Manufacturing Science and Technology Group
Room 305 - Session MS+HI-MoM

Machine Learning for Microelectronics Manufacturing Process Control and Materials Discovery R&D

Moderators: Tina Kaarsberg, U.S. Department of Energy, Advanced Manufacturing Office, **Gary Rubloff**, University of Maryland, College Park

8:20am **MS+HI-MoM-1 Advancing Semiconductor Industry Process Control via Data-Centric AI*, Jeff David,*** PDF Solutions **INVITED**

Data-Centric AI.Over the last several decades, much of the research and work in machine learning has been based on a model-centric approach or software centric approach.[1] In recent years, some of the codebase for core algorithms such as neural networks have reached a level of maturity where those base algorithms now essentially represent a solved problem for a lot of applications.This has created the opportunity to focus more on the data to improve results, where there is still a significant amount of room to improve the approaches to boost overall outcomes.Areas of Data-Centric AI that have received a growing amount of attention recently include[1]: Measuring data quality, Data iteration, Data management tools, and Data augmentation and data synthesis.

While there has been increasing application of Data-Centric AI in other industries, there are also opportunities for the application of Data-Centric AI in the semiconductor industry as well.Below are a two examples of approaches that have been explored and implemented:

Metabinning and generalized model across chip products

It is difficult to train a model using available data that can be applied to other chip products, due to the unique bin assignment across potentially many thousands of products, even though the underlying failure mechanisms at the device level may be similar.A solution to this challenge is to create metabins that group together bin ID's that are the same or very similar, across chip products.By generating metabins as new labels and overriding the original hardbin/softbin ID's (which again may be disparate), a generalized model can be trained with more previously available data and quickly applied to new chip products for failure prediction.

Classification of wafer failure patterns

Key difficulties in applying machine learning to the classification of spatial failure patterns on wafers are the limited number of wafer classifications (labels) and wafer data available to train the model for a new chip product.To address these issues, a Data-Centric AI approach can be applied.The first step is to generate Augmented Data: Wafers with known patterns are generated randomly.Then the new patterns can be quickly added to the model, by expanding the pattern definition library and retraining.Unlike actual data, new patterns from one product type might be considered general learning and useable to upgrade models.

References:

(1)Andrew Ng, NeurIPS Workshop, Data Centric AI, December 2021

9:00am **MS+HI-MoM-3 Paths Toward Autonomous Plasma Process Tool Operation by Pairing of Plasma and Machine Learning Technologies*, Jun Shinagawa,*** *P. Ventzek,* Tokyo Electron America Inc., **INVITED**

"Smart manufacturing" initiative is a means to meet automation and process control requirements set by semiconductor device technology that is now far below the 10 nm critical dimension in manufacturing[1]. We present our holistic approach on pairing first principle in-situ plasma diagnostics with machine learning techniques to build key components of autonomous plasma process tool operation system or advanced equipment control (AEC) system. AEC is a multi-module system consisting of plasma monitor and control and fault detection and classification(FDC) modules. Machine learning techniques are used to enhance accuracy and reliability of embedded models in the aforementioned modules.

REFERENCE

[1] SEMI, "What is smart manufacturing?" [Online], Available: https://www.semi.org/en/industry-groups/smart-manufacturing/what-is-smart-manufacturing [Accessed Nov. 30, 2021]

9:40am **MS+HI-MoM-5 Compliant Hybrid Bonding for Large CTE Mismatched Electronic Materials*, Mieko Hirabayashi Hirabayashi,*** *M. Wiwi, S. Herrera, E. Madison, M. Jordan,* Sandia National Laboratories

We will discuss methods for hybrid bonding utilizing low modulus materials to enable heterogeneous integration with high density (< 20 µm pitch) interconnections of CTE (coefficient of thermal expansion) mismatched materials. Hybrid bonding techniques, where mechanical stability is provided from a direct bond and electrical connection through a metal-to-metal bond are used to make high-density electrical connections for materials like hybridized CMOS imagers. The temperature of formation of the direct bond and the stiffness of the bonding material result in highly stressed interfaced, limiting the materials that can be used for a hybrid bond.

