumed that the majority of plasma generation comes from the inductive power while the bias can independently control the flux and energy of ions needed for processing. In reality, the interaction between the multiple power sources is difficult to isolate and computational modeling becomes a necessity. Typically ICPs are modeled using a fluid approach, which does not correctly model the collision processes at lower pressures (~1-10 mTorr) nor the sheath that forms near the wafer. In this work, we discuss multiple techniques using the particle-in-cell software package VSim [2,3] that can be used for reactor-scale modeling of mixed inductive and capacitive discharge systems to accurately characterize the ion energies impacting a wafer for processing. One method is to use a global model to first compute a near-steady-state system composed of neutrals and plasma. The fluxes and densities from the global model serve as initial conditions for a high-resolution electrostatic capacitively coupled plasma (CCP) simulation to correctly model the sheath near the wafer and ion fluxes onto the wafer. Another approach is to model both the inductive and capacitive power sources in one simulation using a newly developed implicit electromagnetic scheme. We discuss differences between the CCP-only and coupled ICP/CCP systems found in ion energies, ion fluxes and the ion distribution function impacting the wafer, as well as the computational costs of the two methods.

[1] M. A. Lieberman and A. J. Lichtenberg, Principles of Plasma Discharges and Materials Processing, John Wiley & Sons, Inc. (2005).

[2] C. Nieter and J. R. Cary, J. Comp. Phys. 196, 448 (2004).

[3] www.txcorp.com

5:20pm **PS+MS-TuA-10 Hybrid Particle-in-Cell + Fluid Model of Multi-Frequency Capacitively Coupled Plasma with Tailored Voltage Waveform Bias***, **Shahid Rauf,** X. Shi, T. Wang, S. Ganta,* Applied Materials, Inc.

Multi-frequency capacitively coupled plasmas (CCPs) are widely used for thin film etching and deposition in the semiconductor industry. When operated at low pressures, kinetic effects dominate electron dynamics and, therefore, fluid assumptions are inaccurate for electrons in plasma models. Most industrial applications are, however, done using complicated gas mixtures with a variety of ions and neutral species. These plasmas are often electronegative with large concentrations of negative ions. Kinetic modeling for all the species, e.g., by solving the Boltzmann equation or using particle-based techniques, is impractical due to the high computational cost. A hybrid model for multi-frequency CCPs is described in this paper where the electrons are modeled as particles (using the particle-in-cell technique) while the ions and neutral species are treated as a fluid. The equations governing the kinetics of electron pseudo-particles, continuity and momentum equations for ions, Poisson equation for the electric field, and the continuity equations for neutral species are coupled at each time-step, with the time-step typically governed by the light electrons. This model is used to examine plasmas of Ar/CF_4 and $c\text{-}C_4F_8/O_2$ in a parallel plate CCP reactor with a high frequency (40 MHz sinusoidal) and a low frequency (400 kHz tailored voltage waveform) source. A combination of 1-dimensional, 2-dimensional (2D) Cartesian geometry, and 2D axisymmetric cylindrical geometry simulations is used to examine the effect of the low-frequency duty cycle on plasma chemistry and spatial structure of the plasma. The relative flows of the gases in the mixture are varied to understand the dynamics of both electropositive and electronegative discharges. Due to the long electron mean free path (relative to the inter-electrode gap), the plasma spreads out far from the region where the electrons absorb energy. This has major consequences on plasma uniformity in the 2-dimensional model. It is also found that, at a lower duty cycle, the time-averaged sheath at the powered electrode is thinner and the plasma occupies a larger volume. Consequently, for a given HF power and LF voltage, charged and neutral specie densities are higher at a lower duty cycle.

5:40pm **PS+MS-TuA-11 Wafer Edge and Focus Ring Effects on Ion Energy Distributions and Har Features During Plasma Etching Using Low Bias Frequencies***, **Evan Litch,*** University of Michigan*; H. Lee, S. Nam,* Samsung Electronics Co., Inc., Republic of Korea*; M. Kushner,* University of Michigan

Current microelectronic device architectures are continuing to trend towards 3-dimensional devices for higher functionality.A consequence of fabricating 3D devices is the need to plasma etch high aspect ratio (HAR) features of ARs > 100.An example of HAR plasma etching is deep trench isolation (DTI) which is used to isolate 3D logic structures and imaging cells from interfering with each other.These DTI etches are performed in halogen-based mixtures (e.g., HBr/Cl_2) for a Si wafer in inductively coupled plasma (ICP) reactors.

At HARs, the primary etch mechanisms deep within the profile are ion/hot neutral chemical and physical sputtering. In-order to reduce the etch time for these features while maintaining critical dimensions, plasma etching with narrow-angular distributions of incident ions is required.By lowering the bias frequency (100s kHz), ion transit through the sheath is in the thin-sheath limit.(The thin sheath limit refers to ions being able to transit the sheath in a fraction of the RF period.) While this is helpful for ions incident across the majority of the wafer, ion distributions are typically broader and perhaps skewed at these lower frequencies near the edge of the wafer.This is primarily due to charging of the focus ring (FR) due to the longer period exceeding the RC time constant for such charging leading to greater sheath curvature at the edge of the wafer. To maintain critical dimensions of HAR structures at the wafer edge, modifying the FR geometry and/or electrical properties may be necessary to take advantage of lower bias frequencies.

In this work, results from a computational investigation of an ICP using very low bias frequencies for different FR parameters will be discussed.The simulations were conducted with the Hybrid Plasma Equipment Model (HPEM), investigating an ICP sustained in $Ar/O_2/Cl_2$.IEADs, uniformity of fluxes to the wafer and sheath structure for these systems will be discussed.Consequences on etch profiles will also be discussed.

Work was supported by Samsung Electronics Co. and the US National Science Foundation.

6:00pm **PS+MS-TuA-12 Plasma Dynamics During Synchronous RF Pulsing in Dual Frequency Capacitively Coupled Plasma***, **Abhishek Verma,** S. Rauf, K. Bera,* Applied Materials, Inc.*; D. Sydorenko,* University of Alberta Edmonton, Canada*; A. Khrabrov, I. Kaganovich,* Princeton Plasma Physics Laboratory

Low-pressure multi-frequency capacitively coupled plasmas (CCP) are used for numerous etch and deposition applications in the semiconductor industry.Pulsing of the radio-frequency (RF) sources enables control of neutral and charged species in the plasma on a millisecond timescale.In this work, the synchronous (i.e., simultaneous, in-phase) pulsing of both power sources in a dual frequency CCP is examined.To resolve kinetic effects at low gas pressure, modeling has been done using the electrostatic Particle-in-cell/Monte Carlo collision method.The objective of this work is to investigate the sensitivity of the plasma properties to small changes in timing during synchronous pulsing of the 2 RF sources.It is demonstrated that small deviations in the on and off times of the 2 RF sources can lead to major changes in the plasma characteristics. In the simulations, the pulsing parameters (on and off times and ramp rates) are varied and the temporal evolution of plasma characteristics such as electron density,ion energy, ion energy flux, species current at the electrode, and electron temperature are examined.It is demonstrated that if the low-frequency (LF) source is turned on (or off) a few µs before (or after) the high-frequency source, plasma density during the off-state (or on state) undergoes sharp variations due to the frequency coupling effect. Similarly, turning on the LF source with a small delay results in a sharp increase in the plasma density when the HF source is turned on. The study demonstrates the importance of synchronization of RF pulsing in dual frequency CCPs and discusses methods to finetune plasma properties further.

Plasma Science and Technology Division
Room Oregon Ballroom 203-204 - Session PS-TuP
Plasma Science and Technology Poster Session

PS-TuP-1 Sidewall Polymer Removal Challenges by Wet-Etching and the Proposal of High-Density Radical Flux (HDRF™) as a Dry-Etch Solution*, **Sabrina Rosa Ortiz**, J. Tressler, D. Meisner,* Plasma-Therm LLC

Addressing challenges in semiconductor industry often faced by advanced packaging, sensors, and MEMS by promoting cost-effective solutions has been the ultimate challenge throughout the years. This study explores the use of Plasma Dicing technologies such as plasma singulator systems (MDS-100 & MDS-300 SINGULATOR®) to facilitate and promote an increase in die count per wafer establishing a higher production volume with performance. Plasma dicing offers several advantages, including an improved die surface area per wafer promoting an increase in yield per wafer to be processed. The ability to navigate the incorporation of smooth sidewalls, and achievement of street sizes ≤10µm promotes new advantages in the semiconductor industry. Plasma dicing not only removes material in dicing streets by Bosch process implementation but also prevents any physical impact on each die while performed using polymer deposition to facilitate the protection of sidewalls during etching. To enable several applications in the semiconductor industry, including increased device performance, absorption, and electrical conductivity throughout devices, polymer removal and post-etch cleaning are required which has been mainly performed by wet-etching procedures. Wet clean polymer removal has been tested for our standard Plasma-Therm wafer by using both 3M™ Novec™ 7100 Engineered Fluid and EKC265™ separately and analyzed using Energy Dispersive X-Ray Spectroscopy (EDX) to investigate the removal of residues of Carbon and Fluoropolymer. Although successful removal of polymer from the sidewalls was achieved, the amount of liquid required may increase the cost but also the residual waste, preventing proper process control, causing direct damage to the samples due to chemical nature, and handling issues. To address these limitations, we propose the introduction and implementation of dry plasma cleaning solutions that can perform the removal of polymers and photoresist materials without any device damage. At Plasma-Therm, LLC photoresist can be removed by a dry-etching step performed after completion of the Bosch process in a singulator system but also it can be accomplished by using a High-Density Radical Flux (HDRF™) process tool, which not only enables polymer removal but also is designed to perform photoresist strip allowing smoothing of sidewalls for several applications without causing device damage. This tool not only allows us to move from wet-etching by eliminating contamination of samples by particles or residues but also provides a more efficient and effective alternative to wet-etching processes for the removal of polymer and photoresist.

PS-TuP-2 Mass Spectrometric Study of Ar-Diluted Ammonia Borane Plasma for h-BN 2D Film Formation*, **Takeshi Kitajima**, T. Nakano,* National Defense Academy, Japan

Ammonia borane is used as a relatively safe source of BN for the rapid synthesis of h-BN, an important insulating material[1] in the field of two-dimensional electronics[2]. Ammonia borane plasma attracts attention when aiming at high-speed film formation, and analysis of active species in the plasma is necessary. In this study, active species generated from ammonia borane powder irradiated with Ar plasma were analyzed by mass spectrometry.

Parallel plate type 100MHz driven capacitively coupled plasma generated in a high vacuum chamber is used. After placing 0.1 g of ammonia borane (BH_3NH_3) powder on the RF electrode and evacuating, a 10 W glow discharge was formed with an Ar gas flow rate of 30 sccm. A copper sample heated to 800°C was placed downstream, and when BN radicals were supplied at a pressure of 800 Pa, an h-BN atomic film was formed over 30 minutes as shown in the SEM image and Raman spectrum of Fig. 1(a,b). Radical analysis in space was performed with a mass spectrometer at a pressure of 10 Pa. Figure 1(c) shows the difference in the mass spectrum when the plasma is turned on and off. BNH_5(30) is increased by plasma lighting. O_2(32) is produced by plasma decomposition of H_2O(18).

Radicals generated from ammonia borane raw material leading to formation of h-BN atomic film are presumed to be BNH_5 generated by decomposition of BNH_6. Dangling bonds of BNH_5 are thought to generate chemical reaction activity on the substrate.

1 K.H. Lee, et.al. Nano Letters 12, 714 (2012).

2 L. Song, et.al. Nano Letters 10, 3209 (2010).

PS-TuP-3 Plasma Degradation of PTFE Channel in a DBD/Plasma Jet Configuration for Endoscopes Use in Plasma Medicine*, **Juliette Zveny**, T. Serra, A. Remy, A. Nonclercq, J. Deviere, A. Delchambre, F. Reniers,* Université Libre de Bruxelles, Belgium

As plasma medicine is more and more developed and studied for treatment of pathologies such as skin cancer (Terefinkoet al. 2021)or tumorous intestinal cells (Hadefi et al. 2022, Bastin et al. 2020)as well as for decontamination (Deng et al. 2007), the question of the effect of plasma on medical devices rises.

In this work, we are interested in endoscopes and the way plasma could damage them. Indeed, endoscopes working channelscould be used to carry plasma inside a body to a desired target, but the effect of the plasma on the endoscope itself must be investigated. As the surfaces of the channels of endoscopes are coated with PTFE, mainly for its lubricating properties, we studied the plasma-induced degradation of a PTFE tube in a setup that mimics the characteristics of an endoscope device already described in previous work (Bastin et al. 2019). XPS wasused to study the chemical and roughness modifications of the PTFE surface andFTIR was used to study the species ejected to the gas phase.

Given the preliminary nature of current exploratory studies in this field, we employed diverse parameters for our investigation.Different plasma compositions were used: He, He-O_2(3%O_2), He-H_2O, Ar, Ar-O_2(3%O_2), Ar-H_2O, and air withflow rates of 1,5 L/min. The AC electrical power varied from 10 W to 70 W.

Depending on the plasma treatment applied, variable amounts of gaseous fluorinated compounds like $COF_2$and HF have been detected.They result from the degradation of the PTFE polymeric chains by energetic species created in the plasma. In a pure helium plasma, these species are mainly metastable helium and high energy electrons, capable of breaking C-C and C-F bonds, hence creating carbon and fluorine radicals on the surface. Those radicals will then react with surrounding gas species.

The addition of oxygen containing molecules in the gas mixture (H_2O, O_2) creates higher amount of COF_2than without.The amounts observed of those three species is a direct measurement of the ability of the discharge to degrade the PTFE. The $COF_2$is believed to originate directly from the PTFE degradation by atomic oxygen (O^-) (Vandecasteel et al.), whereas the HF should be formed by hydrolysis of COF_2. With pure gases (He and Ar) plasma, some water and air impurities could still introduce oxygen atoms, hydroxyl groups and nitrogen containing groups.

We observed a drastic increase of the concentrations of fluorine species with the Ar-H_2O plasma compared to the He-H_2O plasma.

The XPS analyses show a defluorination of the PTFE surfacethat depends on the plasma composition and power, and in agreement with the production of $COF_2$and HF detected by gas phase IR.

Acknowledgements:

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PS-TuP-4 Effect of Additive Gas on Etch Profile Improvement during Dielectric Etching*, **Hyun Woo Tak**, S. Kim, C. Choi, S. Kim, S. Lee, M. Park, D. Park, D. Kim, ,. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

As the memory device sizes reach scaling limit, the device structures are changing from 2D to 3D device structure. For 3D device structures, it has been known that improving high aspect ratio (HAR) etching process is one of the most important processes in device manufacturing as it determines the density of the devices. To improve the etch properties such as selectivity and etched profiles, various etch techniques have been widely studied including changing process schemes and equipment. But still, changing etch gas is known to be one of the essential solutions in improving plasma etching results. Recently, it has been reported that the etch profiles of HAR etching can be improved by using WF_6 as an additive material, but no detailed results and etch mechanism on the effect of metal-halide containing additive gas have not been reported. Therefore, in this study, the effects of metal-halide containing additives including WF_6 on etching characteristics were investigated. It was found that HAR etch properties can be controlled and improved by using various additive gases containing carbon or fluorine. Therefore, the effect of various additive materials on dielectric etch properties will be reported for next generation HAR etching.

PS-TuP-5 Etch Characteristics IGZO and Chamber Cleaning using CxHyFz Gases*, **Jong Woo Hong**, D. Kim,* Sungkyunkwan University (SKKU), Republic of Korea*; Y. Jeong, H. Cho, D. Jung, Y. Yeo,* Samsung, Republic of Korea*; G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

Indium gallium zinc oxide (IGZO) is used in next-generation semiconductors and displays and requires anisotropic etch profile, fast etch rate, and high mask selectivity.In particular, as IGZO is used for gates in semiconductors and displays, the CD (critical dimension) is getting smaller and smaller, so highly anisotropic etching is crucial. Additionally, it is important to completely clean the etch residue in the chamber after IGZO is etched.In this study, IGZO was etched, and chamber cleaning was performed using various HFC-type gases ($C_xH_yF_z$) in an ICP etcher. The results showed that mixing H and F-based gases was more effective in increasing the etch rate and etch selectivity of IGZO than using them alone. In fact, it is difficult to etch IGZO because zinc is easily etched by halogen gases, but it is found that the gases combined with C, H, and F make it easier to etch zinc. $C_3H_xF_y$ (x+y=8) gas was found to be better than CH_xF_y (x+y=4) gas, as it lowers the binding energy. In addition, by using a H_2/Ar plasma, the etch by-products formed on the chamber sidewall by the etching using HFC-type gases ($C_xH_yF_z$) could be effectivly removed.

PS-TuP-6 Molecular Dynamics Simulation of Vapor-Phase Nucleation of Metal Nanoparticles in a Reactive Plasma Atmosphere*, **Louis Hoffenberg**, D. Graves,* Princeton University*; I. Kaganovich,* Princeton Plasma Physics Laboratory

Metallic nanoparticles (NPs) offer a wide range of applications in electronics, energy, biology, catalysis, and the production of carbon nanomaterials like carbon nanotubes (CNTs). Synthesis of NPs from the vapor phase using plasma methods such as spark discharge generation is promising for industrial scalability. The behavior of nucleating systems in reactive environments, especially reactive *plasma* environments, is understudied. Moreover, charge-induced dipole interactions between ions and neutrals are thought to play a key role in the nucleation, coalescence, and aggregation of NPs in dusty plasmas [1]. Because the lengthscales and timescales associated with vapor-phase NP formation are too small to effectively probe experimentally, a promising alternative is molecular dynamics (MD) simulation. MD can give strong insight into the nanoparticle formation process with its atomic resolution. In this work, we use MD simulations with a reactive forcefield to study iron vapor nucleation in the presence of ions, radicals, and molecular species relevant to the production of CNTs (i.e., H, H_2, C, CH, CH_2, CH_3, CH_4, C_2, C_2H, C_2H_2, and ions). The effects of atomic-scale phenomena on metal vapor nucleation and nanoparticle behavior in a plasma environment will be discussed.

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PS-TuP-7 Elementary Surface Reactions During F- and CF- Based Plasma Cryoetching of Si and SiO_2: A Molecular Dynamics Study*, **Jonathan Romero Cedillo**, G. Cunge, E. Despiau-Pujo,* Univ. Grenoble Alpes, CNRS, LTM, France

Introduced in the early 90s to achieve silicon deep etching, plasma cryoetching consists of using highly reactive plasmas, such as SF_6, to etch materials cooled down to temperatures below -100°C with a high anisotropy. The addition of low 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 fully desorbs when the substrate is brought back to room temperature. Cryogenic processes have the advantage to be polymer-free and clean (no deposition at the reactor walls since passivation layers only form on cooled surfaces), which avoids process drift and makes them suitable to new applications where smooth sidewalls or reduced plasma-induced damage (PID) are required. These characteristics are attractive for porous low-K materials etching in the back-end-of-line (BEOL) of advanced CMOS technology; applications to atomic layer etching (ALE) of conventional materials (Si, Ge, GaN, InP) or emerging 2D materials (graphene, MoS_2) are also envisaged. Even though the understanding and control of plasma cryoetching have been improved over the years, the fundamental mechanisms of the formation and desorption of the SiO_xF_y passivation layer are not well understood. And little is known about the differences between elementary plasma-surface interactions at cryogenic and room temperature processes. In this paper, Molecular Dynamics (MD) simulations are performed to study the interaction between F- and CF- based plasmas with Si and SiO_2 materials. The objective is to study the impact of given plasma parameters (nature, dose, energy of plasma species) on the 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.

PS-TuP-9 Synthesis and Characterization of Antiviral (Doped)-TiO_2 Coatings by an Atmospheric Pressure Dielectric Barrier Discharge*, A. Chauvin,* Université libre de Bruxelles/University of Mons, Belgium*; M. Galais, L. Sauvage, C. Van Lint, A. Op De Beeck,* Université libre de Bruxelles, Belgium*; R. Snyders,* University of Mons, Belgium*; **Francois Reniers**,* Université libre de Bruxelles, Belgium

The recent COVID pandemic raised the necessity to develop strategies to limit the contamination of human populations by viruses. Amongst the routes explored, the development of antiviral and antimicrobial surfaces is an elegant approach as it could represent a long term, passive (no need of chemicals or human action) and sustainable solutions. Although the antimicrobial action of copper surfaces is well known and documented (even in history books), it represents an expensive solution, and the potential toxicity of copper ions for cells can not be neglected. Titanium oxide, in its anatase phase, is known to possess strong oxidative properties, and is used as coating for "self cleaning" or "easy to clean" surfaces. It possesses strong antimicrobial properties. However, the main drawback is that anatase is only active when irradiated with UV light, which prevents the use of such surfaces in interiors. To circumvent this, nitrogen doped TiO2 coatings were developed using an atmospheric pressure dielectric barrier discharge, and exposed to a variety of coronaviruses, including the SarsCOV2.

Coatings were deposited by PACVD from TTIP in an Ar/O2/NH3 discharge (variable O2 and NH3 concentrations) at various substrate temperatures [1], using a new type of heating device [2,3]. They were characterized by XPS, Tauc plot (for the bandgap), and by SEM. Selected coatings were then put in contact with solutions containing coronaviruses and exposed to white light. Negative and positive controls were realized on fully inactive surfaces (plastic), or fully active surfaces (copper), respectively. It is shown that some surfaces exhibit an antiviral activity.

References :

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Acknowledgements :

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PS-TuP-11 Stability Criteria for Radiofrequency Plasmas at Low Pressure**, **Omar Alsaeed**, A. Lietz,* North Carolina State University*; B. Yee, C. Qu, M. Mamunuru, B. Scheiner,* Lam Research Corporation

Uniformity is critical in the plasma processing of semiconductors, and instabilities can give rise to destructive arcing, striations, and plasmoids that can permanently damage equipment or lead to scrapped wafers. The formation of self-organized striations in the direction parallel to the radiofrequency current in low-pressure, high-voltage plasmas has been experimentally reported[1]. We use a fluid description, typically called the nonlocal moment model[2]. The description uses the drift-diffusion approximation and importantly includes the thermoelectric electron energy transport coefficient which proves essential in describing the pattern formation mechanism[3] and is shown to be critical for the evolution of plasmoids in planar capacitively coupled plasmas (CCPs)[4]. The operating conditions under which these striations occur are analyzed in a planar inductively and capacitively coupled argon plasma. This analysis will be extended to Ar with CF_4 gas admixtures. The ionization rates and electron transport coefficients are derived from an electron energy distribution function calculated as a function of the reduced electric field using a multi-term Boltzmann equation solver, MultiBolt[5] [6]. A key assumption of the nonlocal moment model is that transport coefficients and collisions frequencies in the inhomogeneous 1D model are a function of the average energy and bear the same relation as they do in a homogenous 0D Boltzmann equation solution at different values of the reduced electric field[2]. A linear stability analysis is performed to derive a stability criterion on the allowed values of the thermoelectric electron energy transport coefficient as a function of discharge parameters for stable plasma processing. Instability is more likely at higher electron temperatures which leads to the thermoelectric electron energy transport coefficient having positive enough values to destabilize the plasma. The application to practical plasma conditions and system operating parameters, such as pressure and power, is explored to identify process windows.

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PS-TuP-12 Cyclic Isotropic Etching of SiO_2 using NF_3/H_2 Remote Plasma and Methanol Vapor*, **Ji Yeon Lee**, H. Gill, D. Kim, Y. Jang, H. Kwon, G. Kim, D. Kim, D. Kim, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

The wet etchingwhich has been mainly used for the isotropic etching presents challeges in nano-patterns due to the inability to etch the bottom of the pattern or pattern leaning by surface tension. Therefore, the development of a dry etching process for next-generation semiconductor devices is necessary. Currently, the most widely used isotropic dry etching processes of SiO_2 are the HF/NH_3 vapor process and the NF_3/NH_3 plasma process. The conversion of SiO_2 to an ammonium salt such as $(NH_4)_2SiF_6$ occurs in these processes, and the desorption of the reacted compounds is achieved through a heating process. However, the formation of ammonium salts during NH_3-based processes can produce solid powders that may contaminate the substrate and become particle sources in the chamber. Therefore, in this study, gas combinations without NH_3 were used for the cylic dry etching of SiO_2 over Si_3N_4. HF was formed using an NF_3/H_2 remote plasma, and methanol vapors were injected outside the plasma discharge region to eliminate F radicals produced by NF_3 dissociation andinduce spontaneous etching of Si-based materials. Under the optimized conditions, the etching depth per cycle of SiO_2 was about ~13 nm/cycle, and the selectivity with Si_3N_4 was over 50 and the selectivity with Si was over 20. Surface composition and bonding statewere analyzed to confirm surface damage and to investigate the etching mechanism.

PS-TuP-13 Etching Characteristics of Sion Films Using $C_2F_4O/C_2H_2F_2$ with a Low Global Warming Potential*, **Seul Ki Kim**, H. Tak, S. Kim, C. Choi, D. Kim, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

In the semiconductor industry, perfluorocarbon and hydrofluorocarbon gases are widely used as etching gases. However, some currently commercialized gases have a negative impact on the global environment due to their high GWP (global warming potential) values. Therefore, it is essential to replace those with gases with a low GWP and similar characteristics. In this study, evaluation was conducted to replace existing perfluorocarbon and hydrofluorocarbon gases with high GWP, such as CF_4 and CHF_3, with C_2F_4O and $C_2H_2F_2$, which have a relatively high boiling point for easy recovery in a liquid state at room temperature and a low GWP, respectively. In the experiment, SiON (silicon oxynitride) film was etched using $C_2F_4O/C_2H_2F_2$ plasmas in a CCP (capacitively coupled plasma) equipment and the etch rates of PR (photoresist) and SiON films, and PR/SiON selectivity were measured. The etch profiles were observed by SEM (scanning electron microscopy) and XPS (X-ray photoelectron spectroscopy) was used to analyze the surface characteristics of the sample after etching. The results showed that the plasma etching characteristics with mixed gases of $C_2F_4O/C_2H_2F_2$ showed a higher PR/SiON selectivity and anisotropic SiON etching profile compared to those with conventional mixed gases of CF_4/CHF_3. Therefore, selective and anisotropic etching of SiON film masked with PR could be achieved with low global warming gas combination of $C_2F_4O/C_2H_2F_2$. Details of experiments and analysis data will be reported in the presentation.