We demonstrate the joining dissimilar materials utilizing a compliant bonding layer. By changing materials, we allow stress moderation in the bonding layer which reduces the stress on the top and bottom chips. Reliability decreases significantly when the differences in coefficients of thermal expansion (CTE) are large. With large CTE mismatch between a top chip and a bottom chip, one chip expands more than the bottom chip during thermal cycling. If the interface is brittle, the stress due to the difference in CTE induces cracking at the interface. The current method for addressing this issue is to limit the total area bonded –but this limits the advancement of the technology.

This has ramifications for infrared imagers and other applications that combine compound semiconductors with silicon microchips. The size of hybridized infrared imagers, for example, is limited by the mismatch between the different materials that go into them. This presentation will include the methods we have developed to integrate polymers between dissimilar materials to reduce stress due to CTE mismatch and thus increase reliability.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525

10:40am **MS+HI-MoM-8 Machine Learning Accelerated Scale-up for Microporous Materials - An Industrial Perspective*, Di Du,*** *P. Kamakoti,* ExxonMobil Technology and Engineering Company **INVITED**

Microporous materials such as zeolites and MOFs play a crucial role in producing energy and energy products at scale. Traditional approaches for materials development and scale-up are time consuming and involve experience-based trial and error. Two key areas for materials understanding are the critical variables that impact the synthesis and optimization of material properties which are usually described by quantitative synthesis-property relationships (QSPR). This presentation provides an overview of statistical and machine learning approaches to build QSPR. These methods provide a highly efficient path to optimize synthesis parameters towards targets such as purity, crystal size and surface area, and enable us to significantly speed up our materials workflow.

Our workflow combines design of experiments, machine learning, and high-throughput experimentation (HTE). In order to build QSPR, we featurized the characterization data using machine learning and deep learning approaches. For example, we quantified crystal purity using peak deconvolution of powder XRD pattern. We used a deep learning model to calculate crystal size and aspect ratio from scanning electron microscopy (SEM). We performed functional principal component analysis to select the linear region of Brunauer-Emmett-Teller (BET) adsorption curve which is found to be more accurate than Rouquerol's rules. Since the synthesis space for microporous materials is large and complex, we combined Bayesian Optimization and HTE to further accelerate the workflow. The prior knowledge for Bayesian optimization often comes from a sparse matrix. We used an iterative machine learning model to predict and fill the missing values with uncertainty quantification. After optimization, we used feed-forward neural networks to summarize QSPR for extended investigation at different scales.

We validated the accelerated workflow with a known zeolite. Without referring to historical data, we used the workflow to systematically probe a large and complex synthesis parameter space and obtain small pure crystals of the material. The new workflow demonstrated a significant reduction in the number of experiments needed to meet the same goals as past experiments.

11:20am **MS+HI-MoM-10 Optimizing Copper Deposition in High Aspect Ratio Through Silicon Vias**, ***Jessica N. McDow***, *R. Schmitt, M. Hirabayashi, J. McClain, M. Jordan,* Sandia National Laboratories

We show an optimization method for filling high aspect ratio through silicon vias (TSVs) that provides insights into the diffusion and suppression kinetics of a superfilling electroplating chemistry. In general, TSV copper filling processes are designed to be used with thinned wafers (<200 µm), but some TSV last and microelectromechanical systems (MEMS) require full wafer thicknesses. To electroplate full-wafer thickness TSVs, a suppressor only solution utilizes an s-shaped negative differential resistance (S-NDR) mechanism.[1,2]

This suppression/fill mechanism is sensitive to the via geometry as well as the overpotential during the electroplating. Using a suppressor only chemistry consisting of copper sulfate, sulfuric acid, potassium chloride, and Tetronic 701, we demonstrate a time-dependent process window where early on too high of an overpotential results in suppressor breakdown and too low of an overpotential results in complete suppression of the deposition process. By controlling the voltage between -520 mV (MSE) and -560 mV (MSE), we were able to demonstrate complete fill of the TSVs in 30% of the time previously required for filling. We also hypothesize that there is a maximum void-free fill rate for suppressor only chemistries.

Understanding the filling kinetics provides a throughput target for microelectronic devices. Copper filled TSVs are a key technology for 3D heterogeneous integration. TSV designs improve device functionality, increase bandwidth per volume, simplify assembly, and enable system miniaturization. In this work, understanding of copper deposition kinetics in a suppressor only electrolyte and the development of optimized plating parameters utilizing the S-NDR mechanism is outlined.

SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525. SAND2022-7316A

[1]Rebecca P. Schmitt et al 2020 J. Electrochem. Soc. 167 162517.

[2]D. Josell and T. P. Moffat 2018 J. Electrochem. Soc. 165 D23.

11:40am **MS+HI-MoM-11 Advanced Manufacturing using Virtual Metrology and Equipment Intelligence®** , ***David Fried,*** Lam Research Corporation **INVITED**

The semiconductor industry is now confronting a number of metrology and manufacturing challenges due to critical technology requirements at next-node architectures.Advanced patterning techniques, such as EUV, frequency multiplication and selective deposition, are needed to meet cost and variability challenges at smaller line dimensions.Memory technologies, such as NAND, DRAM, and others, are requiring new materials and the transition to 3D topologies that are more challenging to manufacture.Advanced logic (such as GAA architectures) and heterogenous integration are being pursued in order to reduce power, footprint, and speed in next generation devices, but also require new, higher density and more complex manufacturing techniques.These technology requirements are creating additional metrology challenges, such as a need to measure smaller dimensions in complex 3D structures, increased measurement frequencies and additional demands for metrology data integration and analysis.

In this talk, we will discuss innovative concepts to address some of these next node metrology challenges.We will review the concepts of virtual fabrication and virtual metrology, and how they can be used in conjunction with conventional metrology to better support defect analysis and yield optimization at the latest technology nodes.We will also discuss how physical metrology can be used to calibrate a virtual process model, along with how a virtual process model can be used to validate physical metrology measurements made on a 3D NAND device.

In addition, our presentation will review the concept of Equipment Intelligence®, and how sensor-based metrology is being used to improve chamber and fleet variability.We will discuss how data from in-situ and standalone metrology, using machine learning/artificial intelligence, calibrated models, and advanced analytics, can drive real-time feed-forward and feedback optimization. We will show a specific example of next-generation metrology-based optimization, by presenting an advanced, in-situ etch-depth metrology system that uses spectral analysis and machine learning to deliver significant improvements in wafer-to-wafer etch depth control.

In our conclusion, we will summarize the challenges of next node architectures, and discuss how the concepts discussed in this presentation can be used by all participants in the semiconductor technology space to measure, characterize and address these upcoming challenges.

Atomic Scale Processing Focus Topic
Room 317 - Session AP+AS+EL+MS+SS-MoA

Advancing Metrology and Characterization to Enable Atomic Scale Processing

Moderators: Steven M. George, University of Colorado at Boulder, **Rudy Wojteki**, IBM Almaden Research Center

1:40pm **AP+AS+EL+MS+SS-MoA-1 Nanoscale Chemical Analysis and Mapping of Atomic and Molecular Scale Processes via Infrared Photo-Induced Force Microscopy*,* *Sung Park*,** Molecular Vista **INVITED**

As semiconductor device feature sizes move beyond the sub-7 nm technology node, atomic scale processing techniques such as atomic layer deposition (ALD) and atomic layer etching (ALE) are being adopted to gain control over key processing parameters.These techniques are commonly combined with thin polymer barrier layers such as self-assembled monolayers (SAM) that are selectively located to achieve area selective deposition or etching. In protein and DNA chips, monolayers of specific molecules are engineered and patterned to guide the target molecules to specific locations.Common to these devices and processes are the atomic scale thicknesses, nanoscale lateral dimensions, and the combination of multiple materials consisting of organic and inorganic compounds, metals, and 1D/2D materials which demand new metrology and characterization techniques to assess and monitor these advanced processing techniques.Photo-induced Force Microscopy (PiFM) [1] combines infrared (IR) absorption spectroscopy and atomic force microscopy (AFM) to achieve nanoscale chemical analysis via localized IR absorption spectrum and mapping of heterogeneous materials on the surface of a sample (with sub-5 nm spatial resolution).The spectroscopic capability is useful for ascertaining the presence and quality of the molecular species. The mapping capability is useful for investigating surface functionalization and chemical pre-patterns as well as selectively deposited materials in area-selective processes like block copolymer directed self-assembly, sequential infiltration synthesis, and a variety of area-selective deposition techniques. PiFM applications on various atomic and molecular scale processes will be presented.