PS-TuP-14 Isotropic Dry Etching of SiO_2 using NF_3/H_2 Pulsed Remote Plasma and NH_3 Gas Injection*, **DaeWhan Kim**, H. Gil, H. Kwon, D. Kim, Y. Jang, G. Kim, D. Kim, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

These days, for the isotropic etching of nanoscale device fabrication, due to the problems such as pattern collapse to surface tension, difficulty in controlling etch depth, nonuniform etching, etc., dry isotropic etching technology that can replace wet etching is actively investigated. For high selectivity SiO_2 isotropic dry etching, NF3/NH3 remote plasma is generally used to react with SiO_2 to form $(NH_4)_2SiF_6$ which is sublimated and removed through a heating process of 100℃ or higher. However, the process forming $(NH_4)_2SiF_6$ on the surface of a wafer by NF_3/NH_3 remote plasma has the disadvantage of lowering selectivity of SiO_2 over Si or Si_3N_4 because Si and Si_3N_4 are etched by F radicals transported to the wafer form the remote plasma source. in this study, the F radicals transporting to the wafer surface was controlled bt inducing to form HF by discharging NF_3/H_2 in a pulsed remote plasma. $(NH_4)_2SiF_6$ was formed on the surface of SiO_2 by supplying NH_3 to the outside of the plasma discharge region, and then $(NH_4)_2SiF_6$ was removed through heat treatment. through this method, SiO_2 could be selectively etched at a higher etching rate than Si and Si_3N_4. Etching mechanism by the puled remote plasma source was identified through plasma analysis and surface analysis, and possible surface damage during the etching process was also analyzed.

PS-TuP-15 Etched Characteristics of Nanoscale Tio_2 Using C_4F_8-Based and Bcl_3-Based Gases*, **Nam Il Cho**, J. Hong, H. Kim, D. Ji, D. Kim, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

TiO_2 is a material used in various fields such as electronics, optics, environment, etc. For the application to electronic and optical devices, TiO_2 needs to be patterned using reactive ion etching using halogen-based gases. In this study, a TiO_2 masked with ACL pillar pattern was etched using two types of gases such as C_4F_8-based ($C_4F_8/SF_6/Ar$) and BCl_3-based ($BCl_3/CF_4/Ar$), and the effect of etch gas and asynchronous pulsing (separated source power ON time and bias power ON time in a pulse period) on the etch properties such as etch rates, etch selectivity, and aspect ratio dependent etching (ARDE) were investigated. The use of asynchronous pulsing with decreased bias pulsing ratio (high source power ON time and low bias ON time in a pulse period) improved the etch selectivity and ARDE possibly due to the more similar etch environment among different aspect ratio TiO_2 features. The use of BCl_3-based plasma showed higher etch selectivity over ACL compared to C_4F_8-based plasma, however, it showed the lower etch rate and more severe ARDE due to the higher stickiness of Cl compared to F to the sidewall during the etching of high aspect ratio TiO_2.

PS-TuP-16 Study on Atomic Layer Etching of Molybdenum by Formation of $MoCl_x/MoO_xCl_y$*, **Do Seong Pyun**, J. Lee, D. Kim, Y. Jang, D. Kim, H. Kwon, H. Gil, G. Kim, J. Kim, G. Yeom,* Sungkyunkwan University (SKKU), Republic of Korea

Do Seong Pyun[1], Ji Yeon Lee[1],Dae Whan Kim[1], Yun Jong Jang[2], Doo San Kim[2], Hae In Kwon[2], Hong Seong Gil[2], Gyoung Chan Kim[2], Ju Young Kim[2] and Geun Young Yeom[2,3]

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To improve the integrity and performance and to reduce the power consumption of semiconductor, the line width between patterns of interconnects has been shrunk continuously. In order to solve this challange, Cu is currently used as an interconnect material with a barrier material in a damascene structure because it has low resistivity. However, Cu also shows a rapid increase of resistivity in a critical dimension (CD) of less than 10 nm due to long mean free path in addition to a limitation in scaling down due to the requirement of a barrier material. Therefore, the importance of new materials such as Mo, Ru, Co, etc. to substitute Cu has been increased to solve this problem. In this experiment, atomic layer etching (ALE) of Mo has been carried out by using O_2/Cl_2 gases as adsorption process and Ar^+ ion beam for desorption process. By using ICP-type ion beam for desorption step, fine control of the ion energy was possible during the ALE. In the adsorption step, by using O_2/Cl_2 plasmas, the Mo surface was modified into $MoCl_x$ and MoO_xCl_y. In the desorption step, the modified Mo surface such as $MoCl_x$ and MoO_xCl_y was removed using an Ar^+ ion beam. After the ALE process, physical and chemical analysis of the Mo surface was performed using X-ray photoelectron spectroscopy (XPS), atomic force microscope (AFM), etc.

PS-TuP-17 Modeling the Impact of Electronegativity in Capacitively Coupled Argon/Oxygen Discharges with Tailored Voltage Waveforms*, **Sk Azmaeen Bin Amir**, S. Zulqarnain,* North Carolina State University*; J. Prager, T. Ziemba,* Eagle Harbor Technologies*; A. Lietz,* North Carolina State University

Recent developments in power supply technology have made a greater variety of custom waveforms achievable at a scale relevant to semiconductor processing. These custom waveforms provide additional degrees of freedom that can be used to control the ion energy distributions. Dual-frequency capacitively coupled plasmas (CCPs) are often used with a sinusoidal high frequency to generate the plasma and a low-frequency custom waveform to accelerate the ions. Many etching processes use electronegative gases, introducing negative ions which have much lower mobility than electrons and altering the plasma dynamics and sheath behavior.

In this work, we explore the impact of oxygen and the resulting negative ions on the plasma dynamics and the control of the ion energy distribution for dual-frequency CCPs. The focus is on regimes of interest for atomic layer etching (ALE), where the desired ion energy is relatively low (< 100 eV), but must be more precisely controlled. EDIPIC, a particle-in-cell Monte Carlo Collision (PIC-MCC) model, is used to model the plasma in a one-dimensional simulation. A high-frequency (60 MHz) sinusoidal voltage is applied to the upper electrode, and the tailored voltage waveform is applied to the lower electrode at 400 kHz. In this case, the tailored waveform is a triangular positive pulse, with a negative voltage applied in the interpulse period.

The changing plasma dynamics with the varying Ar/O_2 mixtures will be discussed, as well as the impact of the amplitude of the custom waveform. Variations in the waveform, such as the duration of the positive pulse and the magnitude of the negative voltage, may also be explored. The impact on the ion angular and energy distribution, as well as the electric field dynamics in the sheath during the pulse and the role of secondary electron emission, are discussed. In particular, narrow ion energy distributions with a tunable energy are desirable for ALE, with a minimum flux of high energy ions, as these may cause etching that is not self-limiting and destroy the atomic precision.

PS-TuP-18 Kinetic Modeling of Dual-Frequency Capacitively Coupled Argon Discharges Using Tailored Voltage Waveforms*, **Syed M. Zulqarnain**,* North Carolina State University*; J. Prager, T. Ziemba,* Eagle Harbor Technologies*; A. Lietz,* North Carolina State University

As microelectronics technologies become more advanced, high aspect ratio (HAR) etching has become more challenging in recent years. In this work, plasma simulations are used to better understand industrial capacitively coupled plasmas (CCPs) with the goal of controlling ion energies and ion-radical flux ratios using tailored voltage waveforms. The use of a dual-frequency CCP enables high-quality HAR etching by controlling the ion energy and angular distributions. A regime in which ion flux and energy can be more independently controlled is accessed by applying two different frequencies of applied voltage, and tailoring the voltage waveforms can control ion energy and angular distributions. To achieve narrow ion energy and angular distributions, high voltages and low pressures are typically applied. As a result, fluid and hybrid models become inaccurate, and a kinetic approach is required. We investigate the dynamics of low-pressure (7 mTorr) dual-frequency argon plasmas in a 5 cm gap between electrodes using EDIPIC, a Monte Carlo collision-based particle-in-cell (PIC/MCC) simulation. In this work, we introduce the electrical asymmetry effect by tailoring voltage waveforms at the lower electrode (i.e., the wafer). The triangular pulsed tailored voltage waveform of low frequency (400 kHz) is applied to the lower electrode and sinusoidal high frequency (60 MHz) on the upper electrode. The effects of changing the peak-to-peak voltage of the driving voltage waveforms on the ion average energy, ion velocity, and secondary electron yields at the surface of the electrode are discussed. We found that increasing the amplitude of the low-frequency waveforms (100-1000 V) resulted in a tens of eV increase in the average ion energy in bulk regions and a significant increase in ion energy reaching the electrode surface (100-500 eV). Conversely, increasing the peak-to-peak voltage of high-frequency waveforms led to an increased density of bulk plasma but did not significantly change the average ion energy. Furthermore, inclusion of secondary electron emissions (SEE), using energy-dependent SEE yields, resulted in increased electron collisions with the electrodes due to the low-energy electrons emitted from the electrodes. Additionally, during the positive pulse from the low-frequency voltage waveform, electrons only collided with the low-frequency electrode with a slight decrease in ion collisions, which springs back as the positive cycle relaxes.

PS-TuP-19 Patterning of Magnetic Tunnel Junction (MTJ) using RF-biased Reactive Ion Beam Etching*, **Kyoung Chan Kim**, D. Kim, Y. Jang, H. Gil, H. Kwon, J. Kim, G. Yeom,* Sungkyunkwan University, Republic of Korea

Materials such as CoFeB and MgO are used in the Magnetic Tunnel Junction (MTJ) layer of MRAM devices. These materials are mostly used to make small-sized MRAM devices, and ion beam etching (IBE) is used to etch these materials. However, when using the ion beam etching method is used to etch the MTJ layer, hard mask materials or/and materials in the MTJ layer are also etched, leading to the re-deposition of byproducts on the side walls between nano-sized patterns as well as problems with non-vertical etching. To remove these problems, the MTJ layer of the MRAM device is generally etched at a slant angle by tilting the substrate from the ion beam to remove the redeposited layer on the side of the MTJ structure. However, as the distance between the MTJ structures is decreased to nanoscale, it is difficult to tilt the substrate for the removal of the redeposited sidewall byproducts due to the narrow width of the nanoscale patterns. To solve these issues, in this study, H_2/NH_3 reactive ion etching with RF biasing was introduced to etch MTJ layer without tilting the substrate. The MTJ layer was etched through an RF-biased ion beam, and the etch profile, sidewall re-deposition, and etch characteristics were compared with a general reactive ion beam.

PS-TuP-21 Production of Argon Metastable Species in an Electron Beam Generated Plasma*, **Vighneswara Siva Santosh Kumar Kondeti**, N. Chopra, S. Yatom, Y. Raitses,* Princeton University Plasma Physics Lab

Electron beam (e-beam) generated plasmas can produce desirable species for material processing applications by leveraging control of electron energy, while simultaneously maintaining a low electron temperature.[1] In particular, e-beam generated plasmas can be used to produce low energy ions in the periphery of the primary electron beam.[2] This production is enabled by the presence of metastable species in the discharge periphery. In this work, we measured the absolute density of argon ($1s_5$) metastable density in an e-beam generated ExB secondary electron emission plasma source by laser induced fluorescence. We used a Langmuir probe to obtain the electron temperature and density. The measured electron density and Ar($1s_5$) densities were on the order of 10^{16} m^{-3}, while the electron temperature was less than 1eV. The electron density and the Ar($1s_5$) density reduced, while the electron temperature remained constant as a function of distance from the center of the discharge. A one-dimensional continuity equation model showed that there is continuous production of argon metastables even outside the core plasma region. Two distinct regions were identified in the spatial profile of Ar($1s_5$) level inside and outside the core plasma region. These results suggest that there is an additional source of production of Ar($1s_5$) in the core of the plasma in addition to the direct excitation by electrons from the ground state of argon.

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PS-TuP-22 Effect of Plasma Nitrided Layer on the Deflection of Biopsy Needles*, **Hideaki Kuwabara**, T. Yamauchi, P. Abraha,* Meijo University, Japan

Biopsy needle deflection refers to the bending or flexing behavior exhibited by biopsy needles when subjected to external forces during medical procedures. The extent of deflection is influenced by various factors, including needle diameter, length, material, geometry, and applied forces. The addition of a nitride layer, such as titanium nitride (TiN) or silicon nitride (Si3N4), has been reported to alter material properties, such as modulus of elasticity and hardness, impacting the deflection characteristics of biopsy needles. The objective of this research is to treat biopsy needles in an electron beam-induced plasma and diffuse neutral species of nitrogen into the needle surface creating a nitrided layer and investigating its effect on the deflection of biopsy needles. Both experimental testing and finite element analysis (FEA) are utilized in this study.In our experiments, we used neutral nitrogen species from electron beam-induced plasma to diffuse into the stainless steel surface of the biopsy needle, resulting in the formation of the nitrided layer. This process did not involve adding any material to the needle's surface. Additionally, FEA was employed to create a virtual model and analyze the deflection behavior of the biopsy needles under different loading scenarios. The results of our parametric studies, focusing on the impact of nitrided layer thickness on needle deflection, will be presented. These findings will be compared to the experimental testing conducted using a custom-designed setup. By combining experimental and numerical approaches, we aim to gain a comprehensive understanding of the effects of the nitride layer on biopsy needle deflection.

PS-TuP-24 Understanding 3D Grayscale Pattern Transfer: A Plasma Etching Parametric Study for Optoelectronic Devices*, **Assia SELMOUNI**, A. TAVERNIER, A. WARSONO, S. BERARD-BERGERY, N. POSSEME,* Univ. Grenoble Alpes, CEA, Leti, France

The latest promising optoelectronic devices require increasingly complex three-dimensional structures made of specific materials that meet optical, mechanical and ageing requirements. These structures are diverse, for instance: microlenses are needed for image sensing devices in the visible and infrared range [1] while multi-height structures are used in diffractive optics [2]. In this study, these different shapes are patterned in a photoresist layer before being transferred into a non-photosensitive polymer layer by plasma etching. This can cause profile deformation and roughness that may affect device performances.

The experimental setup consists of a low contrast photoresist patterned using Grayscale I-Line lithography [3]. This innovative technique uses a binary mask to allow spatial variation of the light intensity transmitted on the resist surface during the exposure step. Exposing a low contrast resist at different doses results in different thicknesses in the resist film. This allows industrial production of various 3D shapes through a single lithography step. The resist structures are transferred into a non-photosensitive polymer layer using CF_4 chemistry in a 300 mm Capacitively Coupled Plasma (CCP) industrial chamber (Tokyo Electron Vigus™). Samples are characterized using ellipsometry, X-ray Photoelectron Spectroscopy (XPS), 2D and 3D Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy Energy-Dispersive X-ray spectroscopy (TEM EDX).

To understand the impact of plasma etching on roughness and profile deformation, a parametric study is conducted focusing on multi height and microlens structures.

First, we propose etching mechanisms based on the variation of RF power, pressure and plasma chemistry. For instance, our study revealed that increasing high frequency power led to a rougher surface and shape deformation of microlenses as shown by SEM images displayed in figure 1. XPS analysis on etched blanket wafers show a flurorocarbon layer with significant increase in fluorine content at high power. TEM EDX and 3D AFM analysis will also be discussed to support proposed etching mechanism.

Finally, a second part presents means for process optimisation to achieve smooth and conform shapes. For example, chuck temperature increase during microlens etching, illustrated through SEM images in figure 2, has proved to be a simple way to limit edge roughness without significant shape deformation.

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PS-TuP-25 Monocrystalline III-Nitride Films Grown on Sapphire Substrates at 200 °C via Hollow-Cathode Nitrogen Plasmas*, **Narmin Ibrahimli**, I. Saidjafarzoda, A. Mohammed, N. Biyikli,* University of Connecticut

Research efforts on low-temperature (T < 300 ℃) synthesis of crystalline GaN thin films using plasma-assisted ALD utilized various reactor configurations featuring different plasma sources. While our early GaN growth experiments using quartz-based ICP sources resulted in nanocrystalline/amorphous films with elevated oxygen impurities, stainless-steel based hollow-cathode plasma sources revealed polycrystalline GaN films on Si(100) and sapphire substrates. Upon further modification of the hollow-cathode plasma source and reactor chamber design, in this work, we share our experimental findings on the epitaxial growth efforts of GaN,AlN, and InN using hollow-cathode plasma-assisted ALD (HCP-ALD) at 200 ℃.

The films were deposited using metal-alkyl precursors (triethylgallium, trimethylaluminum, trimethylindium) and various nitrogen plasmas (N2/H2, N2-only, N2/Ar, and N2/H2/Ar) at 200 °C substrate temperature and 50 – 150 W RF-power range. In-situAr-plasma annealing cycles were also employed and tested for the binary III-nitride films to enhance the surface crystallization process. In-situellipsometry and optical emission spectroscopy (OES) were employed to monitor the surface ligand-exchange reactions, plasma surface interactions, and reaction byproducts in real-time. Ex-situspectroscopic ellipsometry measurements revealed the growth-per-cycle (GPC) and optical properties of the III-nitride films. When compared to reference films grown on Si(100) substrates, GPC values obtained for III-nitride films on sapphire substrates showed a notable increase. For GaN samples, grazing-incidence XRD (GIXRD) measurements revealed single-phase hexagonal polycrystalline films on Si(100) substrates while GaN/sapphire samples exhibited no crystal peaks at all. Rocking curve XRD scans displayed a strong single (002) peak, confirming the monocrystalline epitaxial character of the synthesized GaN films on sapphire substrates. We attribute this significant improvement in crystal quality to the synergistic impact of a customized HCP-ALD reactor, large-diameter third-generation hollow-cathode plasma source, and optimized growth conditions (plasma gas mixture, rf-power). With further improvement in film properties, we aim to achieve device-quality electrical properties that can be used for logic, memory, power, and sensing applications.

PS-TuP-26 Plasma Delayering for Non-Selective Precision Etching*, **Leonid Miroshnik**, S. Han,* University of New Mexico*; T. Stevens, J. Duree, R. Shul, C. Nakakura,* Sandia National Laboratories

For defect and reliability analysis of microdevices, we have begun investigating precision, non-selective delayering of microdevices where all materials are etched ideally at the same rate, resulting in a planar surface. The desired etch uniformity and precision over the wafer exceed what can be achieved by chemical etching and/or chemical mechanical planarization. In this poster, we will share preliminary results from methyl-acetate and ethyl-acetate-based plasmas in which we can relatively retard the etch rate of dielectric films compared to metal exposed to the same plasma. The surface analysis by spectroscopic ellipsometry and x-ray photoelectron spectroscopy suggests that the polymer films on dielectric and conductor materials are different in nature and likely responsible for relatively retarding or accelerating the etch rate for non-selective delayering.

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**PS-TuP-27 Ion Energy Control in a Capacitively Coupled Plasma with a High Voltage Custom Waveform Bias*, Timothy Ziemba*, *J. Prager, J. Perry, K. Muggli,* Eagle Harbor Technologies, Inc.

Producing high-aspect-ratio (HAR) features with plasma etching is becoming increasingly important as the market demands solid-state non-volatile memory storage. In order to minimize bowing and twisting defects in HAR features, precision control of the ion energy distribution (IED) is required. Eagle Harbor Technologies (EHT), Inc. has previously developed a Rapid Capacitor Charger power system that can charge capacitance to high voltage in tens of nanoseconds and operate at 400 kHz. In this work, EHT is investigating ion energy control with these high-voltage custom waveforms. The experimental test chamber includes a 60 MHz capacitively coupled plasma source and a pedestal that can be biased using the Rapid Capacitor Charger waveforms. EHT will present the chamber modifications, retarding field energy analyzer details, and IED measurements. Based on these measurements, the next steps will be discussed.

PS-TuP-28 Cryogenic Aspect Ratio Etching of SiO_2 at $CF_4/H_2/Ar$ Plasma in a Cryogenic Reactive Ion Etch System*, H. Kwon,* ***In Young Bang****, J. Kim, H. Kim, S. Lim, S. Kim, S. Jo, J. Kim, W. Kim, G. Shin, G. Kwon,* Kwangwoon University, Republic of Korea

In the manufacturing processes of 3D NAND, the high aspect ratio contact (HARC) etching process, which is one of the most critical steps, has encountered a significant challenge. HARC, typically performed at room temperature, has become increasingly difficult to achieve the desired high aspect ratio while maintaining high productivity. This challenge is expected to become harder when considering devices with highly stacked alternating layers of silicon-containing materials, such as SiO_2 and SiN. Therefore, cryogenic HARC technology has emerged as a promising solution to overcome this challenge, as it offers advantages in terms of productivity and better etch profile. Consequently, we conducted cryogenic aspect ratio etching of SiO_2 at $CF_4/H_2/Ar$ plasma in a cryogenic reactive ion etch system. Overall, our results revealed that cryogenic aspect ratio etching of SiO_2 showed a higher etch rate and a higher aspect ratio under the experimental conditions. With these conditions, we conducted the cryogenic aspect ratio contact etching of SiO_2 for the comparison with the etching of SiO_2 at RT as well.

PS-TuP-29 in-Situ Electron Density Measurement in Inductively Coupled Plasma Using Microwave Reflectometer*, Jae Hyeon Kim*, *W. Kim, G. Shin, H. Kwon, J. Kim, I. Bang, S. Lim, H. Kim, S. Kim, S. Jo, G. Kwon,* Kwangwoon University, Republic of Korea, Korea (Democratic People's Republic of)

Low temperature plasma has been widely used in semiconductor manufacturing process. The characteristics of low temperature plasma that are important in semiconductor manufacturing include electron density, electron temperature and electron energy distribution. Specifically, electron density is important to understand plasma physics and plasma process. The electron density is commonly measured using a Langmuir probe. The probe inserts a tip into plasma and voltage is applied to the probe. Charged particles in plasma move to the probe and current generated by the movement is measured to determine plasma density. However, the measured signals interfere with radio frequency and plasma perturbation by the probe distorts the plasma characteristics.

In this study, plasma density was measured using microwave reflectometer without plasma perturbation. The microwave signal radiated by Wi-Fi antenna is reflected by the plasma and collected through the antenna. The electron density measured by analyzing a phenomenon arising from the correlation between the microwave and plasma angular frequencies. The plasma angular frequency is derived using the reflection or transmission phenomenon of microwaves, which depends on the refractive index of the plasma. The refractive index of a plasma N is related to the microwave angular frequency ω and the plasma angular frequency wave ω_p, i.e. $N = (1 - \omega_p/\omega)^{1/2}$. The plasma angular frequency depends only on the plasma density as $\omega_p=(n_e e^2/\varepsilon_0 m_e)^{1/2}$. When the microwave frequency is equal to plasma frequency, the refractive index of the plasma becomes zero and the reflection becomes maximum. The S_{11} parameter is calculated by measuring the intensity of the reflected signals on the frequency sweep. The reflectivity was analyzed by measuring the difference between the S_{11} parameter before and after plasma discharge.

In this experiment, 13.56 MHz RF power source was used in a 300 mm inductively coupled plasma chamber. The applied RF power was 200, 400 and 600 W. The intensity of the reflected signal from the plasma was measured using mixer and RMS to DC converter.

PS-TuP-30 Localized Deposition of Coatings Using Immobilized Streamers of a DBD: Interplay between the Electrode Gap and the Precursor Flow on the Coating Chemistry*, Marie Brabant,* Université libre de Bruxelles, Belgium*; A. Demaude, D. Petitjean, F. Reniers,* Université Libre de Bruxelles, Belgium

Deposition of patterned coatings to generate hybrid surface properties often require a multi-step process, such as the use of masks or lithography [1]. We proposed recently a simple scalable method for the deposition of patterned coatings (morphological and chemical contrasts) [2]. As a case study, the deposition of propargyl methacrylate (PMA) based-coatings was realized, as, due to its structure (one double and one triple bond), this molecule allows very fast deposition, and can lead to hydrophobic coatings, without the need of fluorinated atoms. Moreover, we showed that, depending on the deposition conditions, one could obtain hybrid hydrophilic/hydrophobic patterns. In a recent paper, we showed that pulsing the power (in the ms range) leads to more localized filaments, to a global change in the plasma behaviour and to a change in the coating chemistry [3].

In this poster, we investigate the interplay between the interelectrode gap and the precursor gas flow on the overall plasma discharge and on the resulting (localized) coating. The plasma discharge is characterized by a high speed camera, and mass spectrometry, whereas the coating is characterized using micro-XPS and infrared spectroscopy in IRRAS mode. We show that increasing the gap necessitates an overall higher power to sustain the plasma, resulting in a higher voltage (according to Paschen Law) that leads to a global higher electron energy in the filaments. Such higher power injected into the discharge induces surface discharges between the immobilized filaments. In parallel, increasing the precursor gas flow leads to a higher luminosity in the inter-filament space. The coating thickness and chemistry is similarly influenced by the gap and the precursor flow. Increasing the gap and precursor flow lead to an increase in the coating diameter under the filaments but the thickness of the spots decreases when increasing too much gap. A better preservation of the chemical functionalities of the precursor inside the coating deposits is obtained for higher gas flows and low gaps, which is correlated with the mass spectroscopy analysis of the plasma phase. Results are interpreted in terms of the evolution of the Yasuda parameter.

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PS-TuP-31 the Effect of Rf Bias Frequency on the Ion Energy Distribution in Ultra-Low Electron Temperature Plasma*, Chang-Min Lim, M. Kim, J. Park, C. Chung,* 'Department of Electrical Engineering, Hanyang University, Republic of Korea

The ion energy distributions in an ultra-low electron temperature (ULET) plasma ($T_e < 0.5$ eV) are expected as follows: The mean ion energy is closed to V_{dc} since V_p is nearly 0, and the energy dispersion of the ion energy distribution (ΔE_i) is much narrower. In this study, we measured the ion energy distributions in ULET plasma and ICP at bias frequencies of 27.12 MHz and 60 MHz. It is observed that when V_{dc} ranged from 0 to -40 V, the mean ion energy of ULET plasma is slightly greater than Vdc. Furthermore, the ion energy distributions in the ULET plasma have narrower ΔE_i, which is a monoenergetic distribution compared to those in a conventional bias ICP.