[1] D. Nowak et al., Sci. Adv. 2, e150157 (2016).

2:20pm **AP+AS+EL+MS+SS-MoA-3 Area-Selective Deposition/Patterning of Boron Carbide Layers: Etch Studies*,* *Raja Sekhar Bale*,** *R. Thapa, A. Caruso,* University of Missouri-Kansas City*; J. Bielefeld, S. King,* Intel Corporation*; M. Paquette,* University of Missouri-Kansas City

The semiconductor industry is pushing the boundaries of device scaling by way of novel processing methods and increasingly complex patterning schemes. This requires a variety of functional and patterning-assist materials as well as advanced deposition techniques. For years, silicon-based materials have been used to meet these needs; however, these alone cannot fulfill the range of material requirements moving forward. Boron carbide has shown promise due to its compelling dielectric, thermal, mechanical, chemical, and etch properties. Toward applying this material to next-generation integration schemes, we have been exploring the potential of going beyond traditional growth processes (e.g., plasma-enhanced chemical vapor deposition) and investigating innovative area-selective atomic layer deposition (AS-ALD) strategies. Herein we explore schemes for the selective dielectric on metal/dielectric deposition of boron carbide using monolayer and layer-by-layer methods. In particular, we focus on etch studies (wet and dry) toward understanding the stability and removal of these layers. X-ray photoemission spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy (AFM) techniques are employed for the characterization and imaging of the resulting surfaces.

2:40pm **AP+AS+EL+MS+SS-MoA-4 Smoothing of Surfaces by Atomic Layer Deposition and Etching***, S. Gerritsen, N. Chittock, V. Vandalon, M. Verheijen,* Eindhoven University of Technology, The Netherlands*; H. Knoops,* Oxford Instruments Plasma Technology, Netherlands*; E. Kessels,* ***Adrie Mackus*,** Eindhoven University of Technology, The Netherlands

With critical dimensions scaled down to the nanoscale in current electronics, surface and interface roughness increasingly limit device performance. In this work, we use simulations and experiments to explore whether atomic layer deposition (ALD), atomic layer etching (ALE) and combinations of these techniques can be used to smoothen surfaces, while processing materials with excellent uniformity and atomic scale control. The smoothing is experimentally demonstrated by atomic force microscopy and transmission electron microscopy analysis.

Many previous studies have shown that ALD and ALE can smoothen surfaces,[1,2] but the extent of smoothing has not been systematically characterized and the mechanisms of smoothing are only partly understood. In our studies, finite difference simulations were performed that describe ALD/ALE as a uniform front from which the deposition/etching propagates isotropically at every point. Al_2O_3 ALD experiments using TMA and O_2 plasma validated this uniform front propagation model. A smoothing rate of $5.5\cdot10^{-3}$ nm RMS roughness reduction per nm of deposition was determined, revealing that significant smoothing by ALD requires relatively thick films (e.g. > 20 nm).

Al_2O_3 ALE from TMA and SF_6 plasma[3] resulted in a larger roughness reduction of $9.8\cdot10^{-3}$ nm/nm, which is explained by considering that the fluorination of the surface depends on the local curvature, such that peaks are smoothed more than valleys. In other words, for ALE two mechanisms contribute to the smoothing, i.e. uniform front propagation and curvature-dependent fluorination. In order to benefit from the enhanced smoothing by ALE, especially combinations of ALD and ALE in supercycle recipes can be very effective in smoothing surfaces, as will be highlighted in the contribution.

(1)Elam *et al.*, *Thin Solid Films***414**, 43 (2002)

(2)Zywotko *et al.*, *J. Vac. Sci. Technol. A* **36**, 061508 (2008)

(3)Chittock *et al., Appl. Phys. Lett.* **117**, 162107 (2020)

3:00pm **AP+AS+EL+MS+SS-MoA-5 Thermal Atomic Layer Etching of Amorphous Aluminum Nitride Using Sf_6 Plasma and $Al(Ch_3)_3$*,* *Haozhe Wang*,** *A. Houssain, D. Catherall, A. Minnich,* California Institute of Technology

We report the thermal atomic layer etching (ALE) of amorphous aluminum nitride using sequential exposures of low-power SF_6 plasma and trimethylaluminum ($Al(CH_3)_3$, TMA). ALE was observed at temperatures greater than 200 °C, with etch rates varying with temperature from 0.1 Å/cycle at 200 °C to 1.9 Å/cycle at 300 °C, as measured using ex-situ ellipsometry. The self-limiting nature of the reactions was established by verifying that no etching occurred with only SF_6 or TMA. The etched surface was characterized using atomic force microscopy and x-ray photoemission spectroscopy. After 50 cycles of ALE, the etched surface was found to contain a lower concentration of oxygen compared to the original surface and exhibited a∼35% decrease in surface roughness. These findings have relevance for applications of AlN in nonlinear photonics and semiconductor devices.

3:20pm **AP+AS+EL+MS+SS-MoA-6 Thermal Atomic Layer Etching using MoF6-H2O precursors*,* *Anil Mane*,** *J. Elam,* Argonne National Laboratory, USA

Well controlled atomic layer etching (ALE) processing is needed for the creation of next generation complex 3D devices. A simple semiconductor processing compatible thermal ALE method is preferred for the process integration point of view. Recently we have developed the MoF6-H2O precursors based etching methods for the etching of atomic layer deposited (ALD) TiO2, Ta2O5 and MoS2 in a precise controlled manner. The etch rate and etch behavior of these materials mainly controlled by processing temperature (100-325ºC) and precursors dose times. The MoF6-H2O etching process of these ALD grown TiO2, Ta2O5 and MoS2 was studied by in-situ methods such as infrared spectroscopy (FTIR), quartz crystal microbalance (QCM), and spectroscopic ellipsometry (SE). Additionally, at present we have also developed novel in-situ calorimetry method to measure chemical reaction heat in ALE precursor’s reaction. Here some of latest results on this in-situ ALE-calorimetry method will also be presented.

4:00pm **AP+AS+EL+MS+SS-MoA-8 The Thinner, the Better - Characterization of Ultra-Thin Films by Low Energy Ion Scattering (Leis)*,* *Thomas Grehl*,** IONTOF GmbH, Germany **INVITED**

Current and future thin film processes require quantitative characterization from the early phases of film growth to complex film stacks with a total thickness of only a few nm. While many surface analytical techniques are challenged by this requirement, Low Energy Ion Scattering (LEIS) analysis is ideally suited for ultra-thin film and sub-monolayer characterization. The key property is its single atomic layer information depth.

By scattering noble gas ions from the surface of the sample, LEIS determines the elemental composition of the surface of the outermost atomic layer. Nucleation processes and layer closure are investigated, but

also diffusion from the bulk towards the surface can be studied with in-situ sample heating and continuous monitoring of the surface composition.

In addition to the surface composition, also the distribution of elements over the first few nm of the sample is contained in the spectra. The so-called "in-depth information" is acquired in a virtually non-destructive way, avoiding sputtering and therefore the long measurement times and artefacts associated with it. For sufficiently thin films, the depth resolution is only a few Å. This allows to study the development of the film thickness while also monitoring film closure to determine the growth mode.

In some cases, low energy noble gas sputtering is applied to extend the depth range beyond a few nm or to handle complex materials where "in-depth" and surface information cannot be deconvoluted.

In this contribution, we will highlight a number of examples from quite different materials and film systems. These will be used to illustrate how LEIS is applied in practical way. We will show how LEIS contributes unique information for modern ultra-thin film characterization.