PS-TuP-32 Changes in Ion Density and Electron Temperature Over Time Due to Bias Power*, Park Sung-Joon, E. Hyundong, C. Chin-Wook,* Department of Electrical Engineering, Hanyang University, Republic of Korea

In an inductively coupled plasma (ICP), we measured the electron temperature and ion density over time while applying RF bias power. We observed rapid temporal changes on the order of seconds using a higher time resolution probe (approximately 0.2 seconds). The experiment involved adjusting the antenna power and bias power. Additionally, we installed two types of probes for measurement, one at the plasma bulk and the other at the biased electrode. We noticed that density changes occurred very rapidly, within a few seconds, due to the electron charging effect in response to the bias power. Furthermore, the trends in electron temperature and ion density are similar when the RF bias powers are changed at both positions.

PS-TuP-33 On the Method of Dielectric Thickness Measurement by Using Three Frequencies*, **Hyeon ho Nahm, H. Lee, B. Seo, C. Chung,* Department of Electrical Engineering, Hanyang University, Republic of Korea

Optical emission spectroscopy (OES) is a widely used technique for noninvasive plasma measurement. However, the deposition of polymers on the viewport can lead to a reduction in light intensity, even under the same experimental conditions (e.g., pressure, power). It can be useful to measure the thickness of the deposition layer to compensate for the reduction in light intensity.

We applied three different voltages to an electrical probe to obtain deposition layer impedance. In an equivalent circuit model, the plasma sheath can be regarded as a parallel circuit of sheath resistance and sheath capacitance, representing displacement current and conduction current, respectively. The deposition layer can be considered as a dielectric film. By solving three equations derived from three voltages of different frequencies, we calculated the capacitance of the dielectric and determined its thickness.

However, two problems arose. First, due to the voltages applied to the probe, the floating potential shifted, distorting the plasma sheath resistance. Second, a significantly high impedance ratio between the plasma sheath and deposition layer made it challenging to obtain the thickness of the deposition layer. Therefore, we modulated the amplitude of the applied voltages to minimize distortion and decreased the frequencies to increase the dielectric impedance. Consequently, the error in the measured deposition layer thickness could be greatly reduced.

PS-TuP-34 Etching Characteristics of NF_3 and F_3NO at Reactive Ion Etching Plasma for Silicon Oxide*, W. Kim, **Seong Hee Jo**, H. Kwon, G. Shin, J. Kim, I. Bang, S. Lim, J. Kim, H. Kim, S. Kim, G. Kwon,* Kwangwoon University, Republic of Korea

Nitrogen-trifluoride (NF_3) is mainly used as a reactive gas in cleaning and etching process in the semiconductor and display fabrication. However, NF_3 is a greenhouse gas with a high potential for global warming. As regulations related to the green index are getting stronger worldwide, the need for gas to replace NF_3 is increasing.

In this study, an experiment was conducted on F_3NO gas as a gas to replace NF_3. The plasma etching process was similarly diagnosed by RGA and OES, and the etch rate was calculated by measuring the refection. The etch rate of silicon oxide during F_3NO/Ar plasma etching is approximately 94% of that for NF3/Ar plasma etching. The RGA and OES measurements confrmed that more O^+, NO^+, and O_2^+ ions were generated in the F_3NO plasma than in the NF_3 plasma.

PS-TuP-35 Investigation of Transient Phenomena of Electron Heating in Low-Frequency Pulse-Driven Capacitively Coupled Ar Plasmas Using a Particle-in-Cell Simulation*, **Seoi Choi**, H. Lee,* Pusan National University, Republic of Korea

Pulsed capacitive RF plasma is demanded for the semiconductor etching because it mitigates plasma-induced damage. Repeating pulse-on and pulse-off time lowers ion energy and electron temperature compared to a continuous wave plasma, resulting in less wafer damage. This study performed a pulse-driven two-dimensional (2D) particle-in-cell (PIC) simulation parallelized with a graphics processing unit (GPU) to investigate the plasma dynamics for the time duration of ms. We investigated the effects of a 2D electrode structure empowered low-frequency (LF) pulsed voltage added to a high-frequency (HF) sinusoidal wave on the plasma potential, electron density, and electron temperature by varying frequency and pressure conditions. Plasmas diffuse for a sufficiently long afterglow period in the LF pulse and re-ignited from a lower electron density when the pulse is on again. The electron heating mechanisms are reported for the ramp-up and ramp-down phases at different frequencies.

PS-TuP-37 An Arrival Time Difference-Based Elimination Method of Cavity Resonances for Crossing Frequency Determination of the Cutoff Probe*, **Chulhee Cho**, S. Kim, W. Lee,* Chungnam National University, Republic of Korea*; B. Na,* Korea Institute of Fusion Energy, Republic of Korea*; Y. Seol, Y. Lee, I. Seong, W. Jeong, M. Choi, B. Choi, S. Seo, S. You,* Chungnam National University, Republic of Korea

The crossing frequency method of the cutoff probe, which is composed of radiating and detecting tips, has been recently developed for electron density measurement. However, this method faces challenge in accurately deducing electron density due to cavity resonances, which is caused by the standing wave resonance between the chamber wall and the cutoff probe. In this research, we propose an arrival time difference-based elimination method. As the cavity resonance occurs later in time compared to the directly transmitted between two tips, cavity resonance can be eliminated by adjusting the signal detection time. On the contrary with a conventional frequency sweeping system, we established a ns-pulse radiation and detection system, which can convert signals in time domain to that in frequency domain, so-called S_{21} by using Fast Fourier transform. As a result, by adjusting the detection time, the cavity resonance peaks in S_{21} spectrum were eliminated. By using this method, the crossing frequency can be clearly determined under wide range of chamber pressure and plasma density environments. This research not only addresses the challenges associated with high-pressure plasma measurements but also presents a reliable technique for obtaining precise electron density insides a cavity structure such as a vacuum chamber.

PS-TuP-38 A Global Model with Monte Carlo Collision Method in Sheath for Capacitively Coupled Ar Plasma*, **Inho Seong**, S. Kim, Y. Lee, Y. Seol, C. Cho, W. Jeong, M. Choi, B. Choi, S. Seo, W. Lee, S. You,* Chungnam National University, Republic of Korea

In conventional a global model, ion losses have been considered as the average of sheath voltages, without accounting for the ion energy distribution, making it inaccurate. In this research, we propose a global model with Monte Carlo Collision (GM/MCC) method for Ar capacitively coupled plasma (CCP). The input parameters in the GM/MCC are voltage and current waveforms of the powered electrode. Referenced on a 13.56 MHz Ar CCP source, we compared the electron density calculated through the GM/MCC with that measured by the cutoff probe and as a result, the discrepancy ranges from 30% to 70%. Hence, the GM/MCC is a simple-and-accurate model to analyze a conventional CCP source. Besides, the GM/MCC can be employed as a plasma monitoring sensor accompanied with voltage/current probe of the powered electrode in a CCP source.

PS-TuP-39 Control of Radical Density Through Modulation of Electron Energy Probability Function in a Dual-Frequency (2/27.12 MHz) Inductively Coupled Plasma*, **Yeong Jae Jeong**,* Department of Electrical Engineering, Hanyang University, Seoul, Republic of Korea*; U. Jung, C. Chung,* Department of Electrical Engineering, Hanyang University, Republic of Korea

The effects of 2 MHz and 27.12 MHz power on the electron energy probability functions (EEPFs), electron temperature (Te), absorbed power of plasma, and radical density were experimentally investigated in a dual frequency inductively coupled oxygen plasma. The RF powers are simultaneously applied to two parallel connected antennas. The EEPFs are investigated as a function of pressure and power. Experimentally, it was observed that electron heating and the EEPFs change with pressure and driving frequency. Through the effect of each driving frequency on the EEPFs, we achieved control over the radical density. These results have the potential to control radical density by changing the dual frequency RF power.

PS-TuP-40 Effects of a Non-Sinusoidal Rf Field on Multipactor Discharge in a Parallel Plate Geometry*, **Asif Iqbal**, D. Wen, J. Verboncoeur, P. Zhang,* Michigan State University

Multipactor [1] is a nonlinear discharge phenomenon occurring in RF and microwave components and systems in which a high frequency RF field creates an electron avalanche sustained through secondary electron emission [2] from metallic or dielectric surfaces. It can be detrimental to RF devices creating problems [1,3] such as the breakdown of dielectric windows, erosion of metallic structures, melting of internal components, etc. In addition, multipactor can often detune RF systems, cause multi-tone coupling and signal distortion, limit the transmission or delivery of RF power [1,3].

This work presents a study of two-surface multipactor discharge in a parallel plate geometry induced by a non-sinusoidal Gaussian-type RF field waveform [4,5]. We employ 3D electromagnetic Particle in Cell (PIC) simulations using Computer Simulation Technology (CST) Particle Studio [6,7], and Monte Carlo (MC) simulations [6,7] to examine the effects of RF amplitude and the half peak width of the Gaussian-type electric field on multipactor susceptibility and time dependent physics [4-7].

The threshold peak RF voltage and the threshold time-averaged RF power per unit area for multipactor development increase with a Gaussian-type electric field compared to those with a sinusoidal electric field. The threshold peak RF voltage and RF power for multipactor increase as the full width at half maximum and/or half minimum (FWHM) of the Gaussian profile decreases. Expansion of multipactor susceptibility bands is observed compared to the sinusoidal RF operation. A high initial seed current density is found to shrink the multipactor susceptibility bands in the presence of space charge. The effect of space charge on multipactor susceptibility decreases as the FWHM of the Gaussian profile decreases.

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This work was supported by the Air Force of Scientific Research (AFOSR) MURI Grant Nos. FA9550-18-1-0062 and FA9550-21-1-0367.

PS-TuP-41 Field Reversals in High Voltage-Driven Low Pressure Capacitively Coupled Plasmas, ***De-Qi Wen,*** Michigan State University*; J. Krek,* KLA Corporation*; J. Gudmundsson,* University of Iceland*; E. Kawamura, M. Lieberman,* University of California at Berkeley*; P. Zhang, J. Verboncoeur,* Michigan State University

Low pressure capacitively coupled plasmas (CCPs) are widely used in plasma processing, such as etching, sputtering, cleaning. In recent work, we presented the important role of realistic electron-induced secondary electron emission (SEE), metastable atom and photon-induced secondary electrons from electrodes on the plasma density in low pressure capacitive argon discharges at 13.56MHz. Including the surface processes, the plasma density from the kinetic particle-in-cell (PIC) simulations shows good agreement with experimental measurements [Schulenberg et al Plasma Sources Sci. Technol. 30 (2021) 105003] at low pressure (1-10 Pa). In this work, we investigated the high voltage-driven capacitive discharges at low pressure via the validated PIC model and studied the reversed electric field pointing from the electrode towards the bulk plasma. The reversed field is induced by the strong secondary electron emission during the phase of sheath collapse. Especially, we explored the transition behavior of the formation of field reversal as a function of driving voltage amplitude and found the field reversal starts to be formed at around 750 V for CCP with an electrode spacing of 4 cm at 10 mTorr argon and 13.56 MHz. Accordingly, the electron energy distribution function incident on the electrode shows peaks from around 3 eV to 10 eV while spanning the driving voltage from 150V to 2000 V, showing potentially favorable effects in plasma processing where directional electrons are preferred to solely thermal diffusion electrons. The field reversals found at macroscale will also be examined for microplasmas considering a similarity law.

This work was supported by the Air Force Office of Scientific Research (AFOSR) MURI Grant FA9550-21-1-0367 and NSF-DOE Partnership Grant for DE-SC0022078. the Icelandic Research Fund Grant Nos.163086 and 217999, and a gift from the Applied Materials Corporation, AKT Display Division.

Atomic Scale Processing Mini-Symposium
Room A107-109 - Session AP+PS+TF-WeM

Plasma Deposition and ALD Processes for Coatings and Thin Films

Moderators: Silvia Armini, IMEC, Belgium, **Jessica Kachian**, Intel Corporation

8:00am **AP+PS+TF-WeM-1 Recent Progress in Analysis of the Conformality of Films by Atomic Layer Deposition*, Riikka Puurunen,*** Aalto University, Finland **INVITED**

Conformality is a fundamental characteristic of atomic layer deposition (ALD) thin film growth technique. “Conformal” film refers to a film that covers all surfaces of a complex three-dimensional substrate with everywhere the same thickness and properties. ALD - invented independently by two groups in 1960s and 1970s - has since late 1990s been transformational in semiconductor technology. Apart from semiconductors, conformal ALD films find applications and interest in widely varied fields such as microelectromechanical systems, pharmaceutical powder processing, optical coatings, battery technologies and heterogeneous catalysts.

Conformality follows directly from the “ideal ALD” principles: growth of material through the use of repeated separate self-terminating (i.e., saturating and irreversible) gas-solid reactions of at least two compatible reactants on a solid surface. Obtaining conformality in practice is not self-evident, however. Reasons for deviation from conformality are multiple, ranging from mass transport limitations to slow reaction kinetics and various deviations from ideal ALD (e.g., by-product reactivity or a continuous chemical vapor deposition (CVD) component through reactant decomposition or insufficient purging). Incomplete conformality can also be intentional: a saturation profile inside a feature can be exposed, to enable an analysis of kinetic parameters of the reactions.

This invited talk will explore recent progress especially by the author and collaborators in understanding ALD conformality and kinetics, obtained via experiments and simulations. Experiments have been made with the recently commercialized (chipmetrics.com) silicon-based PillarHallTM lateral HAR test chips (channel height ~500 nm) and spherical mesoporous high-surface-area materials (average pore diameter ~10 nm, sphere diameter ~1 mm). Simulations are presented for 1d feature-scale models and optionally a recently developed 3d code for spheres. Two codes are available on GitHub: DReaM-ALD (diffusion-reaction model, DRM) and Machball (ballistic transport-reaction model, BTRM). Often it is assumed that diffusion during an ALD process in HAR features is by Knudsen diffusion and free molecular flow conditions prevail (Kn >>1). If so, a characteristic “fingerprint saturation profile” can be obtained, and the slope method (derived for DRM-ALD-Arts, GitHub) can be used to back-extract the lumped sticking coefficient. When diffusion is in the transition flow (Kn ~1) or continuum flow (Kn<<1), the shape of the saturation profile depends on process conditions and the slope method is not applicable.

8:40am **AP+PS+TF-WeM-3 ALD Temperature Cycling for Uniform Infilling of Macroscopic Nanoporous Solids*, Benjamin Greenberg,*** *K. Anderson, A. Jacobs, J. Wollmershauser, B. Feigelson,* U.S. Naval Research Laboratory

Uniform ALD infilling of macroscopic nanoporous solids with aspect ratio greater than 10^4 can require precursor dose times on the order of 10^3 seconds, at least four orders of magnitude longer than typical dose times for ALD on wafers. For ALD processes based on relatively stable precursors and straightforward chemistries, such as ALD of Al_2O_3 from trimethylaluminum (TMA) and H_2O, very long doses are generally harmless, but for some ALD processes, precursor decomposition and other side reactions are significant concerns. For example, at a deposition temperature of 180 °C, which has been chosen previously for ZnO ALD infilling to ensure rapid removal of H_2O from nanopores during purging,[1] diethylzinc (DEZ) decomposition[2] and surface Zn deethylation[3] may be substantial on the ~10^3 s timescale.

In this work, we investigate the potential of temperature cycling as a route toward rapid yet controlled infilling of macroscopic nanoporous solids. We infill Al_2O_3 nanoparticle compacts of ~1.5 mm thickness and ~100 nm pore size (aspect ratio > 10^4) with ZnO using DEZ and H_2O as precursors, and we cycle the substrate temperature between ~160 °C (during H_2O purges) and ~120 °C (during all other steps). DEZ infiltration is accomplished via static dosing, wherein DEZ vapor is held in the ALD chamber for >10^3 seconds with the pump valve closed so that, in principle, diffusion/reaction and saturation are observable as a rise (due to byproducts) and flattening of the ALD chamber pressure, respectively. The 120/160 °C cyclical-temperature process produces clear saturation signals in the pressure trace, whereas fixed-temperature processes carried out entirely at 120 or 160 °C do not, apparently due to incomplete H_2O removal at 120 °C and DEZ decomposition and/or other side reactions at 160 °C. We use a variety of characterization techniques, including SEM/EDS, XRD, and electrical conductivity measurements, to assess the uniformity and purity of the ZnO infills.

1. A. Cendejas, D. Moher, and E. Thimsen, J. Vac. Sci. Technol. A **39**, 012406 (2021).
2. J. D. Ferguson, A. W. Weimer, and S. M. George, J. Vac. Sci. Technol. A **23**, 118 (2005).
3. T. Weckman and K. Laasonen, J. Phys. Chem. C **122**, 7685 (2018).

9:00am **AP+PS+TF-WeM-4 Plasmonic Plasma Process for Room Temperature Growth of High-quality Ultra-thin Dielectric Films*, Takeshi Kitajima,*** *M. Miyake,* National Defense Academy, Japan*; K. Watanabe,* National defense Academy, Japan*; T. Nakano,* national defense Academy, Japan

Catalytic surface reactions utilizing gold nanoparticle plasmons have been utilized in various applications in recent years.[1] We have applied hot electrons supplied from gold nanoparticles to plasma surface reactions to use them to form high-quality ultrathin dielectric films at room temperature.[2] We focused on the mixed effect of visible light for plasmon excitation and plasma VUV emission and discovered the effect of green light excitation that promotes radical nitriding. Due to the mercury probe measurement and TEM imaging, the film grown have sperior dielectric feature and uniformity with less plasma induced damage in spite of nonuniform formation of gold nanoparticles.

In the growth sequence, Au was vapor-deposited on a SiO_2 / Si (100) substrate in an ultra-high vacuum chamber with an average thickness of 0.4 nm by electron beam deposition to form Au nanoparticles (C) on the surface. A 30 mTorr N_2-inductively coupled plasma was generated in the attached chamber, and the sample was irradiated with N radicals (R) that passed through a 30 line/inch SUS304 single mesh with the configuration shown in Fig. 1 (a) for 5 minutes. A filter and a white LED controlled the wavelength of light (L), and VUV light from N_2 plasma was mixed. The reaction condition consisting of the above is RLC. Figure 1 (b) shows the dielectric characteristics of the SiON film {leakage current and EOT (equivalent oxide film thickness) when 1 V is applied}. In green light suitable for Au plasmons, the hot electrons (~ 4 eV) generated by the deexcitation of plasmons enabled the bond conversion from Si-O to Si-N the ultra-thin SiON shows the same characteristics as the ideal SiON film. By mixing VUV, it is possible to increase the film thickness further and reduce leakage.

Cross-sectional TEM image of SiON film after plasmonic process is shown in Fig. 1 (c). Beneath the Au particle SiON film with wide range of uniformity is confirmed and the single crystal lattice of Si substrate is clearly identified.

From the above, it is considered that the reaction between the adsorbed N radicals and Si proceeded, and a quality SiON film was formed by superimposing the photoelectron emission from the VUV light on the hot electron injection from the gold nanoparticles by green light irradiation.

1 C. Clavero, Nat. Photonics 8, 95 (2014).

2 T. Kitajima, M. Miyake, K. Honda, and T. Nakano, J. Appl. Phys. 127, 243302 (2020).

9:20am **AP+PS+TF-WeM-5 Time Resolved Energy Diagnostics of HiPIMS Discharges With Positive Cathode Reversal*, Zachary Jeckell,*** *T. Choi, M. Hossain, D. Kepelyan, N. Vishnoi,* University of Illinois at Urbana Champaign*; B. Jurczyk,* Starfire Industries*; 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 the Hiden ANALYTICAL PSM probe that can measure the ion energies as well as perform charge to mass (q/m) measurements. This work builds off other diagnostic work done on the chamber such as time resolved electron energy distribution functions from our time resolved Langmuir probe technique, previous work with measuring ion energy distribution functions using the SEMION probe, as well as preliminary measurements taken with the PSM probe. This work was performed on several different target materials such as Ag, Ti, ZnTe, and W. The diagnostic capabilities of the PSM allows for differentiation between the working gas and target material ions which enables us to calculate the ratio of target ions for a given condition. Previous work we have done has 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, by running the PSM with the filament on and a properly set repelling voltage it was possible to get a sense of the neutral energies as well. This required a deconvolution of the energy that the neutrals gain from the ionization from the filament. The goal was to use the results of those experiments to build a framework of understanding and to use that information to deposit better films, such as increasing the hardness of TiN, reducing the resistivity of N doped ZnTe, improving the crystallinity of W films or improving the optical properties of a Ag thin film.

9:40am **AP+PS+TF-WeM-6 Electron-Enhanced ALD of TiO_2, TiN, and TiCN at Low Temperature Using TDMAT Together with O_2 and NH_3 Reactive Background Gas***, Z. Sobell, A. Cavanagh,* ***Steven George,*** University of Colorado Boulder

Electron-enhanced atomic layer deposition (EE-ALD) was utilized for the growth of TiO_2, TiN, and TiCN films at T < 70 °C.Three Ti-based films were grown using sequential exposures of tetrakis(dimethylamido) titanium (TDMAT) precursor and electrons together with a continuous reactive background gas (RBG) (Figure 1). The electrons accelerated across a grid bias of 100 V desorb surface species by electron stimulated desorption.The electrons also dissociate the RBG as they travel to the substrate.The RBGs utilized to tune the film composition were oxygen (O_2) for TiO_2 and ammonia (NH_3) for TiN and TiCN.

TiO_2 EE-ALD was performed at T < 70 °C using TDMAT together with an O_2 RBG at ~1 mTorr. O_2 is believed to be dissociated by the electron beam, creating O radicals that add oxygen to form TiO_2 and remove N and C from the TDMAT precursor. XPS showed no detectable C or N in the TiO_2 films and a slightly O-rich stoichiometry. Oxygen-rich TiO_2 films may be more photochemically active due to bandgap narrowing and could be useful in photocatalysis.

TiN EE-ALD was conducted at T < 70°C using TDMAT together with an NH_3 RBG at a pressure of ~1 mTorr. NH_3 is believed to be dissociated by the electron beam, liberating H and NH_x radicals that facilitate Ti nitridation and C removal from the film. Electron exposures for 20 seconds led to the rapid nucleation of TiN films with purities of > 96% and ultralow resistivities of < 120 μΩ-cm. These films may be useful as diffusion barriers in backend interconnects.

Incomplete C removal resulted from shorter electron exposures during TiN EE-ALD using TDMAT with NH_3 RBG.This carbon residual provides a pathway for the deposition of TiCN, an important amorphous ternary nitride diffusion barrier.TiCN EE-ALD film growth and properties were explored for electron exposure lengths from 20 seconds to 0.5 seconds.Shorter electron exposures led to an increase of the C:Ti ratio from ~0.03 to ~0.33 as measured by x-ray photoelectron spectroscopy (XPS) (Figure 2).Shorter electron exposures also produced a decrease in film density from ~5.3 g/cm^3 to ~3.3 g/cm^3.In addition, shorter electron exposures yielded an increase in the film resistivity from < 120 μΩ-cm to ~2000 μΩ-cm as measured by ex situ spectroscopic ellipsometry (SE).Consequently, the enhanced diffusion barrier properties of TiCN EE-ALD films will be accompanied by higher film resistivities and lower film densities than TiN EE-ALD films.

11:00am **AP+PS+TF-WeM-10 A Non-Violent Approach to Remove SiN:H Surface Impurities (HCl) at Room Temperature***,* ***Tsung-Hsuan Yang****, T. Wang, G. Hwang,* University of Texas at Austin*; P. Ventzek, J. Zhao,* Tokyo Electron America, Inc.

Our research presents a non-violent approach to remove H^+/Cl^- pairs, a common reaction byproduct, after depositing chlorosilane-type Si precursors (such as dichlorosilane, SiH_2Cl_2) on a SiN surface. While previous studies have suggested the use of H radicals in NH_3 and CH_3NH_2 plasma to remove Cl impurities, these methods have limitations in high-aspect-ratio structures. The recombination rate of radicals may be too fast to reach the bottom of the trench, resulting in the accumulation of Cl and possibly the formation of a salt layer that inhibits further film growth. Through first-principles calculations, we propose an alternative solution by introducing polar molecules, such as NH_3, N_2H_4, CH_3NH_2, and $(CH_3)_2NH$. When these polar molecules are dosed onto the surface, they can first abstract the H^+ from the H^+/Cl^- pair to form a complex with Cl^-. Adjacent polar molecules then solvate the complex, forming a stable "microsolvation cluster." This cluster effectively captures Cl^- while weakening the interactions between Cl^- and surface amine groups, providing a pathway for HCl desorption with a lower energy barrier. Our calculations of free energy surface show that when the surface is saturated with CH_3NH_2 molecules, the energy barrier for HCl desorption can be significantly reduced at 300K. Based on these promising findings, we propose a novel and non-aggressive atomic layer deposition (ALD) scheme to grow SiN at low temperatures while achieving a higher growth rate.