4:40pm **AP+AS+EL+MS+SS-MoA-10 Intrinsic Area Selective Atomic Layer Deposition of MoS_2 Thin Films***, J. Soares, **Wesley Jen**, S. Hues,* Boise State University*; J. Wensel,* Micron Technology Inc*; E. Graugnard,* Boise State University

As the critical dimensions in today's semiconductor devices continues to shrink, new methods for device fabrication are paramount for continued reduction in scaling. These fabrication processes must be adaptable in order to evolve with future technology nodes and scales, while providing flexible material integration techniques within the high complexity of device structures. Area selective atomic layer deposition (ASALD) is a deposition technique that utilizes a bottom-up patterning approach for self-alignment of deposited materials. ASALD operates on the basis that functional groups either present or absent on a growth surface will promote or inhibit nucleation. This contrast can lead to selective deposition. In addition to compatible processing techniques, next generation materials also need to be studied. Layered two-dimensional (2D) molybdenum disulfide (MoS_2) is a semiconducting material that shows great promise due to its atomically thin structure and impressive electrical properties. In this work, we report the ASALD of MoS_2 on patterned template substrates of common dielectric materials versus thermal silicon oxide and nitride. Growth and non-growth surfaces were initially screened with X-ray photoelectron spectroscopy (XPS) characterization of blanket MoS_2 films after numerous ALD cycles. The selectivity parameter between surfaces was calculated using XPS, revealing a high selectivity of S = 0.94 after 20 ALD cycles for growth on ALD alumina versus thermal silicon oxide. These results identified contrasting surfaces that were then patterned to investigate area selectivity. MoS_2 ALD was performed at 200 °C on patterned surfaces that were then annealed at 650 °C for 30 minutes. Samples were characterized using Raman spectroscopy maps of crystalline MoS_2 modes and time-of-flight-secondary ion mass spectroscopy (ToF-SIMS) elemental mapping, which confirmed ASALD. These results hold promise for advancing the integration of 2D materials into device manufacturing.

5:00pm **AP+AS+EL+MS+SS-MoA-11 In Situ Measurements of Surface and Film Stress during Atomic Layer Deposition of Al_2O_3 and AlF_3 using Wafer Curvature Techniques***, **Ryan B. Vanfleet**, E. Sorinto, A. Cavanagh, V. Bright, S. George,* University of Colorado at Boulder

In situ surface and film stress were measured during atomic layer deposition (ALD) using wafer curvature techniques in a new custom reactor. Aluminum oxide (Al_2O_3) ALD using trimethylaluminum (TMA) and H_2O as the reactants was used as a model system to test this new apparatus. Al_2O_3 ALD was explored at different deposition temperatures ranging from 130 to 285°C. The in situ measured film stress during Al_2O_3 ALD is a tensile stress of 450 MPa at 130°C (Figure 1). The tensile stress then decreases with increasing deposition temperature. These in situ temperature-dependent Al_2O_3 ALD film stresses are in good agreement with ex situ film stress measurements for Al_2O_3 ALD films reported in the literature [1].

High sensitivity wafer curvature measurements are also able to measure the surface stress from individual surface reactions (Figure 2). These in situ measurements revealed that the TMA exposure results in a compressive surface stress. This compressive stress is attributed to repulsion between surface methyl species. In addition, the H_2O exposure removes surface methyl species and releases the compressive stress. The compressive surface stress resulting from the TMA exposure grows from 0.4 N/m at 150°C to 0.75 N/m at 285°C. This increase in the compressive surface stress from the TMA exposure can be attributed to the greater relative change in methyl coverage at higher deposition temperatures.

Additional in situ measurements have explored the surface and film stresses during AlF_3 ALD using TMA and HF as the reactants. AlF_3 ALD showed similar surface stress behavior to Al_2O_3 ALD. The TMA exposure again results in a compressive stress attributed to repulsion between surface methyl groups. The HF exposure then removes the methyl groups and releases the compressive stress. At AlF_3 ALD temperatures between 150-200°C, the compressive surface stress resulting from the TMA exposures is ~0.45 N/m. In marked contrast to Al_2O_3 ALD, AlF_3 ALD displayed no film stress during film growth. This lack of film stress in AlF_3 ALD films may be related to the nature of the AlF_3 ALD film as a molecular solid.