11:20am **AP+PS+TF-WeM-11 Influence of Plasma Species on the Growth Kinetics and Properties of Epitaxial InN Films Grown by Plasma-Enhanced Atomic Layer Deposition***,* ***Jeffrey Woodward****, D. Boris,* U.S. Naval Research Laboratory*; M. Johnson,* Huntington Ingalls Industries*; S. Walton,* U.S. Naval Research Laboratory*; S. Rosenberg,* Lockheed Martin Space Advanced Technology Center*; J. Hite, M. Mastro,* U.S. Naval Research Laboratory

The controlled co-delivery of reactive and energetic plasma species during plasma-enhanced atomic layer deposition (PEALD) enables the growth of epitaxial layers at significantly reduced temperatures which are prohibitive to other methods. However, this capability is challenged by the complexity which arises from the reliance on plasma-surface interactions, and it is thus necessary to understand the influence of the plasma properties on the growth kinetics and resultant film properties. Among the III-nitride binary compounds, indium nitride (InN) is particularly well-suited for the investigation of the roles of reactive and energetic plasma species, as high-quality crystalline films can be achieved using trimethylindium (TMI) and a relatively simple N_2/Ar plasma rather than $N_2/Ar/H_2$ or NH_3/Ar plasmas which generate greater varieties of species. This was explored in recent studies of InN PEALD on gallium nitride (GaN) using *in situ* synchrotron x-ray scattering, which revealed that the growth mode is correlated with the relative density of atomic N, while coarsening behavior is influenced by ion flux.[1]

In this work, epitaxial InN films are grown by PEALD on GaN (0001) at approximately 320 °C using TMI and N_2/Ar plasma within various regimes of plasma species generation in order to investigate the influence on the resultant film properties. Optical emission spectroscopy and Langmuir probe measurements are used to correlate the production of atomic N and ions with the N_2 and Ar gas flows into the inductively coupled plasma (ICP) source. The InN films are characterized by atomic force microscopy (AFM), x-ray reflectivity (XRR), high-resolution x-ray diffraction (HRXRD), in-plane grazing incidence diffraction (IP-GID), synchrotron grazing incidence wide-angle x-ray scattering (GIWAXS), and x-ray photoelectron spectroscopy (XPS). The films are found to exhibit wurtzite phase and sixfold rotational symmetry with a clear epitaxial relationship to the GaN. Low fluxes of atomic N are found to promote larger domains, increased crystalline order, and smoother morphology compared to films grown with high atomic N fluxes. For the high atomic N flux condition, increasing ion flux is found to promote a very rough morphology containing large cluster-like features and decreased in-plane crystalline order, but increased out-of-plane crystalline order and a reduction in mosaic twist.

[1] J. M. Woodward *et al*., J. Vac. Sci. Technol. A **40**, 062405 (2022)

11:40am **AP+PS+TF-WeM-12 One Step Synthesis of Patterned Coatings Using Immobilized Filaments in an Atmospheric Pressure Dielectric Barrier Discharge. Effect of Gap and Power Pulsing.***, M. Brabant,* ***Annaëlle Demaude****, D. Petitjean,* Université Libre de Bruxelles, Belgium*; K. Baert, T. Hauffman,* Vrije Universiteit Brussel, Belgium*; M. Gordon,* University of California Santa Barbara*; F. Reniers,* Université Libre de Bruxelles, Belgium

Deposition of patterned coatings to generate hybrid surface properties often require a multi-step process, such as the use of masks or lithography [1]. We proposed recently a simple scalable method for the deposition of patterned coatings (morphological and chemical contrasts) [2]. As a case study, the deposition of propargyl methacrylate (PMA) based-coatings was realized, as, due to its structure (one double and one triple bond), this molecule allows very fast deposition, and can lead to hydrophobic coatings, without the need of fluorinated atoms. Moreover, we showed that, depending on the deposition conditions, one could obtain hybrid hydrophilic/hydrophobic patterns.

To test the flexibility and the limits of the method, we now investigate further this route and try to understand better the effects of the gap between the electrodes and of the pulsed/non pulsed injection of the power. The deposited coating was characterized using μ-XPS, FTIR and contact angle measurements, whereas the discharge was characterized using a high intensity camera, electrical measurements (oscilloscope and Rogowski coil), and mass spectrometry. Due to the DBD configuration, the coating exhibits two distinct areas : the spot (S) area, corresponding to the coating deposited under the filament position, and the between spot (BS) area, corresponding to the coating deposited outside the filament position.

Filaments are immobilized thanks to beads fixed to one of the dielectrics, reducing locally the gap and therefore igniting specifically the discharge at these locations. Here the gap was fixed at 2, 2.5 and 3 mm. it is shown (using a high intensity camera, and electrical measurements) that an increase in gap leads to more energetic discharges inside the filaments. As shown by XPS, this leads to a lower preservation of the precursor structure for the “S”area coating. In parallel, due to higher voltages needed to light up the discharge, surface discharges take place between the filaments leading to subsequent deposition also between the spots located under the filaments.

Pulsing the power (in the ms range) leads to more localized filaments, to a global change in the plasma behavior and to a change in the coating chemistry [3] .

References :

[1]. A. Demaude *et al*., *Langmuir*, 2019, *35* (30), 9677–9683

[2] A. Demaude *et al*., *Advanced Science*. 2022, *9* (15), 2200237

[3] A. Demaude *et al*., *Plasma Chemistry and Plasma Processing*, submitted.

12:00pm **AP+PS+TF-WeM-13 Effect of Bias Pulsed Plasma Enhanced Atomic Layer Deposition for Void-Free SiO_2 Gap-Fill of High Aspect Ratio Trench Structures*, Ye Ji Shin,*** *H. Kim, G. Yeom,* Sungkyunkwan University, Korea

In 3-dimentional (3D) device structures, cells are getting thinner and higher to increase the density of devices which resulted in High Aspect Ratio (HAR) structures. Gap-fill process is one of the processes that could affect the device performance of HAR trench structures. Void and seam are observed after the gap-fill process and they allow penetration of the chemical etchant used in subsequent processes, and which degrades isolation performance and increases leakage currents. To solve this issue, various processes such as thermal ALD processes with inhibitors, plasma enhanced ALD with substrate biasing, etc. have been used but, with increasing the aspect ratio of the structure, it is found to be difficult to fill the gap completely without void or seam in the trench. In this study, bias power with pulsing was introduced to PEALD processes for void and seam free SiO_2 gap-filling. Pulsed bias power with various pulse duty ratio from 30 to 75% were used and compared with continuous wave (CW) bias power and no bias power to identify the effect of bias pulsing. The results showed that, as the bias pulse duty ratio was decreased, void and seam were decreased and disappeared at HAR trench structures even with negative bowing. The pulse biasing with low duty ratio appeared to open the opening of the trench top while the pulse biasing with high duty ratio and CW biasing operation appeared to close the opening of the trench top possibly due to differences in combined effect of ion bombardment flux and deposition. Eventually, void-free SiO_2 gap-fill for HAR trench structures were obtained with bottom-up filling under the pulsed bias conditions. Detailed experimental results and analysis data will be shown in the presentation.

Plasma Science and Technology Division
Room A106 - Session PS-WeM

Exploring Boundaries of Plasma Science (ALL-INVITED SESSION)

Moderators: Michael Gordon, University of California at Santa Barbara, **Mingmei Wang**, Lam Research Corporation

8:00am **PS-WeM-1 Electron Beam Driven Plasmas: Development and Use for Ultra Low T_E Processing*, Scott Walton,*** Naval Research Laboratory **INVITED**

The advantages of plasma-based materials processing techniques are numerous. The capability to rapidly and uniformly modify large areas (> 10^3 cm^2) with high precision is one reason plasmas are widely used in the materials and surface engineering communities. However, with the ever-evolving demand for new materials and single nanometer-scale device dimensions across a variety of applications, some of the limitations of conventional plasma sources are becoming apparent. The lack of process control and excessive ion energies in the development of atomic layer processing strategies are examples.

The Naval Research Laboratory (NRL) has developed a processing system based on an electron beam-generated plasma. Unlike conventional discharges produced by electric fields (DC, RF, microwave, etc.), ionization is driven by a high-energy (~ keV) electron beam, an approach that can overcome many of the problems associated with conventional plasma processing systems. Electron beam-generated plasmas are generally characterized by high charged particle densities (10^{10}- 10^{12} cm^{-3}), low electron temperatures (0.3 - 1.0 eV), and in reactive gas backgrounds, a relatively low radical production rate compared to discharges. These characteristics allow the ability to precisely control the flux of charged and reactive neutrals as well as ion energy at adjacent surfaces. This provides the potential for controllably etching, depositing, and/or engineering the surface chemistry with monolayer precision.

An overview of NRL’s research efforts in developing this technology will be presented, with a focus on source development and operation, plasma characterizations, and how the system can be advantageously applied to the processing of select materials. Examples include graphene, where erosion and damage is a major concern and the etching of semiconductor materials, such as Si, SiN and SiO_2, where the focus is on etch rates and selectivity at low ion energy. This work is supported by the Naval Research Laboratory base program.

8:40am **PS-WeM-3 My Path to AVS Fellow: Non-Volatile Memory Processing from Fundamental Understanding to the Promise of Atomic Layer Etching and Sustainable Etch Precursors*, Eric Joseph,*** IBM T. J. Watson Research Center **INVITED**

Non-volatile memory technologies such as phase change memory (PCM) and magnetoresistive memory (MRAM) have seen various levels of success in manufacturing over the past decade.Intel/Micron’s Optane PCM memory and Everspin’s MRAM are just a few examples of recent products, while in more recent research, these same materials are also being explored as accelerator technologies for AI hardware applications. However, to enable these memory technologies, a significant understanding of plasma processing is required to achieve high fidelity pattern transfer while maintaining device performance. In this talk I will walk through first data highlighting the challenges of material volatility for both PCM and MRAM etching and how process induced modification of the material leads to deleterious device performance.Furthermore, we will review the promise of atomic layer etching in enabling new avenues to address patterning issues for MRAM and PCM and demonstrate how ALE can lead to new opportunities for sustainable future non-volatile memory processing applications.

9:20am **PS-WeM-5 VHF Plasma Enhanced Atomic Layer Deposition of SiN_x using Aminosilane Precursors***, Y. Ji, S. Choi, J. Kang,* Sungkyunkwan University, Republic of Korea*; A. Ellingboe,* Dublin City University, Ireland*; C. Lee,* Merck Korea*; H. Chandra,* EMD Electronics*;* ***Geun Young Yeom***, Sungkyunkwan University, Republic of Korea **INVITED**

In this study, we investigated the plasma enhanced atomic layer deposition (PEALD) of silicon nitride (SiN_x) using the VHF-CCP N_2 plasma and different aminosilane precursors at the process temperature range of 100–300 °C. The combinations of VHF-CCP plasma source instead of conventional HF-CCP plasma source and an adequate aminosilane precursor allowed a high growth rate and high quality films as well as excellent conformality close to 100% at substrate temperature of 300 °C. In addition, when external magnetic field was added during the VHF CCP N_2 plasma generation during the PEALD of SiN_x film, the magnetized VHF CCP N_2 plasma allowed better film quality and higher conformality at low temperature of 200 °C.

11:00am **PS-WeM-10 PSTD 2022 Young Investigator Awardee Talk: Plasma Processing Challenges for Emerging Memory Technology*, Luxherta Buzi*[1]***, IBM Research, T. J. Watson Research Center*; N. Marchack, S. Engelmann, R. Bruce,* IBM Research Division, T.J. Watson Research Center **INVITED**

Continuously shrinking feature size in patterning imposes non-volatile memory processing challenges, particularly for phase change memory (PCM) materials, where damage mitigation is imperative. Optimization of etch process and chemistry in minimizing or eliminating structural or compositional damage is key for the success of this technology. Use of

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[1] **PSTD 2022 Young Investigator Awardee**

halogens is often needed for a better profile control, reduce redeposition, selective metal etching etc., but it can cause structural damage and elemental depletion of PCM materials leading to an increase in the recrystallization time. Ion sputtering with inert gases on the other hand, can cause material re-deposition on the sidewall, poor profile control and worse etch selectivity.

In addition to ion bombardment which is typically responsible for physical sputtering and increased roughness, plasma can generate short wavelength irradiation due to electron-neutral collisions. UV/VUV photons emitted in a plasma can reach high fluxes and thus become important in terms of plasma-surface interaction processes. Elemental depth profiling with ion beam analysis and time resolved laser reflectivity was done to study the phase transition behavior of GST when exposed to different chemistries, temperatures, plasma duration, and various reactor configurations.

Surface oxidation of PCM materials can substantially alter switching properties therefore, in-situ plasma enhanced CVD encapsulation has been viewed as a favorable solution. It is imperative that RIE and encapsulation mitigate damage and oxidation of PCM material during integration. In-situ encapsulation of GST and tuning of plasma parameters, caused controlled SiN film deposition with simultaneous selective etching and damage removal from GeSbTe-based PCM materials.

11:40am **PS-WeM-12 How Can Machine Learning Help Process Development?**, ***Satoshi Hamaguchi***, Osaka University, Japan **INVITED**

The recent development in data science and technology such as machine learning (ML) and artificial intelligence (AI) is now changing the way we perform various tasks, including research and development. Process development for semiconductor manufacturing is so complex that there is much room for improvement in its efficiency by ML and AI. Often one of the major problems in applying ML and AI for process development is the lack or insufficiency of experimental data. One possible remedy is to form “digital twins,”i.e., numerical simulation models of plasmas and plasma-interacting surfaces, and generate a large amount of data that can augment the shortage of experimental data. Even if the simulation results do not agree with experimental observations quantitatively, as long as the simulation data are correlated with experimental observations, such augmented data help us search optimal process conditions and perform a design of experiments. In this presentation, the recent development of data-driven plasma science [1] for low-temperature plasmas and their applications to material processing will be briefly reviewed. Then, more specifically, the prediction of sputtering yields/etch rates of materials by ion beams and the construction of plasma surrogate models will be discussed, which could allow real-time simulation of plasma processing systems for process control and fast survey of optimized process conditions.

[1] R. Anirudh, et al., “2022 Review of Data-Driven Plasma Science” IEEE Trans. Plasma Sci. (2023) to appear/ arXiv:2205.15832

Thin Film Division
Room A105 - Session TF1+PS-WeM
Emerging and Advanced Materials and Processes

Moderators: Subhadra Gupta, University of Alabama, **April Jewell**, Jet Propulsion Laboratory

8:00am **TF1+PS-WeM-1 Modified Reactive Sputter Deposition of Titanium Nitride Thin Films via HIPIMS with Kick-Pulse**, *A. Miceli, D. Santavicca,* ***Stephen Stagon***, University of North Florida **INVITED**

Direct current (DC) and radio frequency (RF) sputtering methods have been commonplace in industry for several decades and widely studied in the literature. Hard films of nitrides, such as titanium nitride (TiN), have been deposited using reactive DC sputtering onto cutting tools and medical devices extensively as well. For these applications, the films require excellent adhesion, high density, and high hardness. High-Power Impulse Magnetron Sputtering (HIPIMS) has emerged over the last several years as a method to produce films with increased density and mechanical properties. Process-structure-property relationships for reactive HIPIMS are not well developed. Additionally, conventional HIPIMS suffers from relatively low deposition rates, which become a challenge or barrier to adoption for applied TiN coatings that are typically greater than several microns in thickness. This work aims to look at increasing this deposition rate while maintaining the beneficial effects of HIPIMS by utilizing the short duration “kick-pulse” in the voltage/current cycle, leading to higher instantaneous deposition rates and increased adatom energy level. TiN films are deposited onto silicon (Si) wafers under varied reactive sputtering conditions, including DC, HIPIMS, and HIPIMS with kick-pulse. Structural characterizations are performed using scanning electron microscopy (SEM) and X-ray diffraction (XRD). Optical and electrical properties of the resulting films are also characterized using reflection UV-Vis spectroscopy and 4-point probe techniques. The deposition rate, morphology, and chemical composition of the films are highly affected by the processing conditions, with the kick-pulse producing significant increase in deposition rate and observed grain size. Further investigation will aim to develop a modified structural zone model to include HIPIMS with and without kick-pulse.

8:40am **TF1+PS-WeM-3 Time-Resolved ALD Reaction Heat**, ***Ashley Bielinski***, *E. Kamphaus, L. Cheng, A. Martinson,* Argonne National Laboratory **INVITED**

Atomic layer deposition (ALD) is a surface synthesis technique that consists of sequential self-limiting surface reactions between molecular precursors and a substrate.Differences in the substrate surface as well as the precursor ligands can have a significant influence on the properties of the deposited film and the formation of interfaces, even within a given material system. ALD processes are often empirically optimized with only a simplified chemical understanding of the surface reactions.While this is sufficient for some applications, emerging technologies such as area-selective ALD and site-selective ALD seek to leverage the chemical selectivity between precursor molecules, inhibitors, and the substrate surface.To better understand and direct ALD surface reactions, we must improve our fundamental understanding of the surface reaction mechanisms and energetics.

Pyroelectric calorimetry enables in situ, time-resolved measurements of the heat generated by ALD surface reactions. We present a pyroelectric calorimeter optimized to operate under standard ALD conditions with resolution down to 0.1 $\mu J/cm^2$ and 50 ns.This process of ALD calorimetry was used to measure the heat generation rates from trimethylaluminum (TMA), tetrakis(dimethylamino)zirconium (TDMAZr) and water to form Al_2O_3 and ZrO_2.The aerial heat generation rates were combined with in situ spectroscopic ellipsometry and ex situ Rutherford backscattering measurements to calculate the reaction thermodynamics on a per atom basis.These results were then compared with computational first principles models as well as calculations of the standard reaction enthalpies.The total measured heat was in good agreement with the standard enthalpies, but the computational models showed greater deviation.Pyroelectric calorimetry provides a unique opportunity to validate and provide benchmarks for computational models, helping to evaluate the accuracy of proposed models and mechanisms.

The heat generation rates were also analyzed to compare reaction kinetics.For example, the water reaction occurred at significantly different speeds on the TMA and TDMAZr saturated surfaces. Due to the high time-resolution, we were able to resolve, for the first time, a multi-step reaction for TDMAZr reacting with hydroxylated ZrO_2. Heat generation rates provide new insight into ALD processes, helping us to untangle the thermodynamics, kinetics, and mechanisms of these heterogenous surface reactions.

9:20am **TF1+PS-WeM-5 Reducing Hysteresis in Atomic Layer Deposited VO_2 Thin Films**, *V. Wheeler,* ***Peter Litwin***, *S. Bennett, M. Currie,* US Naval Research Laboratory

VO_2 is a phase change material that undergoes a first order crystalline phase transition at a critical temperature (T_c = 68°C), resulting in significant changes in intrinsic electrical and optical properties, especially in the infrared. Optical and electrical variations associated with this phase transition are of particular interest as passive and active components of electronic and optoelectronic devices, including RF limiters, thermal regulation, and modulated signaling. Realizing this type of device often requires the integration of thin, conformal VO_2 films with complex, non-planar structures (like metamaterials). Thus, atomic layer deposition (ALD) is an ideal deposition method in these cases.

While ALD is useful for integrating highly uniform and stoichiometric films with dissimilar materials, the low deposition temperature results in amorphous films that do not exhibit the required phase change for device applications. Thin VO_2 films deposited by many methods, including ALD, typically require a post-deposition anneal to induce the crystallization necessary for large, abrupt, usable changes in properties during the phase transition. This anneal can be accomplished in many ways such as a slow traditional anneal in specific partial oxygen environments or using environmentally independent laser processes to rapidly crystallize the film. However, the microstructure and resulting phase change properties are highly dependent on the method of crystallization and can lead to deleterious effects like large hysteresis windows (> 10°C) during heating and cooling through the phase transition of these films. For optimum performance in device applications, the hysteresis needs to be reduced or even eliminated.

In this work, we will discuss developing novel processes towards achieving crystalline ALD VO_2 films and the impact they have on reducing hysteresis, including the introduction of nucleation layers and tailoring of plasma properties during plasma enhanced ALD. As an example, we have found that hysteresis can be reduced to a few degrees using ALD TiO_2 films, independent of crystallinity, phase, or thickness of the TiO_2 film itself, but ALD Al_2O_3 or HfO_2 buffer layers do not impact the hysteresis at all. When possible, we will discuss the possible causes and mechanisms behind hysteretic performance improvements.

9:40am **TF1+PS-WeM-6 Magnetron Sputtering Deposition and Stabilization of the Bismuth Sesquioxide (Bi_2O_3) High-Temperature Equilibrium Phase***, **Sandra E. Rodil,** A. Martinez, O. Depablos-Rivera,* Universidad Nacional Autónoma de Mexico

Bismuth sesquioxide (Bi_2O_3) exhibits a dynamic polymorphism characterized by two thermodynamically stable phases. The first is the monoclinic (α) phase, which remains stable from room temperature (RT) up to 730 °C, while the second is the defect-fluorite cubic (δ) phase, stable above 730 °C and up to the material's melting point (830 °C). Additionally, during the cooling/heating process, two metastable phases (β-tetragonal and γ-bcc) are formed, and their transformation temperature depends on factors such as the cooling rate, ambient conditions (vacuum or air), and oxygen concentration.

The production of the δ-Bi_2O_3 phase as a thin film date back to 1999, when it was first demonstrated using electrodeposition, followed by magnetron sputtering. The crystallographic structure of the films has been analyzed through X-ray diffraction patterns and visible Raman spectra. However, caution must be exercised when interpreting Raman spectra, as the broadband at 600 cm^{-1} associated with the defect-fluorite cubic (δ) phase can also be observed in other phases. To address this issue, we critically analyzed the assignments provided in the literature for this broad Raman mode and proposed an alternative explanation consistent with its observation in all films. Our proposal attributes the 600 cm^{-1} band to the presence of residual-weakly bonded $[BiO_n]$ units located at the grain boundaries of the nanocrystalline films. This band is not exclusive to the defective fluorite cubic structure of Bi_2O_3. Interestingly, we found a similar signal in the Raman spectra of the Bi_4O_7 phase, which had not been reported before, suggesting possible incorrect assignments to the δ-phase. We employed a density functional approximation of the Bi_4O_7 molecular structure to gain further insights to calculate the Raman active bands. The theoretical estimations showed excellent agreement with experimental data, reinforcing the validity of our proposed explanation.

Finally, our investigations revealed that doping with heterovalent ions allows for stabilizing films exhibiting the δ-Bi_2O_3 phase within a temperature range from room temperature to 600 °C. This exciting discovery opens new possibilities for using these films as ionic conductors, potentially finding applications in various technological fields.

Plasma Science and Technology Division
Room A106 - Session PS1+AS-WeA

Plasma Chemistry, Catalysis and Applications for the Environment and Sustainability

Moderators: Michael Gordon, University of California at Santa Barbara, **Kenji Ishikawa**, Nagoya University

2:20pm **PS1+AS-WeA-1 Synthesis of Hydrogen and Structural Carbon Materials from Methane Using Radiofrequency Nonequilibrium Plasma***, **Elijah Thimsen**,* Washington University in St. Louis **INVITED**

The production of hydrogen from methane by dehydrogenation of carbon is up to 6 times less energy intensive than water splitting and involves no intrinsic CO_2 byproduct. If hydrogen were used as a fuel at societal scale, billions of tons per year of carbon co-product would be produced. Steel and concrete are manufactured goods that are used at a scale of billions of tons per year, for structural applications. To avoid massive waste, the carbon co-product from hydrogen production could be used in structural applications, perhaps to displace concrete and steel. In this talk, I will focus on the use of radiofrequency capacitively coupled electrodeless discharges in a tubular flow-through configuration for methane dissociation. The plasma step of our process currently operates in the pressure range from 0.025 to 0.125 bar, and the goal is to synthesize an equimolar mixture of C_2H_2 + HCN from CH_4 + N_2. The mixture of C_2H_2 + HCN is an intermediate between the plasma and a downstream thermocatalytic reactor. The downstream thermocatalytic reactor synthesizes acrylonitrile, which is a critical precursor to structural carbon fiber, from the C_2H_2 + HCN mixture that elutes from the plasma. Remarkably, the plasma synthesis of C_2H_2 + HCN from CH_4 + N_2 is highly selective. We have been able to achieve >95% methane conversion with >90% nominal yield of a stoichiometric mixture of C_2H_2 + HCN. Downstream of the plasma in the thermocatalytic reactor, selectivity is somewhat challenging, but yields of the desired acrylonitrile in the range from 20 to 40% based on C_2H_2 + HCN have been achieved at the time of writing. For technoeconomic context, the results will be compared against the industrial standard SOHIO ammoxidation process for the synthesis of acrylonitrile. Furthermore, I will take this opportunity to reflect on the prospect of running a gas-phase synthesis process at a reduced pressure of approximately 0.1 bar and a production rate of minimum 10,000 tons per year.

3:00pm **PS1+AS-WeA-3 Kinetics of Hydrocarbon Decomposition in Plasmas Operating Up to 5 bar***, **Norleakvisoth Lim**, M. Gordon,* University of California at Santa Barbara

Hydrogen is a promising energy carrier to replace fossil fuels in response to the rise in global warming from CO_2 greenhouse gas emissions. Unfortunately, hydrogen is predominantly produced industrially via steam methane reforming, where the reaction itself and process heating requirements generate CO_2. Direct methane pyrolysis for hydrogen generation has recently regained interest due to its potential for net zero CO_2 emission. This process requires high operating temperatures due to high C–H bond energies (4.55 eV for methane) and collateral issues such as catalyst poisoning via coking. As an alternative, plasma–based conversion of methane to hydrogen and carbon (as well as other hydrocarbons) is an attractive process due to its potential ability to generate reactive species that can overcome activation barriers, improve CH_4 conversion, and use less energy than required for water electrolysis. Thus, understanding the mechanism and kinetics of CH_4 dissociation in thermal and non-thermal plasmas is a crucial step to evaluate the efficacy of plasma conversion of hydrocarbons.

This talk will highlight conversion, selectivity, and kinetics measurements of plasma-based decomposition of CH_4 and C_2 hydrocarbons using various plasma excitation schemes (AC arc and nanopulse) at pressures up to 5 bar in a batch configuration with different electrode gaps. H_2 selectivities up to 80% were observed in AC-excited thermal arcs, with specific energy requirements (SER) decreasing with increasing pressure to ~300 kJ/mol CH_4. In general, plasma-based conversion has fast rates and seems to not encounter the typical pseudo-equilibrium limit, i.e., due to hydrocracking of products back to CH_4, that is typically encountered with thermal pyrolysis of CH_4 at temperatures from 900-1300 °C. Other CH_4 decomposition products (<30 mol %) observed include C_2H_2 and C_2H_4, and plasma-decomposition of C_2H_4 was also studied. Product distribution with pressure and various CH_4:H_2 ratios will be discussed, along with characterization and management of the solid C product. This work suggests that higher operating pressures can potentially improve the efficiency of plasma conversion of hydrocarbons.

3:20pm **PS1+AS-WeA-4 Plasma Pyrolysis of Liquid Hydrocarbons to Produce H_2 and Solid Carbon***, N. Lim, **Michael Gordon**,* University of California at Santa Barbara

Understanding and engineering reacting systems that enable 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 the energy density of liquids to produce clean H_2 and solid carbon without CO_2, could be game changing. In this work, we investigate the potential of directly exciting plasmas in liquid hydrocarbons to create unique, multi-phase reaction environments, i.e., environments where plasma (ionized gas), gaseous H_2, gaseous and liquid hydrocarbons, and solid carbon are all present simultaneously, to produce clean H_2 and carbon. The ultimate target is direct transformation of liquid hydrocarbons to gaseous H_2 and solid, easy-to-separate carbon using electricity that can be provided from any source and/or points of use.

As a proof of concept, we have recently demonstrated that it is indeed possible to strike and sustain plasma discharges in liquid hydrocarbons such as hexane, to simultaneously generate gaseous H_2 and solid carbon at high rates. Significant H_2 generation along with small amounts of other light hydrocarbons was observed. Initial, un-optimized experiments have been promising: a single pin-to-pin AC-driven, high voltage plasma discharge running at ~18 W (estimated from the plasma current-voltage transient) in liquid hexane produced ~80-100 sccm of H_2, which is equivalent to an energetic input of ~ 240 kJ/mol H_2 = 33 kW*hr/kg H_2. This energy requirement for an un-optimized system is considerably lower than for water electrolysis (40 kW*hr/kg H_2 (theoretical), but 60 kW*hr/kg H_2 in practice), and promisingly competitive with other plasma-based hydrocarbon conversion processes. Preliminary experiments show that (i) the plasma is not simply vaporizing the liquid - so the system's specific energy input (SEI) is preferentially driving hydrocarbon cracking; (ii) small amounts of C_2-C_4 products are also produced, where selectivity depends on plasma operating conditions; and (iii) the liquid hydrocarbon phase immediately turns yellow and then quickly black due to rapid formation of suspended carbon particulates. Hydrocarbon conversion, reaction rates, and characterization of the gas (MS), liquid (GC/MS), and solid (C/H analysis, SEM, Raman) phase products as a function of plasma operating conditions and hydrocarbon source will be discussed.

4:20pm **PS1+AS-WeA-7 Plasma-Surface Interaction in CO_2 Containing Plasmas***, **Olivier Guaitella**, E. Baratte,* Ecole Polytechnique - CNRS, France*; V. Guerra,* Instituto Superior Técnico, Portugal*; D. Sadi, S. Bravo, C. Garcia-Soto,* Ecole Polytechnique - CNRS, France*; T. Silva,* Instituto Superior Técnico, Portugal **INVITED**

The use of Non Thermal Plasmas to convert CO_2 is a very promising way of meeting environmental challenges. However, there are two main obstacles to their use and optimisation:

i) the complexity of the kinetics of these plasmas makes it very difficult to predict their chemical reactivity,

ii) while it is relatively easy to dissociate the CO_2 molecule in a plasma, it is difficult to avoid reverse reaction mechanisms that reduce the energy efficiency of conversion.

To address the first point, complementary experimental set-ups have been developed in this work to enable step-by-step validation of 0D kinetic models including electronic, vibrational and chemical kinetics. This systematic approach relies on discharges as simple as pulsed glow discharge and radiofrequency discharges in batch reactor, monitored with in situ time resolved absorption spectroscopy. Thanks to these studies, models of pure CO_2 but also, CO_2/N_2, CO_2/H_2 and CO_2/CH_4 have been thoroughly validated against a large range of experimental conditions. Once these plasma sources have been well characterized, they can be used to study the fundamental mechanisms of plasma-catalyst interaction. The combination of a cold plasma and a catalyst is indeed the solution most often proposed to overcome reverse reaction processes and improve selectivity and energy efficiency. However, the design of materials truly capable of benefiting from the vibrationally or electronically excited species of the plasma relies on an understanding of these mechanisms.

In addition to plasma-catalysis, new concepts are currently emerging for continuously shifting chemical equilibria in the plasma phase, thereby improving yields.The use of ionic membranes (perovskite or Yttrium

Stabilized Zirconia) or water used as solvent opens up new routes for improving plasma CO_2 conversion processes, but once again raises the question of how these plasmas interact with complex surfaces. Examples of these approaches will be given.

5:00pm **PS1+AS-WeA-9 Study of Plasma-Catalyst Surface Interactions for Methane Dry Reforming***, **Michael Hinshelwood**, G. Oehrlein,* University of Maryland, College Park

Plasma enhanced dry reforming of methane (DRM) at atmospheric pressure is a promising technique for converting greenhouse gases (CH_4 and CO_2) into syngas (H_2 and CO), which can be further used for producing fuels and chemicals. The exact mechanism of enhancement of DRM due to plasma is not fully understood, however plasma-generated reactive species are thought to play an important role. Enhancement in DRM can take the form of increased product formation or reduced carbon coking which can deactivate the catalyst. We use a remote plasma-catalysis setup that enables the study of certain plasma-catalyst interactions by infrared spectroscopic methods [1]. Species adsorbed on the catalyst surface are analyzed in-situ using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), while gas phase products from the interaction are analyzed with Fourier Transform Infrared Spectroscopy (FTIR). The catalyst used is Ni, commonly used for dry reforming reactions, on a SiO_2/Al_2O_3 support. The catalyst is exposed to either Ar/CO_2 or Ar/CH_4 plasma, while other gas mixtures are introduced into the reaction chamber downstream from the plasma. This allows for evaluation of the effect of reaction species specific to either gas. DRIFTS measurements reveal that exposure to CH_4 plasma results in the buildup of CH_2 (2930 cm^{-1}) and CH_3 (2960 cm^{-1}, 2860 cm^{-1}) containing species on the catalyst surface. Build-up of such species also occurs during catalyst coking and deactivation. Exposure to CH_4/Ar plasma may be able to replicate coking at low temperatures where reaction rates are lower and surface mechanisms easier to resolve. If CH_n (n=1-3) buildup at room temperature is followed by Ar plasma exposure, the CH_2 and CH_3 surface coverages are reduced at similar and temporally decreasing rates, but not eliminated. Comparing the effect of Ar plasma and Ar/CO_2 plasma on surface CH_n, is used to evaluate the potential of Ar/CO_2 plasma to reduce catalytic deactivation during dry reforming. Our setup allows for variation of the catalyst temperature to test the impact of plasma on DRM at various degrees of catalyst activity. Increased understanding of the time-dependent relationship between downstream products (FTIR) and surface adsorbed species (DRIFTS) will shed light on the plasma enhancement of DRM to inform development of future systems.

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1.Y. Li, J. Jiang, M. Hinshelwood, S. Zhang, P. J. Bruggeman, and G. S. Oehrlein, "Characterization of plasma catalytic decomposition of methane: role of atomic O and reaction mechanism," J. Phys. D: Appl. Phys., 55, 155204, (2022). doi: 10.1088/1361-6463/ac4728.

5:20pm **PS1+AS-WeA-10 Silver Nanoparticle Synthesis in Low-Pressure Plasmas: The Roles of Free Electrons and Photons***, **Chi Xu**, J. Held, H. Andaraarachchi, U. Kortshagen,* University of Minnesota

The interactions of plasmas with liquids enable considerable electron and vacuum ultraviolet (VUV) photon fluxes to the solution surface, contributing to subsequent reduction processes and emerging as a novel technique of nanomaterials synthesis. To date, the solvated electrons were mostly proposed to be the critical reducing agent while the effect of photon-driven reactions on nanoparticle synthesis has not been fully understood. In this work, we use glycerol, a major co-product of biodiesel production as the solvent. Using this solvent, we investigate the silver nanoparticle formation in silver nitrate ($AgNO_3$)-glycerol solutions delivered as droplets to a low pressure nonthermal plasma, opening new synthetic pathways over previous bulk reactions. We demonstrate that this system allows the formation of monodispersed sub-20 nm silver nanoparticles. By inserting crystal filters having various cut-on wavelengths between the plasma and the glycerol droplet, UV radiation from the plasma-liquid emission at wavelength ranges between 150 and 280 nm is differentiated, while plasma-generated electrons are prevented from reaching the droplet. To quantify the nanoparticle yield, the final silver ion concentration was measured using a colorimetric method. We find that UV radiation contributes ~ 70% of the integral plasma effect in reducing silver ions to atoms, likely driven by H radicals attributed to the photodissociation of glycerol with an energy threshold of ~ 5 eV. The UV emission was traced to originate from carbon species released into the plasma from the glycerol solvent. The effects of aldehydes are minimal, which was evaluated by scavenger study and colorimetric assay kit, respectively. Using water as the solvent instead, silver nanoparticle formation in aqueous solutions instead of glycerol does not exhibit a strong dependence on UV emission under the same operating conditions.

The research was sponsored by the Army Research Office and was accomplished under Grant No. W911NF-20-1-0105.

5:40pm **PS1+AS-WeA-11 Plasma Synthesis of Hydrogen from Ethanol Solution***, D. Lojen,* Université libre de Bruxelles, Belgium*; T. Fontaine,* Université libre de Bruxelles/ University of Mons, Belgium*; L. Nyssen,* Université libre de Bruxelles/Ghent University, Belgium*; D. Petitjean,* Université libre de Bruxelles, Belgium*; R. Snyders,* University of Mons, Belgium*; N. De Geyter,* Ghent University, Belgium*; **Francois Reniers**,* Université libre de Bruxelles, Belgium

In the quest for green energy sources, hydrogen is often presented as the fuel of the future. However, as such, hydrogen must be synthesized. Among the many synthesis routes, those which don't directly produce CO2 are privileged. In this regard, water electrolysis, plasma splitting or pyrolysis of methane are intensively explored, sometimes already at the industrial or preindustrial scale. However, all routes present advantages and drawbacks. For instance, plasma splitting of methane has to deal with the removal of solid carbon from the reactor, and water electrolysis suffer from the high intrinsic energy cost to break the water molecule into H2 and O2. In this paper, we present preliminary results of the plasma induced splitting of liquid ethanol, using a nanopulsed generator, as this route could be an intermediate between the high energy cost of water splitting, and the solid carbon problem evidenced in CH4 plasma. Moreover, ethanol could be from renewable sources origin, and according to previous studies, its main oxygenated degradation product could be CO, which is useful for the chemical industry. The plasma reactor consists of a pin-to-plate electrode geometry, with the plate electrode being submerged in ethanol. The gases produced are quantified using atmospheric mass spectrometry (Hiden), and the discharge is characterized using a high speed photron camera, and electrical measurements. The main body of the reactor is glass-based, with selected entries for OES, mass spectrometry, gas inlet and outlet. Results show that the thickness of the liquid ethanol layer over the plate electrode plays a tremendous role as it generates two plasma regimes: up to 2.5 mm, the plasma is hot, with a high current and a reasonable peak voltage, whereas above 2.5 mm, the plasma changes to a DBD-like configuration, with ethanol playing probably the role of a dielectric. This induces an increase in voltage and a drop in current. Hydrogen production is directly related to the current injected in the discharge. In the hot plasma configuration, hydrogen is produced with 55% selectivity, dropping to <50 % at higher ethanol thicknesses. A change in the byproducts selectivities is also observed (C2H4, C2H2, CH4, C2H6, CO), with the change in plasma regime. Results also show the effect of the nanopulse duration and frequency and the electrode polarity.

Acknowledgements:

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Plasma Science and Technology Division
Room A107-109 - Session PS2+MS-WeA

Plasma-Surface Modeling

Moderators: Emilie Despiau-Pujo, Univ. Grenoble Alpes, CNRS, LTM, **Jun-Chieh Wang**, Applied Materials

2:20pm **PS2+MS-WeA-1 Modeling and Simulation of Plasma-Surface Interactions in Nanofabrication***, **David Graves**,* Princeton University **INVITED**

Plasma-enhanced atomic layer deposition (ALD) and etching (ALE) in principle offer an unprecedented opportunity to control surface composition and structure. By modulating process time, frequency, energy, and chemistry, it is possible to vastly increase the range of conditions and surface modification effects at surfaces. ALE/ALD can simplify the process by separating, for example, a chemical surface modification step from addition of energy through rare gas ion bombardment. It might be possible to design novel etch and/or deposition precursor molecules to take advantage of ALE/ALD modulation-oriented approaches. However, process modulation introduces the complexity of having the surface state change in time during the exposure. To understand and control these processes, an atomic scale plasma-surface interaction simulation is essential. In this talk, I briefly review the use of molecular dynamics (MD) simulations in plasma-surface interactions and how they have been used to help understand conventional plasma etching and deposition. I then use our recent studies of PEALE to highlight both successes and limitations of the current state of the art when used for modulated atomic layer processes. The key issues of interatomic force fields for many new chemistries and materials; using MD to simulate an intrinsically multi-timescale process; and the need to couple well-diagnosed experiments with atomistic simulations are emphasized.

3:00pm **PS2+MS-WeA-3 Mechanisms of Phosphorus Halides Gas Boosting Cryogenic Dry Process Etch Rate: A Quantum Chemistry Investigation***, **Yu-Hao Tsai**, D. Zhang,* TEL Technology Center, America, LLC*; T. Orui, T. Yokoyama, R. Suda,* Tokyo Electron Miyagi Limited, Japan*; T. Hisamatsu,* TEL Technology Center, America, LLC*; Y. Kihara,* Tokyo Electron Miyagi Limited, Japan*; P. Biolsi,* TEL Technology Center, America, LLC

3D-NAND fabrication requires ultrafast etch rate (E/R) of the dielectric material stacks to deliver the high-aspect-ratio contact (HARC) etch with an economical fashion. In a sperate report submitted about the cryogenic dry etch process development, we introduce the results of the drastically higher E/R of Ox/SiN (ONON) than the room temperature ones. We also reveal the catalytic etching reaction which enables the fast-etch process. We then identify the E/R booster gases: phosphorus halide, which brings the E/R to a higher level. To advance the booster-process development, a fundamental understanding of how the performance enhancing gases work is unavoidably crucial. This paper focuses on the mechanisms of phosphorus halides booster making the ONON E/R faster than the non-boosted cryogenic etch processes. Using the density functional theory (DFT), we identify the major chemical reactions behind the E/R enhancement. Based on the findings, we highlight the major properties required for the booster gases to function. The experimental results verify the mechanisms built upon the DFT study. In addition, we discuss the impact from the halogen atoms of the molecules on the etch performance. The paper does not only provide the insight toward an even higher E/R but also shed a light on the synergy of combing the experiments and atomistic modeling for the advanced node manufacturing technology developments.

3:20pm **PS2+MS-WeA-4 Molecular Dynamics Simulations of Diamond Surface Processing via Low-Energy Hydrogen and Argon Ion Bombardment***, **Jack Draney**,* Princeton University*; J. Vella,* Princeton University Plasma Physics Lab*; A. Panagiotopoulos, D. Graves,* Princeton University

Nitrogen-vacancy (NV) centers in diamond are promising for multiple applications in quantum information processing and sensing [1,2]. NV centers can locally detect and measure physical quantities such as magnetic and electric fields. However, these devices are currently limited by surface defects that compromise charge stability and spin coherence [1,2]. In this work, we explore plasma-assisted atomic layer etching of diamond using classical molecular dynamics (MD) simulations. We performed MD simulations of low-energy hydrogen (<50 eV) and argon (<200 eV) ion bombardment of diamond surfaces. Argon ion bombardment can be used to locally smooth initially rough diamond surfaces via the formation of an amorphous C layer, the thickness of which increases with argon ion energy. Subsequent exposure with hydrogen ions (or fast neutrals) will selectively etch this amorphous C layer, leaving the underlying diamond layer intact if the H energy is maintained between ~2–5 eV. The simulations suggest that combining Ar^+ smoothing with selective H removal of amorphous C could be an effective strategy for diamond surface engineering, leading to more reliable and sensitive NV center devices.

[1] Sangtawesin, S., Dwyer, B. L., Srinivasan, S., Allred, J. J., Rodgers, L. V., De Greve, K., ... & De Leon, N. P. (2019). Origins of diamond surface noise probed by correlating single-spin measurements with surface spectroscopy. *Physical Review X*, *9*(3), 031052.

[2] Stacey, A., Dontschuk, N., Chou, J. P., Broadway, D. A., Schenk, A. K., Sear, M. J., ... & Hollenberg, L. C. (2019). Evidence for primal sp2 defects at the diamond surface: candidates for electron trapping and noise sources. *Advanced Materials Interfaces*, *6*(3), 1801449.

4:20pm **PS2+MS-WeA-7 Yesterday, Today, and Tomorrow for High-Aspect-Ratio Contact Etching: Unraveling the Mysteries of Plasma-Surface Interactions with Modeling and Simulations***, **Du Zhang**, Y. Tsai,* TEL Technology Center, America, LLC*; M. Iwata, M. Yokoi, K. Tanaka,* Tokyo Electron Miyagi Limited, Japan*; T. Hisamatsu,* TEL Technology Center, America, LLC*; Y. Kihara,* Tokyo Electron Miyagi Limited, Japan*; P. Biolsi,* TEL Technology Center, America, LLC **INVITED**

The ever-growing demand for big data storage and processing has driven advancements in both the design and process technologies of advanced memory devices. In particular, the fabrication of high-aspect-ratio contacts (HARC) is a key process step. Etch throughput and profile control are crucial for reducing manufacturing cost and ensuring device performance. To meet these challenges, multiscale mechanistic understandings are essential for driving process and design optimization.

In this paper, we will discuss the fundamental etch mechanisms of plasma-surface interactions for HARC etching assisted by atomistic / plasma / profile modeling. We will review the underlying surface reaction mechanisms of the conventional fluorocarbon gas chemistry. We will also discuss the typical process challenges with etch rate and profile control, as well as various possible mitigation methods. Moreover, we will introduce how hydrogen admixture into the fluorocarbon chemistry can alter the behavior of dielectric etch rate and surface chemistry in a way that breaks conventional wisdom, especially at lower wafer temperatures. By unraveling and utilizing these underlying mechanisms derived from multi-scale simulations, we have been able to design new processes to achieve enhanced performance.

5:00pm **PS2+MS-WeA-9 Optimization of Model Parameters in Simulations of High Aspect Ratio Plasma Etching***, **Florian Krüger**,* University of Michigan, Ann Arbor*; D. Zhang, M. Park, A. Metz,* TEL Technology Center, America, LLC, USA*; M. Kushner,* University of Michigan, Ann Arbor

Computational investigations of feature evolution during plasma etching of micro- and nano-electronics devices are highly dependent on a robust reaction mechanism and precise knowledge of reaction probabilities and coefficients to accurately represent the physical behavior of these processes. The increased complexity of the structures and use of novel gas compositions coupled with the necessarily reduced reaction set used by numerical investigations of feature evolution makes it difficult to choose these critical parameters from first principles. This problem is exacerbated by the fact that many of the physical and chemical processes occurring during plasma etching are based on different fundamental principles - i.e., physical sputtering, chemical sputtering, chemisorption, physisorption, spontaneous etching – that have different functional forms.

The aim of this work was to accelerate the development of reaction mechanisms for feature profile evolution during plasma etching.This is accomplished by selecting a subset of reaction rates and angular dependencies and matching the predictions of feature profiles to experimental data using autonomous optimization methods. To that end a series of etches of high aspect ratio (HAR) SiO_2 features using a C_4F_6 / C_4F_8 / Ar /O_2 plasma was performed and relevant quantities such as etch depth, etch rate, aspect ratio as well as critical widths at several depths were determined using scanning electron microscopy.

The same process was reproduced using gas phase and profile scale simulation tools, HEPM (Hybrid Plasma Equipment Model) and MCFPM (Monte Carlo Feature Profile Model), respectively. Some of the input parameters used by the MCFPM were coupled to a multi variate 2-step optimizer that adjusted relevant input parameters in to achieve the best match between simulation and experiments.Thus, the profile etch simulation effectively acts as an objective function on which the optimization is based. Due to the specific nature of the data and objective function with respect to spatial discretization, the 2-step approach – a combination of gradient descent and Nelder-Mead optimization - proved most effective.

The outcome and development this optimization process will be discussed.The resulting reaction mechanism was used to simulate features using similar but quantitatively different processing conditions to demonstrate how broadly the mechanism can be applied.

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* Work supported by Tokyo Electron, Samsung Electronics and the National Science Foundation.

5:20pm **PS2+MS-WeA-10 Prediction of Surface Morphology and Composition Evolution during Atomic Layer Deposition via Combined Ab-Initio and Monte Carlo Approach***, **Ting-Ya Wang**, G. Hwang,* University of Texas at Austin

Atomic layer deposition (ALD) has been proposed as a method for achieving greater precision and control over film thickness, conformality, and impurity levels as compared to traditional chemical vapor deposition. It uses alternating cycles of two half-cycle reactions to achieve sequential and self-limiting deposition. However, finding the optimal conditions for the desired film properties and surface states for a certain material has largely relied on a trial-and-error approach. To expedite the search process, understanding the underlying mechanisms that influence surface chemistry and structure is crucial. However, currently available experimental methods may be limited in their ability to non-invasively observe surfaces at the atomic level or hindered by overlapping signals.

Theoretical methods have their own set of limitations. First-principles calculations, such as density functional theory (DFT), can be used to study the electronic structure of atoms and have been applied extensively to study surface reaction pathways. However, they are generally limited to a few hundred atoms and do not consider temperature and pressure effects. Ab-initio molecular dynamics (AIMD) simulations allow for studying dynamic processes, but they are similarly limited by both length and time scales. Monte Carlo (MC) simulations provide a way to study the thermodynamic properties of larger systems, and kinetic MC (KMC) allows for real-time simulation of system evolution. However, without a description of potential for each atom, both MC methods rely on predetermined lists of allowed events, which limit their accuracy and applicability.

Combining MC with DFT can potentially enhance the accuracy and applicability of simulations. However, in order to make these methods more reliable in describing various systems and include unknown reaction mechanisms, streamlining the integration of these two methods and the auto-generation of required information for MC simulations is important. In our work, we have applied this approach to investigate the evolution of surface structure and film morphology during plasma-enhanced ALD. Film morphology is a critical factor affecting film properties such as refractive index and wet etching rate, while surface structure determines the surface chemistry and thus affects deposition kinetics. We have examined the effects of plasma and different types of precursors on ALD processes and film properties, as well as the impact of process conditions, such as temperature and pressure.

5:40pm **PS2+MS-WeA-11 Modeling Reaction and Diffusion at a Plasma-Liquid Interface***, **Sean Peyres**,* University of Illinois at Urbana-Champaign*; N. Üner,* Middle East Technical University, Turkey*; N. Abuyazid, R. Sankaran,* University of Illinois at Urbana-Champaign

Low-temperature, atmospheric-pressure plasmas can promote reactions at a liquid surface for various applications including nanoparticle synthesis, water purification, treatment of skin wounds, and chemical production. At the core of these processes, plasma-produced species, such as electrons and hydroxyl radicals, cross the gas-liquid boundary and rapidly react with solution-phase species, including the solvent, within a few nanometers to micrometers distance of the interface. A key consequence of the highly localized reactions is that the reaction rates are limited by mass transport of the solution species from the bulk liquid to the plasma-liquid interface. Previous experimental studies have observed such mass transport limitations, but a fundamental description of the mass transport has yet to be developed.

Here, we present a simple reaction-diffusion model for the reaction of plasma-produced species at a gas-liquid interface. The model consists of a set of nonlinear differential equations describing the reaction and diffusion of a single plasma species (referred to as a radical) and a single solution-phase species (referred to as a scavenger). The plasma-produced radical reacts both with the scavenger and itself in the solvent via recombination. To solve the equations analytically, simplifying assumptions were necessary. First, quasi-steady state was assumed, where the radical and scavenger concentrations quickly obtain a profile that can be solved for a given time. Then, various assumptions were made to solve the equations under limiting cases. Examples include negligible radical-scavenger reaction, uniform scavenger concentration, and fast reaction with the scavenger (compared to radical recombination). These results could be summarized by using dimensionless numbers that relate the competition between the radical-scavenger and radical recombination reactions along with the transport freedom of the scavenger. Furthermore, we solved the full set of equations numerically and compared with the analytical solutions for the limiting cases. Finally, by adding a boundary condition for the diffusive layer, the bulk scavenger concentration could be calculated as a function of time and compared with previous experimental reports. We show that the model can be used to quantitatively predict and explain mass transport effects on reaction yields and selectivity.

6:00pm **PS2+MS-WeA-12 Integrated Modeling of Diamond Growth and the Surface Composition in CH_4/H_2 Plasma***, Y. Barsukov,* Princeton University Plasma Physics Lab*; A. Khrabry,* Princeton University*; **Igor Kaganovich**,* Princeton University Plasma Physics Lab

Microwave plasma generated in a mixture of CH4 highly diluted in H2 is typically used to grow diamonds. According to the broadly accepted mechanism, most of the surface of the growing diamond is unreactive because it is covered by hydrogen atoms. At a small fraction of the surface, hydrogen is removed by the so-called hydrogen-atom abstraction mechanism resulting in the formation of reactive sites (surface activation). Radical species produced in the CH4/H2 plasma are adsorbed on the reactive surface sites, changing the surface composition and promoting the diamond film growth. Atomic H radicals play a key role in the surface activation, allowing for the CH3 radicals to be adsorbed on the reactive sites which leads to the growth of diamond. Nevertheless, the main by-product of CH4 decomposition in the plasma is C2H2, but its role in the growth process is still debated. A complex kinetic model which links fluxes of gaseous reactants from the plasma to the surface composition is needed to identify the role of each reactant.

To consider complex plasma-surface chemistry we performed a 0D kinetic modeling, where 83 surface reactions between CH4, CH3, H, H2 and C2H2 gaseous species are considered. The rates of all 83 reactions were calculated under the same approach, namely, we used WB97XD DFT functional and transition state theory. The DFT functional was validated for gaseous reactions, for which rate constants were measured. The following processes were considered in the model: 1) surface activation/passivation by H, H2, CH3 and CH4, 2) adsorption/desorption of CH3 and C2H2 on the reactive surface sites, 3) hydrogen abstraction from the adsorbates, 4) incorporation of C atom from the adsorbate into the diamond network (sp3 phase), and 5) formation of sp2 phase from C2H2 adsorbate.