[1]O.M.E. Ylivaara et al., *Thin Solids Films* **552**, 124 (2014)

Manufacturing Science and Technology Group
Room 305 - Session MS+AP+AS+TF-MoA

Advanced Characterization and Metrology for 3D and ML for Microelectronics Materials Discovery

Moderators: Alain Diebold, SUNY Polytechnic Institute, **Jeremy Mehta**, U.S. Department of Energy

1:40pm **MS+AP+AS+TF-MoA-1 Semiconductor Metrology for Dimensional and Materials Scaling***, **Bryan Barnes**,* NIST **INVITED**

Dimensional and materials scaling are two key drivers for advancing computational capabilities beyond the conventional scaling trends of the last several decades. Future device metrology solutions must be developed now without clarity as to which combinations of proposed architecture(s) and novel materials will prove best suited for integration into high-volume manufacturing. This presentation briefly reviews these possible pairings and the near-term and long-term metrology challenges as identified in the *IEEE International Roadmap for Devices and Systems*. As device dimensions further approach near-atomic and atomic scales, many of the several existing metrology techniques will face new tests, illustrated here using examples and solutions from our optics-based semiconductor metrology research. No single metrology technique can address all issues faced in modern process control and inspection; thus we address complementary techniques across semiconductor metrology are required to address dimensional and materials scaling

2:20pm **MS+AP+AS+TF-MoA-3 Towards a Digital Twin for Spatiotemporal Experiments***, **Subramanian Sankaranarayanan**,* Argonne National Laboratory **INVITED**

We will present our ongoing efforts at creating a virtual platform or "DigitalTwin", wherein the users can exhaustively explore experimental controls and obtain synthetic read-outs – a small subset that displays the most interesting physics and/or phenomena can be explored in the actual experiments. We take advantage of the fact that most experimentalspatiotemporally-resolved measurements at SUFs in real or reciprocal space can be derived from the accurate prediction of atomic configurations and their dynamical evolution across time- and length. We will use representative examples to demonstrate how Digital Twins can be utilized for accelerated materials discovery and design.

3:00pm **MS+AP+AS+TF-MoA-5 Autonomous Scanning Probe Microscopy: from Streaming Image Analysis to Learning Physics***, S. Kalinin, **Yongtao Liu**,* Oak Ridge National Laboratory **INVITED**

Machine learning and artificial intelligence (ML/AI) are rapidly becoming an indispensable part of physics research, with domain applications ranging from theory and materials prediction to high-throughput data analysis. However, the constantly emerging question is how to match the correlative nature of classical ML with hypothesis-driven causal nature of physical sciences. In parallel, the recent successes in applying ML/AI methods for autonomous systems from robotics through self-driving cars to organic and inorganic synthesis are generating enthusiasm for the potential of these techniques to enable automated and autonomous experiment (AE) in imaging.

In this presentation, I will discuss recent progress in automated experiment in scanning probe microscopy, ranging from real-time image segmentation to physics discovery via active learning. The applications of classical deep learning methods in streaming image analysis are strongly affected by the

out of distribution drift effects, and the approaches to minimize though are discussed. I will further illustrate transition from post-experiment data analysis to active learning process, including learning structure-property relationships and materials discovery in composition spread libraries. Here, the strategies based on simple Gaussian Processes often tend to produce sub-optimal results due to the lack of prior knowledge and very simplified (via learned kernel function) representation of spatial complexity of the system. Comparatively, deep kernel learning (DKL) and structured Gaussian Processes methods allow to realize both the exploration of complex systems towards the discovery of structure-property relationship, and enable automated experiment targeting physics (rather than simple spatial feature) discovery. The latter is illustrated via experimental discovery of ferroelectric domain dynamics in piezoresponse force microscopy. For probing physical mechanisms of tip-induced modifications, I will demonstrate the combination of the structured Gaussian process and reinforcement learning, the approach we refer to as hypothesis learning. Here, this approach is used to learn the domain growth laws on a fully autonomous microscope. The future potential of Bayesian active learning for autonomous microscopes is discussed.

4:00pm **MS+AP+AS+TF-MoA-8 New in-Line Metrology for Advanced Semiconductor Nodes***, **Cornel Bozdog**,* Onto Innovation **INVITED**

Scaling in Semiconductor Device Manufacturing means "more devices per unit area". The traditional "device shrink" scaling path was already replaced by "stack vertically" in non-volatile memory devices, now up to few hundred devices occupying the same real estate on the wafer, and growing. Gate all-around allowed logic devices to stack multiple transistors, and volatile memory is following suit. Different devices and sub-devices are now bonded together to further optimize scaling. To integrate, optimize and control the multi-thousand-step manufacturing line, in-line metrology plays the critical role. Here we will review the metrology challenges for Advanced 3D devices, present the latest advancements in traditional optical, scatterometry, electron-beam and atomic force techniques, and discuss novel x-ray, acoustic, and mid-IR metrology solutions that enable accurate profile reconstruction, in-device characterization and hybrid metrology schemes.