The model reproduces the experimental observation that the rate of diamond growth strongly depends on the substrate temperature and has a peak near 1200 K. Detailed analysis of the surface composition shows that the growth is suppressed at low temperature due to formation of sp2 phase. (The mechanism of sp2 phase formation is similar to the mechanism of soot growth). At temperatures higher than 1200 K, the growth is suppressed due to reverse reactions leading to separation of C atoms from the diamond network into the adsorbed state and their subsequent desorption. Thus, our 0D kinetic model allows to link fluxes of plasma reagents with the surface composition and growth rate. The model will be expanded with reactions leading to doping of diamond, which are critical for the synthesis of sensors and cubits.

Plasma Science and Technology Division
Room A106 - Session PS1+MS-ThM
AI/ML in Plasma Applications

Moderators: Robert Bruce, IBM Research, T. J. Watson Research Center, **Yu-Hao Tsai**, TEL Technology Center, America, LLC

8:00am **PS1+MS-ThM-1 Approaches to Accelerate Etch Process Optimization by Using Virtual Experiment***, **Tetsuya Nishizuka**, R. Igosawa, T. Yokoyama, K. Sako, H. Moki, M. Honda,* Tokyo Electron Miyagi, Ltd., Japan **INVITED**

High Aspect Ratio Contact (HARC) hole etching is one of the processes which require a lot of efforts to optimize etch condition. As the aspect ratio increases, some issues such as “distortion” and “twisting” which are hole circularity degradation and deviation from vertical etch respectively, have been critical. Since they cause asymmetric profile along hole axis, not only vertical but also horizontal cross section is necessary to observe 3D profile image, it takes more time to conduct a series of experiments, and then it makes the optimization more difficult.

In this study, we created a model for a topography simulation which is based on Monte Carlo method, so that we can conduct “virtual experiment” on the simulator and expect to reduce the number of experiments by understanding etch mechanism. With respect to practicability for model building, we employed a procedure that representative ion and radical parameters which associate with etching behavior are carefully fitted to actual experimental results [1].

As the result, while this kind of asymmetric distortion profile is supposed to come from stochastic variation and charging in the hole [2], we found there is another systematic factor that is an interaction between re-deposition of sputtered etch material and initial mask profile by analyzing Amorphas Carbon Layer (ACL) etching precisely [3]. This model is consisted with the fact that the distortion deteriorates under low temperature condition. It was also applied to oxide-nitride (ON) layers etch and well reproduced twisting profile on the simulator.

Additionally, we attempted an automatic parameter fitting by using ML optimization for the purpose to minimize efforts in case of converting the model to the other applications than HARC.

[1] Ohmine et. al., Jpn. J. Appl. Phys. 50 (2011)

[2] Huang et. al., J. Vac. Sci. Technol. A 37 (2019)

[3] Igosawa et. al., Proceedings of international symposium on dry process 2022

8:40am **PS1+MS-ThM-3 Recipe Optimization for Plasma Etching with Machine Learning Model Trained by Initial Dataset Using D-Optimal Design***, **Ryo Morisaki**, T. Ohmori,* Hitachi, Ltd., Japan

The development of semiconductor fabrication processes is becoming more difficult due to a growing need for the miniaturization of semiconductor devices to the nano-scale level. Furthermore, growing demands for cutting-edge semiconductor devices of superior performance necessitate the swift development of the fabrication processes.

Plasma etching is a pivotal technique for semiconductor processes. Machine learning (ML) methods have been applied to optimize the recipe for these processes, which is a control parameter set including items such as plasma generation power, wafer bias power, gas species for plasma generation, and the flow rate of gases[1][2]. Datasets for training the ML model consist of recipes and their corresponding etching profiles. Generally, the recipes are curated by expert process engineers to reduce the cost of the etching experiments. On the other hand, design of experiments (DoE) methods can be utilized to obtain the training datasets without expert knowledge. Therefore, DoE has the potential to increase of the number of engineers who can optimize recipes for difficult etching processes.

In this work, two distinct approaches for creating an initial dataset for the training are compared to evaluate the efficiency of recipe optimization using an ML model. In the first approach, the initial dataset is created on the basis of the plasma etching knowledge of expert engineers, as has been conventionally practiced, and in the second approach, it is created on the basis of elementary knowledge for etching tool operations and a DoE method with the D-optimal criterion is used[3]. In the latter approach, a preliminary range of values for the recipe parameters, in which plasma generation and etching can occur, is established on the basis of fundamental knowledge of plasma etching. Subsequently, D-optimization is conducted on the recipe parameters within the specified range to generate a high-quality and diverse initial dataset that can improve the ML model for optimizing the recipes and profiles. In contrast to the conventional DoE with orthogonal array, this DoE with the D-optimal criterion method has no limitation on the number of experiments, thus making it suitable for creating small initial datasets to reduce the cost of the etching experiments. We report detailed comparison results of the efficiency of the etching optimization using each approach.

[1]T. Ohmori et al., in Proc. Int. Symp. Dry Process, pp. 9–10 (2017).

[2]H. Nakada et al., in Proc. Int. Symp. Dry Process, pp. 53–54 (2019).

[3]J. Keifer, Journal of the Royal Statistical Society. Series B (Methodological), vol. 21, no. 2, pp. 272–319 (1959).

9:00am **PS1+MS-ThM-4 Digital Twin Model to Compensate for Variations in Plasma Etching Process***, T. Nakayama, T. Ohmori,* Hitachi, Ltd., Japan*; **Naoto Takano**,* Hitachi High-tech America, Inc.

The miniaturization of semiconductor devices based on Moore's Law has necessitated increasingly demanding precision in the mass production of devices. To achieve a target etching profile with nano-scale accuracy during the manufacturing process, plasma etching systems must be equipped with technologies to minimize variations of the etching. A set of parameters for the control function of the etching system is called a recipe, which is used as input data for the system. While the same recipe is used for all systems in mass production, the etching profiles are varied due to the drift of etching chamber conditions or differences in the conditions of the inner chamber parts replaced at the time of chamber maintenance. Etching rate (ER) data are often utilized to check the variations of chamber conditions and construct a compensation model, but a large ER dataset is required for the model, which is time consuming.

Therefore, we have been investigating a compensation method that requires only a small amount of data. In our method, first, a reference digital twin (DT) model utilizing neural networks is trained by sufficient data. A large amount of the training data consisting of recipes and ER can be prepared in advance by experiments using a reference chamber. Further, in addition to the experimental ER, simulation data of ion and radical fluxes correlating with ER (calculated by a plasma simulator) are used for the training data [1]. The simulation data can also be prepared in advance. Next, a small amount of ER data is obtained from a target chamber that has a different ER from that in the reference chamber. A target DT model is obtained by additionally training the reference DT using the small amount of ER data. Finally, a recipe that compensates for the ER difference is predicted using the target DT.

We prepared several hundred experimental ER data and calculated fluxes data using the reference chamber and the plasma simulator, respectively. Several tens of ER data were obtained as a small amount of data using a target chamber. Predicted recipes by the trained target DT model for ER compensation were experimentally verified in the target chamber. As a result, the ER difference used to check the variation of chamber conditions was decreased by our compensation method using DT models.

[1] T. Nakayama et al., Proc. Gaseous Electronics Conf., Sendai (2022).

9:20am **PS1+MS-ThM-5 Deep Learning-Enabled Plasma Equipment Design Optimization in Semiconductor Manufacturing**, *S. Ahn, **Jinkyu Bae**, S. Yoo, S. Nam,* Samsung Electronics, Republic of Korea

In plasma reactors, a focus ring which surrounds the wafer plays an important role in improving uniform fluxes and energy across the wafer. To ensure the uniformity and consistent processes, sophisticated design for the focus ring is necessary. However, focus ring design is very challenging due to the complexity of the design space and the high-dimensional geometry of the focus ring. Furthermore, the multi-scale and multi-physics nature of low-temperature plasmas (LTPs) makes it difficult to develop accurate simulation models that can capture the dynamics of plasma discharges. Simulating LTPs is the need to consider multiple physical and chemical processes that occur simultaneously, such as ionization, recombination, excitation, and attachment. These processes can be highly nonlinear and require a large range of integrating time scales from picosecond to millisecond. In this study, we present a Deep Neural Network framework employing the DeepONet, which is pre-trained deep neural operators between each physical quantities on behalf of physical governing equations. The training data is generated using HPEM (The Hybrid Plasma Equipment Model) plasma simulation solver. The framework involves two network types. The first network reduces the dimensions of the focus ring geometries to a latent representation. We used a geometric attention mechanism in Variational-Auto-Encoder (VAE) allowing us to discover the latent geometric features of focus ring parts. The high-dimensional design space was effectively reduced by the neural network model. We proposed the concept of using this latent representation in combination with the pre-trained neural networks. We pre-trained deep neural operators that can predict independently physical quantity fields, given general inputs. It is an efficient way of incorporating the plasma physics without embedding the partial differential equations into the loss function of the neural network.The proposed framework is shown to be efficient and effective in optimizing the focus ring design for different objectives, and the effects of variations in the design are thoroughly investigated based on very few measurements using pre-trained deep neural operators. This paper aims to develop framework for predicting plasma dynamics and carrying out focus ring design in reactors.

9:40am **PS1+MS-ThM-6 Wafer Arcing Detect Algorithm Using LSTM Autoencoder in Hardmask Strip Equipment with CCP Source**, ***Heewoong Shin,*** PSK, Republic of Korea

“Wafer arc” is one of the phenomenon that occur in semiconductor manufacturing equipment that utilizes plasma, rather than being limited to arc discharge in plasma science. In this study, we discuss the possibility of successfully classifying normal manufacturing process of semiconductor equipment using CCP and the abnormal data by using deep learning methodology. In general, since wafer arcs data have an obvious characteristics that engineers can easily notice, it is thought that they can also easily be detected by general SPC methodology. But in some cases, there are pattern anomalies that cannot be detected by SPC, or there are problems such as requiring the subjectivity of engineers for determining the data is normal or not because it is hard to find common in each abnormal data. Because wafer arcs might cause serious malfunctions in most equipment and are a major cause of yield reduction, so a function that can diagnose abnormalities in advance is required. However, wafer arcs are generally known to be difficult to reproduce to make abnormal data, and there are problems such as requiring high-resolution optical equipment to detect the arc phenomenon which also costs additional charge. In this study, we used specific parameters in lotlog of CCP equipment as an input of DL model. By training with LSTM-autoencoder, it shows the possibility of classifying normal and abnormal data successfully through simple learning. When the result of this research can be applied in mass-production, it is highly expected that it will effectively detect and predict wafer arcs and other anomaly related to electrical/plasma parameters, and will greatly benefit the yield of semiconductor equipment.

Plasma Science and Technology Division
Room A106 - Session PS2+AS+SS-ThM

Plasma-Surface Interactions I

Moderators: Lei Liu, Lam Research Corporation, **Pingshan Luan**, TEL Technology Center America

11:00am **PS2+AS+SS-ThM-10 Remote Plasma-Activated and Electron Beam-Induced Etching of Ruthenium and Its Comparison to Tantalum**, ***Yudong Li***[1], University of Maryland College Park; *C. Preischl, M. Budach, H. Marbach, D. Rhinow,* Carl Zeiss SMT, Germany; *G. Oehrlein,* University of Maryland College Park

Refractory metals are of importance in microfabrication, which necessitates patterning of these materials. One issue is to reduce near-surface modifications of materials during processing, which is often due to ion bombardment and atomic mixing. Recently, we have developed a novel technique of combining electron beam (ebeam) and remote plasma (RP) for materials processing [1, 2]. Material damage is significantly reduced since energetic ion bombardment is prevented. The RP generates reactive neutral precursors and the ebeam provides energy deposition to enable further precursor-materials interactions.

Here we investigate the effects of ebeam and RP on Ru and Ta with the goal of selective etching. The simultaneous irradiation of ebeam and RP with Ar and O_2 as the feed gas induces Ru etching. The Ru ER increases with emission current, electron energy, and O_2 flow rate, while it shows less dependence on RP power. A pretreatment step by ebeam/RP or RP only with $Ar/O_2/CF_4$ significantly enhances the subsequent Ru ER induced by ebeam/RP with Ar/O_2. This effect is likely associated with the reactor wall passivation by the introduction of CF_4 through RP, which reduces recombination of O atoms on reactor surfaces. For Ta, RP with fluorine-rich $Ar/O_2/CF_4$ induces Ta etching at a high rate. If instead an O_2-rich gas mixture is used, we observe Ta oxidation. The RP sustains the spontaneous Ta etching by generating F which interacts with Ta and forms volatile tantalum fluoride. Contrary to the Ru metal, where the ebeam induces etching, the ebeam is found to promote oxidation of Ta. The opposite roles of ebeam on Ru and Ta and the sensitive dependence on CF_4 flow rate of Ta etching provides the opportunity to achieve Ru over Ta etching selectivity.

We gratefully acknowledge the financial support of this work by Carl Zeiss SMT GmbH

References:

1. Lin, K.-Y., et al., SiO2 etching and surface evolution using combined exposure to CF4/O2 remote plasma and electron beam. Journal of Vacuum Science & Technology A, 2022. 40(6).

2. Lin, K.-Y., et al., *Electron beam-induced etching of SiO2, Si3N4, and poly-Si assisted by CF4/O2 remote plasma.* Journal of Vacuum Science & Technology A, 2022. **41**(1).

11:20am **PS2+AS+SS-ThM-11 Plasma Surface Ionization Wave Interaction with Single Channel Structures**, ***Joshua Morsell,*** *S. Shannon,* North Carolina State University

The interaction of atmospheric pressure plasma jets (APPJ) with materials has found promising applications in the fields of plasma medicine, catalysis, and material treatment. One area of interest is the surface ionization waves (SIW) present in these plasmas. SIWs interactions with complex interfaces is critical to these applications and require further study. A complex interface is any target with non-uniform electrical properties and/or non-planar surface morphology. The focus of this work is to study how surface ionization waves interact with single channel structures in dielectric media. The results show that the fraction of the SIW that escapes the channel is dependent on both driving voltage and channel width.

The plasma source in this study is an APPJ powered by a nanosecond DC pulse of positive polarity with helium as the working gas as used in [J. Morsell et al., J. Phys D: Appl. Phys. 56 (2023), 145201]. Voltage and current data are collected via integrated current and high voltage probes at the source head. Time resolved ICCD imaging is used to image SIW propagation. The single channel targets consist of a 25 x 50 mm glass slide which has had a single channel etched across its minor axis. There are six total channel samples with different widths and depths. These samples are mounted to a target stage, which has another glass slide with an optically transparent conductor acting as a ground plane allowing imaging through the substrate.

SIW velocities in the system have been measured. The first is the SIW velocity within the channel, the second is the radial velocity of the portion

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[1] **PSTD Coburn & Winters Student Award Finalist**

of the SIW that escapes the channel. Both velocities increase with increasing voltage but show no significant trends with channel geometry. Velocity magnitudes for radial surface waves are 40-70 km/s and in-channel velocities are determined to be 60-130 km/s. Total light emission from the discharge is used to determine the fraction of the SIW escaping the channel. There exists a strong dependence of SIW portioning with channel geometry and driving voltage. As voltage increases the SIW is less confined and the fraction of the SIW escaping the channel increases. As channel width increases less of the SIW is allowed to escape the channel. No conclusive trends are observed with respect to channel depth. Observation also reveals that the fraction of the escaping SIW relates to the sample area exposed to the discharge. A smaller area of the substrate is exposed to the SIW for low voltages and large geometry channels.

This work is supported by the U.S. Department of Energy, Office of Science, Office of Fusion Energy Sciences under Award Number DE-SC0020232.

11:40am **PS2+AS+SS-ThM-12 Plasma-wall Interactions: Implications for Advanced Chamber Materials Requirements***, **John Daugherty**,* Lam Research Corporation **INVITED**

In semiconductor device fabrication, plasma-assisted processes dominate both the deposition and etching of materials.Over 50 years of successive technology nodes have motivated innovations and continuous improvements in plasma reactor technology, and the semiconductor industry now employs a sophisticated portfolio of plasma reactors that use a wide variety of chemistry and operating approaches. Today, many aspects of the fabrication process must achieve process variations of ~1% and often must contribute particle contamination of less than one particle per wafer pass.Despite dramatic improvement in reactor design and in chamber materials, it remains challenging to achieve current variation requirements because plasma reactors still suffer from process drift, molecular contamination, and particulate contamination that originate from plasma-modification of the chamber materials. The first consideration in choosing a chamber material is the expected maximum ion bombardment energy.The plasma conditions within a single chamber are quite nonuniform, and the ion energy may fall into several ranges. Some parts experience <20 eV ions, and while these parts can be engineered for very long lifetime, challenges remain in meeting performance requirements.Other parts experience ion energies >100 eV (sometimes >1 keV in etch processes).These parts are almost always cost-sensitive consumables. There is an intermediate range of ~50 to 100 eV where there is considerable materials design complexity because of the desire to maintain process stability for thousands of wafers while operating very near the energy thresholds for ion-enhanced chemical modification of the wall material. Another design consideration is that the chamber materials must withstand a repeating sequence of multiple chemistries and plasma conditions followed by *in situ* plasma cleans using still different chemistry.The variety of chemically reactive molecules and free radicals include mixtures containing multiple halogens, hydrogen, oxygen, and depositing species from fluorocarbons, hydrocarbons, complex deposition precursors, and etch products. Recently we have adapted sophisticated materials metrology to examine the materials modifications that occur throughout the lifecycle of real production parts. We have also performed control experiments that allow us to infer the dominant plasma processes that cause the materials modifications we observe on production parts used in various applications.The implications for what types of materials are suitable for different parts of a plasma reactor are explored in this presentation.

Plasma Science and Technology Division
Room A106 - Session PS1-ThA

Plasma-Surface Interactions II

Moderators: Lei Liu, Lam Research Corporation, **Pingshan Luan**, TEL Technology Center America

2:20pm **PS1-ThA-1 A Pseudo-Wet Plasma Etching Mechanism for SiO_2 at Cryogenic Temperature Using Hydrogen Fluoride Gas with*in-Situ* Surface Monitoring***, **Shih-Nan Hsiao**, M. Sekine,* Nagoya University, Japan*; Y. Iijima, R. Suda, Y. Ohya, Y. Kihara,* Tokyo Electron Ltd., Japan*; T. Tsutsumi, K. Ishikawa,* Nagoya University, Japan*; M. Hori,* nagoya University, Japan

The mainstream of every platform requiring data storage for mobile device applications is the 3D NAND flash memory, which boasts increased data capability. Despite its promising properties, the increasing number of stacking layers to enhance data capability poses various challenges, not only in terms of manufacturing process but also from a fundamental scientific perspective. The intensive development of the stacking number has led to significant advancements in deep hole etching, such as high-aspect-ratio contact (HARC) etching, for the stacking layers. Recently, an ultra-high speed etch process at cryogenic temperature for 3D NAND has been presented [1]. To explore the etching mechanism, the SiO_2 cryogenic etching using hydrogen fluoride (HF) plasma was investigated with *insitu* monitoring techniques including spectroscopic ellipsometry and attenuated total reflectance Fourier transformation infrared spectroscopy (ATR-FTIR). A dual frequency capacitively coupled plasma reactor was used to etch the PECVD-prepared SiO_2. The T_s was controlled from 20 to –60 °C by circulating a coolant through the bottom electrode. The etch rate (ER) of the SiO_2 dramatically increased by a factor of approximately 8, from 1.4 to 10.6 nm/s, as T_s was decreased from 20 to –60 °C (see supplemental document for details). The presence of physisorption of HF and H_2O at lower temperature was confirmed by the results obtained using the *in-situ* ATR-FTIR. The absorbance spectra acquired at different T_s clearly display that the HF-related molecules were generated by the HF plasma and absorbed on the surface of the SiO_2 film. The ER exhibiting the increasing trend is consistent with the absorbance intensity of the HF-related molecules (also see supplemental document). This indicates that the absorption of HF and the incorporation of HF-related molecules contribute great impact on etching of SiO_2 at low temperature. Based on these results, a "pseudo-wet" etching model and surface reactions of SiO_2 using HF plasma at low temperature is proposed.

[1] Y. Kihara et al., VLSI symposium T3-22023.

2:40pm **PS1-ThA-2 Coalescence/De-Coalescence Plasma Patterns on a Plasma-Liquid Interface***, **Jinyu Yang**, O. Dubrovski, P. Rumbach, H. Chang, D. Go,* University of Notre Dame

Self-organized anode patterns in plasma electrolysis have recently gained substantial interest, yet a comprehensive fundamental mechanistic understanding of the pattern formation and self-organization remains elusive. Here, we report observations of a distinct mode consisting of coalescence and de-coalescence oscillations (CDO) between plasma patterns when operating the cathodic glow discharge at a moderate current of ~-26 mA. Fast-imaging measurements resolve a liquid conductivity- and viscosity-dependent CDO frequency of ~200 Hz, indicating a potential transport-limited process as the frequency is far lower than any reaction timescales inherent to plasma processes. We therefore propose that advective transport of liquid phase ions (cations) due to surface capillary waves that arise from the electrostatic Maxwell pressure on the plasma-liquid interface is responsible for the observed CDO plasma patterns. A theoretical model for viscous capillary waves, coupled with the electrostatic Maxwell stress, is developed. Both the theoretical and the experimental data collapse onto a single universal curve, suggesting a strong correlation between the measured CDO frequency and the induced capillary waves. Further experimental investigation using laser-assisted visualization reveals the existence of surface capillary waves when CDO plasma patterns are being generated, confirming the hypothesized connection between the unexpected dynamics of the plasma and the dynamic liquid behavior.

3:00pm **PS1-ThA-3 Plasma-Surface Interactions at Atmospheric Pressure: From Liquids to Catalytic Surfaces***, **Peter Bruggeman**,* University of Minnesota **INVITED**

The unique non-equilibrium conditions of low temperature atmospheric pressure plasmas enable the delivery of highly reactive plasma species to substrates at (near) ambient temperatures which is beneficial for a broad range of applications. For example, plasmas interfacing with liquids enable plasma-aided decomposition of recalcitrant organic pollutants in water, decontamination of liquids and material synthesis. In addition, the interaction of plasmas with catalysts offers a sustainable electrically driven route to synthesize chemicals such as ammonia, a molecule that is vital for sustaining global food production or can be used to enhance catalytic reactors used for the removal of trace compounds like VOCs and NO_x from polluted air streams.

In this presentation, we will discuss advances in our understanding of the underpinning mechanisms of plasma-induced liquid phase chemistry in the context of plasma-driven liquid phase redox reactions for nanomaterial synthesis and chemical conversions and gas phase plasma-catalyst interactions enabling the formation of NH_3 from N_2 and H_2 at near ambient conditions. We will show that a detailed experimental characterization of well-designed reactors allows us to develop simplified models of the complex plasma-substrate interactions leading not only to a conceptual but also quantitative understanding of the key species involved in the interactions and the rate limiting processes. We will for example show that a detailed knowledge of the gas phase OH and electron densities, allows us to quantitatively explain liquid phase plasma-induced redox reactions [1] and a detailed measurement of gas phase reactive species fluxes to the catalytic substrate enables one to conclude that NH_3 formation by plasma-catalysis is consistent with surface reactions involving N radicals [2].

References

[1] Y. Yue, S. Exarhos, J. Nam, D. Lee, S. Linic, and P. J. Bruggeman, *Plasma Sources Sci. Technol.***31**(2022) 125008

[2] B. Bayer, P. Bruggeman and A. Bhan., *ACS Catal.***13** (2023) 2619-2630

Acknowledgements

This work was partially supported by the US Department of Energy under Award Number DE-SC-0016053, the National Science Foundation under Award Number CBET-2234270 and the Army Research Office under Grant Number W911NF-20-1-0105.

3:40pm **PS1-ThA-5 Enabling Dry Etching of sub-10 Nm Features at Cryogenic Temperature***, S. Srinivasan, J. Li, X. Yang, S. Joshi, T. Liu, **Sumit Agarwal**,* Applied Materials, Inc.

As the DRAM density scaling continues, there is an ever-increasing challenge in shrinking pattern space to sub-10 nm to enable higher pattern density. Sub-10 nm features induce considerable challenges for ICP based dry etching since the etching needs to be highly directional and spontaneous chemical etching needs to be minimized. With sub-10 nm space, however, the chemical etching is inevitable at room temperature and we observe tapered profile and top space enlargement even with extensive process optimization. To tackle this challenge, we evaluate carbon and oxide etch at cryogenic temperature, and observe significant improvement. For both carbon and oxide etch, cryogenic temperature was able to improve profile angle, shrink space CD as well as reduce defectivity by orders of magnitude, which were hardly achievable at room temperature. We attribute these improvements to the unique cryogenic temperature regime which have (1) stronger sidewall passivation due to higher radical sticking coefficient, (2) less spontaneous chemical etching due to lower reactivity and (3) unique reaction regime to enable new catalyst and passivation. The higher sticking coefficient at cryogenic temperature also allows leaner chemistry to be used, which reduces passivation at etch front and further increases etch rate and selectivity. We expect these process differentiations will benefit other applications with small features and high aspect ratios as well.

4:00pm **PS1-ThA-6 Study of Nonequilibrium Electron and Vibrational Response During Plasma Excitation***, **Sara Makarem**, P. Hopkins,* University of Virginia

Plasmas have long been used for the synthesis and manipulation of materials because of their unique ability to deliver both energy and chemically active species to the surface of plasma exposed materials - an attribute that separates them from other approaches to materials processing. Indeed, that feature provides the ability to drive the surface out of thermal equilibrium with the bulk material thus enabling local physicochemical processes that can be harnessed to establish unique material properties. Traditionally, our understanding of energy delivery from these energetic species is developed using a variety of ancillary plasma diagnostics, temperature measurements, models, and perhaps post-treatment, ex situ surface characterizations to “re-construct” energy deposition and absorption. While certainly of value, none of these approaches provide a direct measure of the localized, transient response associated with the energy flux at the surface.

In this study, with the use of in-situ ultrafast optical detection and sub-picosecond laser systems, we resolve the influence of the various energetic species in an atmospheric plasma on the resulting electronic and thermal response of materials in real time. Through the development of new plasma diagnostics with sub-picosecond to microsecond temporal resolution, we measure the optical response of material surfaces subjected to various types, intensities, and temporal profiles of atmospheric pressure plasma excitations. Through control over both the photon energy and temporal resolution of the laser probe using sub-picosecond and continuous wave lasers of various wavelengths, we selectively probe the optical response of the plasma excited surface, which in turn is related to the electronic structure, scattering dynamics, thermal transport, and elastic and mechanical properties of the lattice. Thus, by utilizing these novel in situ laser-based probes of the electronic, mechanical, and thermal properties of plasma-excited surfaces, we investigate highly non-equilibrium states and properties of materials during plasma exposure.

Plasma Science and Technology Division
Room B117-119 - Session PS2-ThA

Plasma Modeling and Characterization

Moderators: Catherine Labelle, Intel Corporation, **Du Zhang**, TEL Technology Center America

2:20pm **PS2-ThA-1 Control of the Ion Angle and Energy Distribution by an Embedded Electrode in a Focus Ring for a Capacitively Coupled Rf Plasma***, **Seoi Choi**, H. Lee,* Pusan National University, Republic of Korea

With the recent advancements in semiconductor processes reaching the nanoscale, research is underway to enhance the uniformity of plasma in plasma etching reactors. The non-uniformity of the etch process is noticeable at the edge of the wafer due to inhomogeneous electrical characteristics. We investigate a mechanism to control the plasma sheath above the wafer edge for a uniform etching process over the dielectric focus ring by changing the electric field and ion flux uniformly across the wafer surface using a two-dimensional particle-in-cell simulation parallelized with a GPU. An appropriate waveform on the electrode inserted inside the focus ring changes the sheath oscillation and ion flux to improve the ion energy and angular distributions (IEADs) to achieve a better etch rate.

2:40pm **PS2-ThA-2 Plasma Etch Chemistries for High Aspect Ratio Application with Low Emission***, **Phong Nguyen**, C. Jennings, S. Biltek, N. Stafford,* Air Liquide

In recent years, several countries and semiconductor manufacturing companies have announced targets for net-zero carbon emission by 2050. Plasma etch processes are responsible for a high percentage of emission for chip manufacturing especially in high aspect ratio (HAR) dielectric etch. Such an etch process involves employment of high global warming potential (GWP) fluorocarbon gasses such as C4F8, CH2F2. In the past decades, Air Liquide R&D has developed multiple alternative chemistries in HAR applications with very low GWP. However, while the gas entering the plasma etch chamber may be high or low GWP, it is difficult to predict the emission gases post plasma due to the complexities of the breakdown and recombination processes within the plasma.

In this study, we demonstrate that the plasma etch chamber emission gas stream can be analyzed and quantified by Fourier Transform Infrared Spectroscopy (FTIR). Complementary to FTIR analysis, Quadrupole Mass Spectrometry (QMS), a powerful tool, is implemented to help identify emission species in the chamber via studying positive ion fragments present inside the plasma. In addition, these Air Liquide novel chemistries have shown improved etch performance with lower CO2 equivalent emission as compared to that of current baseline in HAR etch processes.

3:00pm **PS2-ThA-3 Two and Three-Dimensional Kinetic Modeling of Capacitively Coupled Plasma Discharge in Cylindrical and Cartesian Geometry***, **Willca Villafana**, A. Powis,* Princeton University Plasma Physics Lab*; S. Rauf,* Applied Materials*; I. Kaganovich,* Princeton University Plasma Physics Lab

In a Capacitively Coupled Plasma (CCP) discharge, the processing rates and uniformity of the wafer depend on key parameters such as the ion flux, ion energy distribution function (IEDF), and plasma homogeneity. The non-Maxwellian nature of the IEDF requires a kinetic treatment, which can be achieved with Particle-In-Cell (PIC) simulations.

In this work, we develop a procedure to control the plasma uniformity and its dynamics using a weak magnetic field with a 2D cylindrical axisymmetric model. The present investigation takes leverage of PIC modeling and uses the explicit EDIPIC-2D code [1]. A detailed analysis of the sheath structure, the ion flux, and IEDF at the wafer will be performed. Additionally, we will also report recent examples and progress regarding 3D PIC modeling using the in-house LTP-PIC code [2].

[1] https://github.com/PrincetonUniversity/EDIPIC-2D

[2] T. Charoy, et al, “2D axial-azimuthal particle-in-cell benchmark for low-temperature partially magnetized plasmas,” Plasma Sources Sci. Technol. **28**(10), 105010 (2019).

Acknowledgments:

This Research was funded by the US Department of Energy through CRADA agreement with AMAT.

3:20pm **PS2-ThA-4 Effect of Feed Gas Content and Substrate Temperature on RIE of SiN$_x$ with Ar/C$_4$F$_6$/O$_2$ Plasma***, **Xue Wang**,* Colorado School of Mines, USA*; R. Gasvoda,* Lam Research Corporation, Tualatin*; E. Hudson, P. Kumar,* Lam Research Corporation, Fremont*; S. Agarwal,* Colorado School of Mines

Effect of feed gas content and substrate temperature on RIE of SiN$_x$ with Ar/C$_4$F$_6$/O$_2$plasma

Xue Wang[1]*, Ryan J. Gasvoda*[2]*, Eric A. Hudson*[3]*, Prabhat Kumar **[3]*, Sumit Agarwal **[1]

[1]Colorado School of Mines, Chemical and Biological Engineering, Golden, CO, USA

[2]Lam Research Corporation, Tualatin, OR, USA

[3]Lam Research Corporation, Fremont, CA, USA

In reactive ion etching (RIE) with fluorocarbon-based plasmas, the etch selectivity of SiO$_2$ relative to SiN$_x$ is controlled by tuning the F to C ratio in fluorocarbon feed gas, and by tuning the ion energy. Previously, we showed that the substrate temperature is one potential process knob to control the etch selectivity for SiO$_2$ over SiN$_x$ during C$_4$F$_6$/Ar plasma RIE. Our *in situ* optical diagnostics show that increasing the substrate temperature during RIE of SiN$_x$ from 70 to 120 °C creates an etch-stop layer and lowers the etch rate of SiN$_x$, with no noticeable effect over the same temperature range during RIE of SiO$_2$. *In situ* infrared spectroscopy and *ex situ* X-ray photoelectron spectroscopy (XPS) show that the fluorocarbon layer on the SiN$_x$ surface is more defluorinated at 120 °C, likely forming a graphitic etch stop layer which lowers the etch rate.

In this work, we explore the substrate temperature dependence on RIE of SiN$_x$ as a function of O$_2$ dilution of a C$_4$F$_6$/Ar plasma. Using *in situ* four-wavelength ellipsometry, we measured the steady-state etch rate of SiN$_x$ over 200 s. In our experiments, we varied the O$_2$ to C$_4$F$_6$ flow ratio over the range of 0.29 to 1.75. Consistent with previous studies, the etch rate of SiN$_x$ increased with increasing O$_2$ to C$_4$F$_6$ flow ratio in the feed gas at both substrate temperature of 70 and 120 °C. High-resolution spectra of the C 1s and F 1s regions were measured for SiN$_x$ surfaces after 200 s of RIE with *ex situ* XPS for O$_2$ to C$_4$F$_6$ flow rate ratios of 0.29, 0.75, and 1.75. Analysis of the XPS data shows that addition of O$_2$ results in a thinner CF$_x$ layer, which enhances the etch rate of SiN$_x$. More interestingly, we found that the etch rate of SiN$_x$ is higher at 120 °C than that at 70 °C at low O$_2$ to C$_4$F$_6$ ratios (< 1.25). This temperature dependence flips for O$_2$ to C$_4$F$_6$ ratios >1.25. We speculate the thickness of CF$_x$ layer and mixing layer are influenced by the substrate temperature, which leads to this temperature dependent etch behavior.

Oral Presentation Requested

3:40pm **PS2-ThA-5 Characterization of Ion and Reactive Species in Perfluorocarbon Gas ($C_4H_2F_6$-Z) Plasma for Mitigating Global Warming Potential*, Minsu Choi,*** Chungnam National University (CNU), Republic of Korea*; Y. Lee,* Institute of Quantum Systems (IQS), Chungnam National University (CNU), Republic of Korea*; C. Cho,* Chungnam National University (CNU), Republic of Korea*; S. Kim,* Institute of Quantum Systems (IQS), Chungnam National University (CNU), Republic of Korea*; I. Seong, W. Jeong, B. Choi, S. Seo,* Chungnam National University (CNU), Republic of Korea*; Y. Seol,* Institute of Quantum Systems (IQS), Chungnam National University (CNU), Republic of Korea*; H. Tak,* Sungkyunkwan University (SKKU), Republic of Korea*; G. Yeom,* Sungkyunkwan University (SKKU), SKKU Advanced Institute of Nano Technology (SAINT), Republic of Korea*; S. You,* Institute of Quantum Systems (IQS), Chungnam National University (CNU), Republic of Korea

In semiconductor and display manufacturing, Perfluorocarbon (PFC) gases are widely used for cleaning post-etching and deposition. With the adoption of advanced patterning like Double Patterning Tech (DPT) and Quadruple Patterning Tech (QPT), PFC gas consumption is rising. However, PFC gases are chemically stable, leading to a high Global Warming Potential (GWP). Reducing PFC gas emissions is essential due to their long-lasting global climate impact.

Transitioning to alternative gases requires understanding ion and active species distribution and plasma density, critical factors dependent on the plasma source. This study focuses on the comprehensive characterization of ion and active species in C4H2F6-Z gas and compares it to the conventional process gas, CHF3. Additionally, an essential plasma parameter, plasma density, is measured using a cut-off probe. Experiments in uniform chambers with Capacitively Coupled Plasma (CCP) and Inductively Coupled Plasma (ICP) sources reveal changes in ion and active species with power, pressure, gas ratio, and pulsing frequency.

Comparative data between the conventional and new gases are discussed. This research contributes to the development of alternative precursors to reduce the impact of global warming.

4:00pm **PS2-ThA-6 Cryogenic Aspect Ratio Etching of SiO_2 at $CF_4/H_2/Ar$ Plasma in a Cryogenic Reactive Ion Etch System*, Hee Tae Kwon,*** *I. Bang, J. Kim, H. Kim, S. Lim, S. Kim, S. Jo, J. Kim, W. Kim, G. Shin, G. Kwon,* Kwangwoon University, Republic of Korea

In the manufacturing processes of 3D NAND, the high aspect ratio contact (HARC) etching process, which is one of the most critical steps, has encountered a significant challenge. HARC, typically performed at room temperature, has become increasingly difficult to achieve the desired high aspect ratio while maintaining high productivity. This challenge is expected to become harder when considering devices with highly stacked alternating layers of silicon-containing materials, such as SiO_2 and SiN. Therefore, cryogenic HARC technology has emerged as a promising solution to overcome this challenge, as it offers advantages in terms of productivity and better etch profile. Consequently, we conducted cryogenic aspect ratio etching of SiO_2 at $CF_4/H_2/Ar$ plasma in a cryogenic reactive ion etch system. Overall, our results revealed that cryogenic aspect ratio etching of SiO_2 showed a higher etch rate and a higher aspect ratio under the experimental conditions. With these conditions, we conducted the cryogenic aspect ratio contact etching of SiO_2 for the comparison with the etching of SiO_2 at RT as well.

Atomic Scale Processing Mini-Symposium
Room C124 - Session AP+PS-FrM

Atomic Scale Processing Late Breaking Atomic Layer Etching and Area Selective Deposition

Moderator: Eric Joseph, IBM T.J. Watson Research Center

8:20am **AP+PS-FrM-1 Atomic Layer Etching of SiO_2 via H_2/SF_6 Plasma and TMA***, **David Catherall**, A. Minnich,* California Institute of Technology

The quality factor of ultrahigh Q silica microdisk resonators has reached values exceeding one billion but remains at around an order of magnitude below intrinsic upper limits 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. Here, we report an ALE process for etching of SiO_2 using sequential exposures of TMA and $Ar/H_2/SF_6$ plasma. The $Ar/H_2/SF_6$ plasma has been reported to enable in-situ production of HF, enabling HF exposures in the ALE process without the need for an external source of HF vapor. We observe etch rates up to 0.6 Å per cycle and examine the effect on surface roughness. This work advances a process of relevance to ultrahigh Q silica resonators which are fundamental elements of on-chip photonic devices such as frequency combs.

8:40am **AP+PS-FrM-2 Area Selective Deposition of HfO2 on Oxide and Nitride Surfaces***, **ByungChan Lee**,* Incheon National University, Republic of Korea*; C. Nguyen,* Incheon National University, Viet Nam*; S. Shim, Y. Kang, H. Lee,* Incheon National University, Republic of Korea

Due to the scaling down in the Si device fabrication, the aspect ratio and complexity of 3D device structures is rapidly increased, leading to the limitation of the conventional fabrication process including deposition, etching, lithography and so on. Area selective deposition (ASD) has received great attentions from the Si industry as one of the unit processes to overcome the limitations. ASD is developed based on the atomic layer deposition (ALD) which has the unique self-saturation surface reaction mechanism. The surface chemical properties are modified by using the promoter or inhibitor which promotes or inhibits the thin film growth, respectively. Accordingly, the ALD thin films are selectively deposited on the desired area. At the beginning of the ASD research, the self-assembled monolayers (SAMs) were commonly used as an inhibitor. But the inherent size of SAMs has potential problems for the pattern interference in nm-size scale. In this study, we investigated the ASD using a small molecule inhibitor (SMI). We selected the aldehyde molecules as SMI to inhibit the nitride surface but not on oxide surface. By using density functional theory (DFT) calculation, adsorption behaviors and energetics of the aldehydes was studied on nitride and oxide surfaces. From the experiments, it was observed that the aldehyde selectively adsorbs on only nitride surface but not on oxide surface and block the HfO_2 deposition until 15 cycles. The inhibition of nitride surface using SMI can contribute to many unit processes of Si device fabrication by simplifying the process scheme.

9:00am **AP+PS-FrM-3 Surface Functionalization of SiN_x over SiO_2 with Aldehydes to Enable Area-Selective Atomic Layer Deposition***, **Andrew Kaye**,* Colorado School of Mines, USA*; S. Agarwal,* Colorado School of Mines*; B. Zope, A. Derecskei, R. Pearlstein, X. Lei,* EMD Electronics, USA

As the semiconductor device dimensions continue to shrink, area-selective atomic layer deposition (AS-ALD), which is a bottom-up technique, can address the challenges associated with device fabrication. SiO_2 and SiN_x are two of the most commonly used dielectrics in semiconductor devices, and deposition on one dielectric with minimal deposition on the other can simplify processing. For example, in 3D-NAND structures, there are alternating layers of SiO_2 and SiN_x, and during processing, it is desirable to grow a metal oxide on SiO_2 with no growth on SiN_x. In AS-ALD, inhibitor molecules can be used to functionalize SiN_x because very few ALD precursors have an inherent binding selectivity to SiO_2 over SiN_x. Finding inhibitor molecules that selectively adsorb on SiN_x over SiO_2 is also challenging since on SiO_2 films contain SiOH groups, which react readily with many compounds such as chlorosilanes, alkoxides, and aminosilanes. We have previously shown that aldehydes selectively adsorb on SiN_x with minimal adsorption on SiO_2.

This work focuses on the adsorption mechanisms of two aldehydes, 3,5,5-trimethylhexanal (TMH) and dodecanal (DDA), on plasma-deposited SiN_x films characterized with *in situ* attenuated total reflection Fourier transform infrared spectroscopy. We show that TMH adsorbs on SiN_x forming silyl ethers, amino alcohols, enamines, and imines with surface $-SiH_x$ and $-NH_x$ groups being the reactive sites. Reaction of DDA with SiN_x leads to the formation of similar surface species except for enamines. Amino alcohols are reaction intermediates formed due to the reaction of surface amines with aldehydes — the complete reaction should result in the formation of imines with H_2O as the byproduct. The presence of amino alcohols is not desirable since the -OH group may react with metal ALD precursors and reduce selectivity. We show that once the amino alcohols are formed on the surface, they cannot be converted to imines by increasing the substrate temperature. The surface composition of the underlying SiN_x film greatly affects the uptake of the aldehyde and the relative ratio of the surface species formed after adsorption of both aldehydes. The aldehydes desorb from the surface when the substrate temperature is increased, and further desorption occurs over time at elevated temperatures. After desorption at a constant temperature, TMH can be replenished by redosing. In practical applications the SiN_x surface is partially oxidized upon exposure to the atmosphere. To understand the effect of surface oxidation, the plasma-deposited SiN_x films were exposed to the atmosphere for several days. The atmosphere exposed SiN_xfilms were then cleaned with D_2 plasma to possibly etch the surface oxide layer to enhance reactivity by restoring $-SiD_x$ and $-ND_x$ surface species.

9:20am **AP+PS-FrM-4 Surface Reactions During Atomic Layer Etching of Platinum by High-Density Nitrogen-Oxygen Plasma and Organic Acid Vapor***, **Thi-Thuy-Nga Nguyen**,* Nagoya University, Japan*; D. Akagi, T. Uno, T. Okato,* AGC Inc., Japan*; K. Ishikawa, M. Hori,* Nagoya University, Japan

Anisotropic patterning process of metal layers in complex nanostructures is a big challenge. Pt is a promising material, but it is a hard-to-etch material. Dry etching of Pt thin film has been developed by using halogen-based plasmas of SF_6, CF_4, or Cl_2 gas. However, the anisotropic etch profiles of Pt films in most cases have not achieved due to the redeposition of the etch residues that produces fences or tapered sidewall. Recently, non-halogen chemistry for noble metal etching has been developed using atomic layer etching (ALE) with surface modification by oxidation and removal of the oxide layer by vapor of organic compounds [1].

Our developed floating wire-assisted high-density plasma at medium pressure significantly increases the chemical reaction rate to the sample surface, that was applied in the reduction of SnO_2 [2] and dry etching of TiAlC [3]. Here, we have demonstrated ALE of Pt via high-density plasma oxidation and removal of the modified layer by organic acid vapor or organic acid plasma. High-density nitrogen-oxygen based plasma (N-O plasma) was generated to fully oxidize Pt surface and form a dominant oxidation state (Pt^{4+}). Surface modifications after the reactions of Pt with N-O plasmas and the modified layer with organic acid vapor or plasma were analyzed by X-ray photoelectron spectroscopy. The film thickness was characterized by ellipsometry and X-ray reflectivity. Surface roughness was analyzed by atomic force microscopy, and patterning profiles were observed by transmission electron microscopy. The N-O plasmas and organic acid plasmas were diagnosed by high-resolution optical emission spectroscopy.

The formation and desorption of organometallic compounds on Pt surface are able to be atomic-level controlled at low temperature (less than 100 ^{o}C). A smooth surface of Pt film was obtained with the etch depth per cycle from 0.3 to 0.7 nm/cycle. The exposure of Pt film to N-O plasmas determines the dominant oxidation state, surface roughness, and thickness of the modified layers, that strongly affects to etching performance of Pt film. The non-halogen atomic layer etching of Pt has been successfully developed in this study.

[1] J. Chang and J.P. Chang, J. Phys. D: Appl. Phys.50, 25 (2017).

[2] T.T.N. Nguyen et al., Plasma Process. Polym. 19, 6 (2022).

[3] T.T.N. Nguyen et al., Sci. Rep. 12, 1 (2022).

9:40am **AP+PS-FrM-5 Isotropic Plasma-Thermal Atomic Layer Etching and in-Situ Atomic Layer Deposition Passivation of Aluminum Films for Superconducting Quantum Devices***, **Haozhe Wang**,* Duke University*; I. Chen, D. Catherall, A. Hossain, A. Minnich,* California Institute of Technology

Metallic and dielectric film surface imperfections negatively impact the performance of superconducting quantum devices, including qubits and microwave kinetic inductance detectors. Despite considerable exploration into the effects of these imperfections on decoherence and low-frequency fluctuations, contemporary microfabrication methodologies fall short in rectifying them. Here, we report an atomic layer etching and in-situ deposition (ALE/ALD) process that enables the etching of the native oxide and passivation of aluminum films, all in high vacuum. The process for both ALE and ALD involves sequential exposures to SF_6 plasma and TMA at temperatures around 300 °C; whether the exposures lead to deposition or etching is controlled by adjusting the duration of each dose at the selected temperature. The resulting films are characterized using x-ray photoelectron spectroscopy, high-resolution transmission electron microscopy, and energy-dispersive spectroscopy. The characterization methods indicate that the ~ 40 Å thick native oxide was removed and the resulting surface passivated with ~ 10 Å of AlF_3. Using x-ray photoelectron spectroscopy, we confirmed that the films are resistant to re-oxidation after exposure to the atmosphere for nine months. Our approach to engineer the surfaces of superconducting films at the atomic scale may enable superconducting quantum devices with improved performance.

Plasma Science and Technology Division
Room A107-109 - Session PS+NS-FrM

Advanced Patterning and Plasma-Engineered Materials

Moderator: Angelique Raley, TEL US

8:20am **PS+NS-FrM-1 EUV Lithography Patterning towards Devices Nano Scaling**, ***Danilo De Simone,*** IMEC, Belgium **INVITED**

Nowadays, the device scaling driven by the Moore's law is continuing by the deployment of the 0.33NA extreme ultraviolet lithography (EUVL) in high volume manufacturing further driven by the need to improve cycle time and cost. To further simplify and improve EUV patterning reducing cost and enable 2nm technology and below, high NA EUV lithography (0.55NA) is under development. At the same time, as the nanoscale is pushed further down, the stochastic nature of the patterning process and the thinning down of the films become the major patterning roadblocks. To enable the high NA technology, new knobs and faster learning cycles on patterning process development are needed to improve the process window. This presentation will show the latest development on EUV patterning materials and their challenges and provide an insight status of overcoming these obstacles towards the devices scaling at nanometric level.

9:00am **PS+NS-FrM-3 Break Healing and LER Mitigation for Low Dose EUV Exposure**, ***Rémi Vallat****, P. Bézard, B. Chowrira,* IMEC, Belgium*; A. Fathzadeh, W. Halim,* KU Leuven, Belgium*; F. Lazzarino, K. Ronse,* IMEC, Belgium

Challenges introduced with High NA EUV lithography will be defectivity management with ultra-thin resists while using low EUV dose[1]. Reducing the density of bridges and breaks is thus a major point of focus for its introduction[2]. Ultra-thin resists, at low EUV dose, may come with high bridge/ break density (positive/ negative-tone resist, respectively). In the case of bridges, a descum step is traditionally introduced, which creates breaks instead (in ultra-thin resists) and further reduces the resist budget for underlayer patterning. Therefore, recovering breaks is a strategic capability for defect reduction.

The proposed way to recover breaks is to use non-conformal PECVD deposition on top of spin-on-glass (SoG). Since, the resist budget is going to be ultra-thin, the underlayer beneath will also have to be ultra-thin, leading to its failing as an hard-mask (break creation) during transfer into an amorphous carbon layer. Depositing extra Silicon-based polymers on top of the ultra-thin underlayer addresses that issue, by increasing the hard-mask etch budget. However, the polymer must be deposited on SoG, selectively to amorphous carbon to prevent the formation of an etch-blocking layer. This approach is presented in figure 1.

The selectivity of deposition is successfully developed, and results are shown in figure 2. The underlayer budget is clearly increased using PECVD. Also, the reduction in break density is demonstrated in figure 3 using a radical ion etching and/or quasi-atomic layer etch into aC, designed to maximize the break density in order to easily observe any improvement brought by the PECVD. The line-edge roughness is improved as well, due to the reduced contribution of breaks.

[1] L. Meli et al,*Proc. SPIE* 11609, 116090P (2021)

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

9:20am **PS+NS-FrM-4 Carbon Resist Microlens Etching in DF-CCP CF_4 Plasmas: Comparison between Modeling and Experiments***, P. Ducluzaux,* Univ. Grenoble Alpes, CNRS, LTM / STMicroelectronics, France*; D. Ristoiu,* STMicroelectronics, France*; G. Cunge,* ***Emilie Despiau-Pujo,*** Univ. Grenoble Alpes, CNRS, LTM, France

Over the past decade, the development of image sensors used in smartphones has focused on reducing pixel size to improve photography resolution. Microlenses are a key component of these sensors, as they focus the incident light on the photodiode, enhancing the sensor's quantum efficiency. However, the manufacture of resist microlenses requires an etching step in low-pressure fluorocarbon plasmas, in which complex chemico-physical reactions can lead to a final 3D shape that is difficult to control.

In this paper, we propose to investigate numerically the influence of tunable operating conditions (RF power, pressure, etc.) on the etching of carbon resist microlenses in CF4 plasmas, to better understand the link between process parameters, plasma properties and the final microlens shape. Using a 2D hybrid model (Hybrid Plasma Equipment Model), we simulate the CF4 plasma gas-phase in a dual-frequency capacitively coupled plasma reactor. We then use the plasma properties obtained from this simulation (densities, fluxes, and energies of charged and neutral species) as entry parameters for an etching profile model (Monte Carlo feature profile module). First, we investigate numerically and experimentally (ellipsometry, TOF-SIMS) the impact of pressure (30-200 mT) and RF powers (100-1500 W) on the etch rate and on the cross-sectional structure (chemical composition, reactive layer thickness) of resist blanket wafers. Then, we analyze the impact of these parameters on the etching of spherical resist microlenses, comparing the simulated 3D final shape with experimental profiles (AFM, SEM) obtained in an industrial reactor.

Our results show that the low-frequency (13.56 MHz) power increases the F penetration in the resist due to an increase in the ion energy, while the high-frequency (40 MHz) power increases the etch rate due to an increase in the ion flux. The impact of operating conditions on the microlens profiles will be discussed in details during the presentation and provide insights into the chemico-physical mechanisms involved in carbon resist etching.

9:40am **PS+NS-FrM-5 Investigations of Surface Reaction Mechanisms in Euv Induced Hydrogen Plasmas***,* ***Tugba Piskin,*** University of Michigan*; V. Volynets, S. Nam, H. Lee,* Samsung Electronics Co., Inc., Republic of Korea*; M. Kushner,* University of Michigan

The deployment of extreme ultraviolet lithography (EUVL) is enabling a few nm critical sizes in microelectronic processing.In one implementation, the EUV photon beams are produced by ablating and ionizing tin droplets with a pulsed laser.The ionized tin species emit photons with 13.5 nm wavelength—where these photons are collected by reflective optics and transferred to the scanner unit.The collector mirror is exposed to the tin plasma, which potentially results in a decrease in reflectivity and lifetime.Pumping H_2 through the EUV chamber can help resolve this problem as an in-situ cleaning technique of deposited tin on the mirror. The hydrogen slows down fast tin radicals by reacting with them in the gas phase and etching. Photoionization of the H_2 by the EUV produces a plasma which etches the deposited tin on the mirror by producing stannane.

EUV photons with 92 eV energy are capable of photo-dissociating and ionizing hydrogen gas while producing energetic electrons and H atoms. Ions, energetic electrons, and photons in turn produce secondary electron emission from surfaces, the latter of which can also produce energetic electrons.In this work, we computationally investigate the etch rate of tin and the redeposition of stannane in a generic EUV lithography tool by the EUV produced hydrogen plasma using a modified version of the Hybrid Plasma Equipment Model (HPEM).The consequences of secondary electron emission from the surfaces by electrons and photons will be discussed.The fluxes of hydrogen radicals and ions to the collector mirror are the most significant factor for the in-situ cleaning. The energy and angular distributions and fluxes to the collector mirror of hydrogen radicals and ions for pressures of a few to hundreds of Torr and hundreds of Watts EUV power will be discussed.

Work supported by Samsung Electronics and the US National Science Foundation.

10:00am **PS+NS-FrM-6 Area Selective Processing Based on Physisorption to Improve Functions of Extreme Ultraviolet Resist***,* ***Van Long Nguyen,*** *N. Maldonado, G. Denbeaux, C. Vallee,* SUNY Polytechnic Institute, Albany

In semiconductor manufacturing, ~10 nm critical dimensions are already in production by using EUV lithography [1]. The smaller critical dimensions require better line edge/width roughness (LER/LWR) or local critical dimension uniformity (LCDU) of EUV resists to ensure the quality of patterning features, as well as device performance. Furthermore, ultrathin EUV resists (20- to 40-nm) are currently utilized to minimize the risk of pattern collapse, which however results in poor etching selectivity to underlying layers for post-lithographic pattern transfer. Recently, employing area selective deposition as a post-treatment method on the EUV resist patterns has been reported as a promising strategy to improve the function of EUV resists [2]. In this research, we tried to improve the local roughness and thickness of the EUV resist by developing an area selective (AS) processing including both deposition and infiltration based on the physisorption mechanism, instead of the conventional chemisorption mechanism. We achieved AS physisorption based on the difference in Van der Waals interactions of surfaces/bulks with a specific gas molecule. The interaction of physisorbed molecules with samples is calculated based on a classical model. SO_2 gas was chosen based on the theoretical calculation to test its selective physisorption capability to the Sn-based resist versus SiO_2. After SO_2 exposure, we observed a significant thickness increase in the case of Sn-based resist (Figure S1a) but not in the SiO_2 (Figure S1b), as shown in the supplemental document. The observed thickness increase suggested SO_2 could both selectively physisorbed onto the surface and into the bulk of the resist due to its porosity. These selective physisorbed molecules onto the surface and into the bulk of the resist are then converted to chemisorbed molecules by a dissociation process using energetic Ar plasma to complete a cycle of AS deposition and AS infiltration, respectively. Ellipsometry, angle-resolved X-ray photoelectron spectroscopy, and atomic force microscopy are employed as key techniques to characterize changes during and after the AS processing. This work is funded by Semiconductor Research Corporation (SRC).

[1] https://irds.ieee.org/editions/2022/executive-summary for International Roadmap for Devices and Systems (IRDS), 2022 Edition.

[2] Nye, Rachel A., et al. "Enhancing Performance and Function of Polymethacrylate Extreme Ultraviolet Resists Using Area-Selective Deposition." Chemistry of Materials 35.5 (2023): 2016-2026.

10:40am **PS+NS-FrM-8 Recent Advances in Ga_2O_3 Material Development at AFRL**, *S. Mou, T. Asel, A. Neal, Y. Kim,* ***Brenton Noesges****, A. Charnas, J. Li, T. Back, K. Burzynski, B. Newton, A. Green, J. Blevins,* Air Force Research Laboratory, Materials and Manufacturing Directorate, USA **INVITED**

Ga_2O_3 has been of interest due to its critical electric field (8 MV/cm)[1], its ability for native substrates to be grown from the melt, and the ability to controllably dope thin films of Ga_2O_3 via growth methods such as molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD). All of these properties make Ga_2O_3 an attractive candidate for high power electronic applications and the ability to grow substrates from the melt make it economically feasible in this space when compared to other materials such as GaN and SiC. The Air Force Research Lab (AFRL) has invested into substrate development with Northrup Grumman Synoptics to provide a domestic source of substrates. Czochralski grown (010) Fe and Mg doped Ga_2O_3 has been demonstrated up to 2 inch wafers by Northrup Grumman Synoptics and challenges in surface polishing have been overcome by using a 2 step process that removes subsurface damage and produces a surface that is ready for epitaxial growth. AFRL's in house research on epitaxial films via plasma assisted MBE has identified sources of unintentional doping during the growth of Ga_2O_3. It was demonstrated that both the oxidation of the Si doping source material and the quartz bulb used to provide the oxygen plasma during growth were contributing significant amounts of Si in the grown films. By adjusting the plasma power to reduce the etching of the quartz plasma bulb we were able to demonstrate epitaxial films with unintentional doping levels $<1 \times 10^{16}$ cm^{-3}. Control of the intentional Si doping was achieved in collaboration with Cornell University by modifying the Si doping source to include a "showerhead" to reduce the effect of the oxidation of the Si source material[2, allowing control from 8×10^{16} cm^{-3} to 1×10^{19} cm^{-3}. Additional thin film development was done in collaboration with Agnitron on MOCVD grown Ga_2O_3 films. High purity Ga_2O_3 films were demonstrated using trimethylgallium as the source for gallium during the growth. The MOCVD grown films' mobility and carrier concentration were measured via temperature dependent Hall Effect at AFRL and exhibited a record electron mobility of 23,400 cm^2/Vs at 32 K, with a low acceptor concentration of 2×10^{13} cm^{-3}, further demonstrating the purity of the films grown via this method[3]. These results demonstrate the investment that AFRL has in Ga_2O_3 and present the contributions that AFRL has made to the development to Ga_2O_3 material system.

[1] M. Higashiwaki et al. Appl. Phys. Lett. **100,** 013504 (2012).

[2] J.P. McCandless et al. Appl. Phys. Lett. **121,** 072108 (2022).

[3] G. Seryogin et al. Appl. Phys. Lett. **117**, 262101 (2020).

11:20am **PS+NS-FrM-10 Reverse Lift-Off Process to Avoid Sidewall Artifacts Resulting from Dry Etching "Challenging" Materials**, *D. Lishan,* Plasma-Therm, LLC; *V. Genova,* Cornell University; *S. Norris,* Axoft; *K. Dorsey,* Physical Sciences, Inc.; ***Sabrina Rosa-Ortiz****,* Plasma-Therm LLC

This work explores a process to avoid sidewall redeposition issues when dry etching materials that do not readily form volatile and desorbing etching byproducts under common operating temperatures. Common dry patterning approaches for these challenging thin films use methods relying on physical mechanisms (i.e., sputtering with accelerated ions) and often result in material being redeposited on the sidewalls of the masking material. Upon removing the mask, the resputtered sidewall material remains and forms features projecting above the material. These features, sometimes referred to as rabbit or dog ears, fences, and veils, may fall over, break and cause particles, or penetrate over layers. We present an etching approach that avoids these issues. Materials such as Pt, Au, Ni, $LiNbO_3$, Cu, Ni, Fe, Mn, Co, Mn, PZT, ScAlN, and perovskites fall in the category of "challenging" to etch materials and impact applications such as MRAM, PiezoMEMS, quantum devices and photonics.

Lift-off patterning requires line-of-sight deposition which is typically an evaporative process that constrains thermal budgets and materials that can be deposited. We discuss a technique derived from this well-known additive method of patterning thin metal layers but using a subtractive approach. In this "reverse -lift" off approach, a layered structure with an undercut in a sacrificial layer is also used. Following etching, the material that was sputter etched and redeposited on sidewalls is removed along with the sacrificial layer. Unwanted redeposition is avoided with the proper choice of sacrificial layer material, mask, and undercut structured or with familiar lift-off resist patterning (LOR). Importantly, the dry etching can be done in common parallel plate RIE and ICP configurations and does not require an ion gun source, thus making the method more accessible.

Results demonstrate physically etching a difficult material without the consequences of resputtered material. Pt was used as a test vehicle with film thicknesses up to 200 nm. Positive results were obtained with LOR patterning, with SiO_2 as the mask with a Si sacrificial layer, and with a Cr sacrificial layer. Both IBE and ICP configurations were used with similar results showing that the expected feature dimensions were maintained without the profile changes typically observed with tilt and rotation IBE. Modeling considered feature spacing, resputter distribution (cosine ejection), and incident ion angles to better understand the limits and dimensions of the lift-off structure. This work offers a process technique that can solve the issue of dog ears when plasma etching low or nonvolatile materials.

11:40am **PS+NS-FrM-11 Control of Ge/Si Core/Shell Nanoparticles Growth In Pulsed Nonthermal Plasmas**, ***Yifan Gui****, J. Polito, M. Kushner,* University of Michigan

Core/Shell nanoparticles(CSNPs) are a type of nanomaterial that has the characteristic structure of a core and an outer shell composed of distinct materials. CSNPs have received increasing attention over the past decade due to their tunable optical properties and wide applicability in the biomedicine, semiconductor and catalyst fields. The major challenges in synthesizing CSNPs with consistent specifications lie in the variation of size uniformity, core and shell purity as a result of diverse operating conditions.

While continuous-wave nonthermal plasma approaches for synthesis of CSNPs have enabled crystalline growth at low reactor temperatures, pulsing the plasma could give an edge in CSNPs production by addressing these issues. Both computational and experimental prior works have demonstrated the capability of pulsed nonthermal plasma in synthesizing nanoparticles with improved size uniformity[1,2].

The aim of this work is to computationally investigate the consequences of pulsed power nonthermal plasmas on size uniformity and core/shell purity of Si/Ge CSNPs using the Hybrid Plasma Equipment Model (HPEM) coupled with DTS Dust Transport Simulation Module (DTS). The test system is an inductively coupled plasma (ICP) having two plasma sources intended to enhance CSNP size uniformity while utilizing separate core and shell synthesis zones for better core/shell purity control. CSNPs are produced under operating conditions of a few Torr, 10 W of ICP power with pulse period of 50 µs, with Ar/GeH_4 and Ar/$SiH\text{-}_4$ gas mixtures flowing from top and middle inlets. The consequences of process parameters such as pulse period, duty cycle and ICP power, and the corresponding impacts on CSNP properties will be discussed and compared to CSNP properties resulting from continuous-wave operation.

Work supported by Army Research Office MURI Grant W911NF-18-1-0240, the National Science Foundation (PHY-2009219), and the Department of Energy Office of Fusion Energy Science (No.DE-SC0020232).

[1] S. J. Lanham, et al. Journal of Applied Physics **132,** 073301 (2022)

[2] J. Schwan, B. Wagner, et al. J. Phys. D: Appl. Phys. **55**, 094002 (2022)

Plasma Science and Technology Division
Room A106 - Session PS+SE-FrM

Atmospheric Pressure Plasmas and Their Applications

Moderators: Michael Johnson, Naval Research Laboratory, USA, **Floran Peeters**, LeydenJar Technologies

8:20am **PS+SE-FrM-1 Electrolyte Engineering for Nitrogen Fixation by Plasma Electrolysis***, **Brandon Kamiyama,*** University of Illinois at Urbana Champaign*; M. Eslamisaray,* University of Illinois Urbana-Champaign*; R. Pierrard, R. Sankaran,* University of Illinois at Urbana Champaign

The fixation of nitrogen is critical to our most basic need, the growth of plants for food. Industrially, nitrogen is fixed to ammonia (NH_3) by the Haber-Bosch process which has a large physical and environmental footprint. The development of alternative methods that are sustainable and deployable at a small scale has become one of the active areas of research. Among the different approaches being explored, plasma-based electrolytic reactors have shown the most promise, capable of activating nitrogen in air or with water as a source of hydrogen at atmospheric pressure and near room temperature without any catalyst and using only electricity which could in the future come from renewable sources. However, a key challenge is selectivity of products with typical processes producing NH_3, nitrates (NO_3^-), and nitrites (NO_2^-).

In this work, we studied direct-current plasma in contact with an electrolyte solution. Various products were characterized in the liquid phase including NH_3, NO_3^-, NO_2^-, as well as hydrogen peroxide (H_2O_2). To control the product selectivity, various conditions were mapped including gas feed, cathodic vs. anodic polarity, and pH. Our most promising result was that the pH and more generally, the electrolyte composition, was found to greatly influence the product distribution. At low pH, the product distribution shifted more to the reduced form, NH_3, and at high pH, the distribution shifted more to the oxidized form, NO_3^-, We also found a strong effect on the presence of O_2 (in air) and humidity. These results can be used to selectively synthesize nitrogen products, elucidate product formation mechanisms, or to inform scale up of similar plasma-liquid systems for sustainable nitrogen fixation.

8:40am **PS+SE-FrM-2 Two Atmospheric Pressure Plasma Jets Driven by Phase-Shifted Voltages: A Method to Control Plasma Properties at the Plasma–Surface Interface***, **Michael Johnson,*** Huntington Ingalls Industries*; G. Brown,* University of Texas, Austin*; D. Boris, T. Petrova, S. Walton,* Naval Research Laboratory

Atmospheric pressure plasma jets project plasma away from their electrodes, enabling the treatment of remotely located surfaces, and making them appealing for a diverse range of surface treatment applications. However, their small effective areas pose a challenge to broader adoption and utilization. To circumvent this limitation, multiple plasma jets can be used in tandem to increase their effective area. The objective of this study is to examine the interactions between two plasma jets and leverage this relationship to manipulate plasma properties at the plasma-surface interface. The jets are positioned at a 130° angle from each other, converging at the surface of a glass substrate. Each jet is driven by an individual piezoelectric transformer, powered by identical but phase-shifted voltage waveforms, which provides precise control over their relative timing and influence plasma properties. As phase difference between the two jets is varied the jet behavior changes from a regime where the two jets repel each other to a regime of enhanced jet interaction, resulting in an expanded effective area for the plasma. Interestingly, increasing this phase difference led to reduced power consumption while simultaneously enhancing electron density at the intersection point. Consequently, this technique of utilizing phase-shifted jets presents a method for increasing the effective area of the plasma and controlling plasma properties at an interface, potentially benefiting a wide array of applications.

This work supported by the Naval Research Laboratory Base program

9:00am **PS+SE-FrM-3 Plasma Chemistry in Atmospheric Pressure Gases and Liquids: Fundamentals and Novel Applications***, **Alexander Fridman,*** Drexel University, Nyheim Plasma Institute **INVITED**

The presentation is focused on fundamental and applied aspects of the non-equilibrium plasma chemical processes performed in high pressure gases and liquids. As an example of the gas-phase processes, the plasma synthesis of NO from atmospheric pressure air is considered, with especial attention on minimizing energy cost of the process. As an example of the plasma-chemical processes in liquid water, the PFAS abatement in considered with especial attention to complete mineralization of these important impurities. As an example of plasma chemistry in cryogenic liquids, the plasma synthesis of polymeric nitrogen is considered. The process is accomplished in liquid nitrogen using the nanosecond-pulsed discharges organized with creation of bubbles during the synthesis.

9:40am **PS+SE-FrM-5 Integrated Circuit Manufacturing with Plasma Activated Chemical Treatment (IMPACT): Effect of Plasmas on Photoresist and Cleaning Solutions in Semiconductor Processing***, **Christian Williams,** S. Dubowsky, D. Curreli, M. Sankaran, D. Ruzic,* University of Illinois at Urbana-Champaign

Low-temperature, atmospheric-pressure plasmas open various chemical and material applications because of their ability to be in contact with temperature-sensitive surfaces such as plastics and liquids. In this work, we investigated the potential of plasmas to modify two key components of semiconductor processing [1]: the photoresist and cleaning solution used to remove the photoresist after lithographic exposure. Two different plasma sources were used in experiments, a dielectric-barrier discharge and a pulsed direct current discharge jet. Characterization of the gas phase was performed by optical emission spectroscopy (OES) and the chemical modification of the treated solutions was examined using ion chromatography (IC). Ultraviolet-visible (UV/Vis) spectroscopy was also used to measure OH radical concentrations in the treated samples. In parallel, a reaction network was constructed using CRANE, a MOOSE-based tool for plasma chemistry modeling. Simulations provided the concentrations of species which could then be compared to experiments to understand potential reaction mechanisms.

10:00am **PS+SE-FrM-6 Increasing Adhesion of Polyurethane Painting on Aluminum by Atmospheric Pressure Plasma Jet Treatment***, **Jorane Berckmans,** C. Tubier,* Chemistry of Surfaces, Interfaces and Nanomaterials (ChemSIN), Faculty of Sciences, Université Libre de Bruxelles, Brussels, Belgium*; R. Revilla Castillo,* Research Group Electrochemical and Surface Engineering (SURF), Department of Materials and Chemistry, Vrije Universiteit Brussel, Brussels, Belgium*; C. Poleunis,* Unité Physico-Chimie et de Physique des Matériaux (PCPM), Université Catholique de Louvain, Louvain-la-Neuve, Belgium*; H. Terryn,* Research Group Electrochemical and Surface Engineering (SURF), Department of Materials and Chemistry, Vrije Universiteit Brussel, Brussels, Belgium*; A. Delcorte,* Unité Physico-Chimie et de Physique des Matériaux (PCPM), Université Catholique de Louvain, Louvain-la-Neuve, Belgium*; F. Reniers,* Chemistry of Surfaces, Interfaces and Nanomaterials (ChemSIN), Faculty of Sciences, Université Libre de Bruxelles, Brussels, Belgium

Nowadays, industries are looking for replacement of chromium VI in aluminum pretreatment. In this quest, plasma treatments could represent an interesting approach. Indeed, atmospheric plasmas enable a wide range of possible modifications of materials (etching, grafting, surface functionalization) but also allow an easy industrial upscale.[1,2]

In this work, aluminum 99,99% surfaces were modified by an atmospheric pressure plasma jet (APPJ) and the effect on polyurethane paint adhesion was studied. The difference in wettability, chemistry and roughness induced by plasma treatments were investigated by water contact angle, X-ray photoelectron spectroscopy and atomic force microscopy respectively. In parallel, optical emission spectroscopy (OES) was used to characterize the plasma phase. The correlation between plasma species, identified by OES, and the resulting surface modification was investigated. Then, the adhesion of the polyurethane coatings on the plasma-modified surfaces was studied by a tape test according to ASTM D3359. The coating – aluminum substrate interface has been also characterized by Tof-SIMS, to identify specific fragments characteristics for bonding.

Different plasma sources were used, with different plasma conditions (PlasmaTreat Openair FG5001, 2 bars of dry air, at varying distances from 5 mm to 10 mm and treatment times of 0,5 to 60,0 s by tuning the number of scans and the scan rate of the APPJ over the surface, SurfX Atomflo 600, with 30,0 L/Min of Ar at varying flow of oxygen from 0,00 to 0,60 L/ Min, distance from 5 mm to 30 mm and treatment times of 0,04 s to 25 s by tuning the number of scans and the scan rate of the APPJ over the surface). Varying humidity containing in plasma, by water injection, was also studied with the SurfX Atomflo 600.

It is shown that, for most of the plasma treatments used, an increase of the adhesion of polyurethane coatings is observed (Fig. 1) and associated with the surface modification of the aluminum and with the plasma chemistry.

References

[1] H. Butt, K. Graf, M. Kappl, Phys. Chem. Interfaces 2013, 28,1379.

[2] K. G. Kostov, T. M. C. Nishime, A. H. R. Castro, A. Toth,L. R. O. Hein, Appl. Surf. Sci. 2014, 314, 367.

Acknowledgements

This work is partly supported by the ULB-VUB “joint research group” fund.

10:40am **PS+SE-FrM-8 Fundamentals of Atmospheric Pressure Discharges for Plasma Catalytic Applications**, ***Judith Golda***, *D. Steuer, R. Labenski, H. van Impel, M. Böke, V. Schulz-von der Gathen,* Ruhr-University Bochum, Germany **INVITED**

A central challenge of our time is the energy transition from fossil energy sources to renewable ones. Plasma catalysis is one of the promising techniques that has been proposed to contribute to this transition. Research shows that synergies between classical catalysis and plasma processes can be obtained due to the distinct non-equilibrium character of atmospheric pressure plasmas and their interaction with surfaces. However, the underlying mechanisms are hard to entangle as typical reactor designs for plasma catalysis are packed bed reactors. While advantageous for industrial processes, the diagnostics of these reactors is challenging.

In this talk, we give an insight into the diagnostic challenges of plasmas for catalysis as well as possible approaches to overcome them. We will discuss alternative reactor designs for fundamental studies such as micro-structured surface dielectric barrier discharges. We will give an overview of global and local diagnostic techniques: Current-voltage characteristics for dissipated plasma power and estimation of electron densities, emission-based techniques for reactive species densities such as atomic oxygen (state-enhanced actinometry) or temperature (rotational bands), and electric field estimation (Stark splitting and shifting).

This research is funded by the German Research Foundation within CRC 1316 in project A6.

11:20am **PS+SE-FrM-10 Atmospheric Pressure Inductively Coupled Torus Torch System for 3D Printing the Silicon-Nanofiber (Si/CNF) Anodes for Li-ion Batteries**, ***Yuri Glukhoy,*** Nanocoating Plasma Systems Inc; *M. Ryaboy,* UC Berkeley

Our approach to environmentally-friendly manufacturing low-cost Si anodes with the core-shell heterostructure includes 3D plasma beam printing. Excitingly, because of the merits of low price, high doping content, and no toxic emission during the process, Si sawdust, which is a waste of the solar cell industry, can be a fascinating raw material for Si shells with well-tailored functions and electrical properties. However, the transition of the Si sawdust requires a long resident time in the high-temperature plasma and a high RF power to sustain it. We offer a new method of generation of Si vapor and the simultaneous lamination of CNFthrough the recirculation of both Si and CNF in the high-temperature torus plasma torch. It allows the incremental sublimation of Si particles, while Si vapor is deposited in the fly on the fibers' preheated surfaces. This torus torch recirculated in the high-temperature doughnut-like reactor is generated by two tangentially injected in the opposite direction axial atmospheric plasma beams in the swirling mode. Besides the high-temperature plasma species, these beams are designed to bring the liquid Si droplets from the melted Si powder injected into the high-temperature plasma discharge generating such a beam.Two inductors with transversal RF fields are positioned on the opposite sides of the doughnut and surround this profile. They boost this torus plasma torch, increasing the plasma density and current until its magnetic field pinches into the high-temperature plasma cord. But RF power applied to the inductor should be limited to avoid melting the CNF at 3550 °C. This recirculation process in the high-temperature plasma reactor should provide a conformal Si lamination of CNF in the fly to achieve the Si shell's thickness of around 1 um. Two outlets are welded to this doughnut to extract the Si/CNF composites and generate the plasma sprays. Ended with the nozzles and directed to the opposite sides of the copper tape serving as a current collector, they provide 3D printing of the Si/CNF anodes in the roll-to-roll mode.

11:40am **PS+SE-FrM-11 Design and Functionality of a Low-Frequency Pulsed Plasma System**, *M. Gulan,* Technological University Dublin, Ireland; ***Vladimir Milosavljevic,*** Technological University Dublin, Ireland & Faculty of Physics, University of Belgrade, Serbia, Ireland

This study presents the design and functionality of a kHz pulsing plasma generator at atmospheric pressure, which can be used for a range of applications, such as sterilization in food processing or plasma-based treatments for biological samples. This next generation plasma system is developed to operate in ambient air or on an argon/helium/oxygen/nitrogen gas mixture at atmospheric pressure, making it suitable for a range of applications such as surface modification, plasma-based sterilization, and material processing. The system's unique design allows for improved efficiency, higher plasma density, and greater control over plasma parameters compared to previous systems. The plasma tool is particularly suitable for sensitive and fragile materials. This work describes the development and operation of a non-thermal, dielectric-free atmospheric plasma system designed for use in surface treatment and modification applications. The system was developed in-house to meet the specific technological needs, and includes detailed information on the design and operating parameters of the system. The new plasma system allows an increase in the plasma-surface interaction selectivity and reduces plasma induced damages to the surface. The innovative design of our plasma system led to the development of unique plasma parameters that are not currently available on the market. Specifically, the system allows for precise control of plasma temperature, density, and composition, which are essential for effective plasma treatment of a range of materials. These unique parameters were designed with the goal of simplifying plasma treatment in industrial applications such as surface modification, cleaning, and sterilization, where precision and efficiency are critical factors for success. The system creates a plasma discharge in gap from 5 to 60 mm in space of hundreds of cm^2. The plasma source is based on a pulse resonance circuit which allows the creation of high voltage pulses with the ability to control and reduce a current of the plasma discharge. The study also includes different setting of plasma source to control the ion flux, the ion energy and the plasma chemistry. Plasma pulsing allows new domains of ion energy and radical fluxes to be reached, thereby extending the operating range of plasma generators. The plasma diagnostics in this work include the absorption spectra of oxygen and nitrogen based molecules and their dependence on the process parameters such as duty cycle, discharge frequency, pick-to-pick voltage, etc.

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