4:40pm **MS+AP+AS+TF-MoA-10 Applications of Artificial Intelligence AI and Machine Learning ML to Semiconductor Materials Discovery and Optimization***, **Brian Valentine**,* DOE **INVITED**

Semiconductor elements such as silicon and gallium are applied in a wide variety of electronic, optical, and energy conversion applications; new elemental, compound, and dopant compositions are continually sought to improve known semiconductor characteristics to find unknown but desired semiconductor material characteristics. In this paper some applications of AI and ML to semiconductor material design and optimization are reviewed, along with limitations of AI and ML techniques applied to materials design and development and forward directions in these materials design and development methods.

Plasma Science and Technology Division
Room 315 - Session PS2+MS-TuM

Modelling of Plasmas and Plasma Driven Processes, and Machine Learning

Moderators: Mingmei Wang, Lam Research Corporation, **David Lishan**, Plasma-Therm LLC

8:00am **PS2+MS-TuM-1 Molecular Dynamics Simulation of Oxide and Nitride Etching by CF_3^+ and Cl^+***, **Charisse Marie Cagomoc**[1], S. Taira, M. Isobe, T. Ito, K. Karahashi,* Osaka University, Japan*; L. Belau, E. Hudson,* Lam Research Corporation*; S. Hamaguchi,* Osaka University, Japan

High-aspect-ratio (HAR) etching is one of the key processes in the fabrication of 3D NAND flash memory devices. HAR etching requires the formation of an etched hole channel hole with a high aspect ratio through all deposited films such as silicon dioxide (SiO_2) and silicon nitride (Si_3N_4). By having a high aspect ratio, more memory cells can be integrated into a single device, thereby increasing its storage capacity. However, the difficulty in creating a perfect hole profile increases as the aspect ratio increases. As such, this study aims to investigate and understand the surface reaction mechanisms involved in the HAR etching process. In this study, molecular dynamics (MD) simulations and ion beam experiments were used to analyze HAR etching processes, especially those of SiO_2 and Si_3N_4 etching by energetic (up to 6keV) CF_3^+ ions as CF_3^+ ions are typical reactive ions emitted from fluorocarbon plasma. Etching simulations of SiO_2 and Si_3N_4 multilayers (ONO) used in 3D NAND by incident CF_3^+ ions were also performed. The results showed that, at low energies, the etch rates observed in the multilayer were similar to those of individual materials, as expected. However, it was observed that the change in the rate occurred before the etching passed through the initial height of the interface. At high energies, a mixing of the oxide and nitride layers became significant and, when the thickness of each layer was thinner than the ion penetration depth, a single etch rate was observed throughout the multilayers. We also performed SiO_2 and Si_3N_4 etching simulations with simultaneous injections of energetic Cl^+ and CF_3^+ ions, which represents ion irradiation from Cl containing fluorocarbon plasmas. The interplay between Cl^+ and CF_3^+ ions for the etching reactions will be discussed.

8:20am **PS2+MS-TuM-2 Molecular Dynamics Simulations of High-Energy Ion Bombardment ALE Processes for Smooth Surfaces***, **Joseph Vella**,* Princeton Plasma Physics Laboratory*; D. Humbird,* DWH Consulting*; D. Graves,* Princeton Plasma Physics Laboratory, Department of Chemical and Biological Engineering Princeton University

Atomic-layer etching (ALE) has emerged as a promising technology in the semiconductor industry in order to continue to shrink the size of advanced electronics. ALE differs from other etching processes in that a substrate is etched by two steps: a surface modification step and a removal step. These steps are separated either in space or in time.[1] Both of the ALE steps have several parameters that can be varied which may lead to different results. For example, recently it has been demonstrated in a silicon-chlorine-argon ALE cycle, that a removal step with higher argon ion energies (>500 eV) and shorter exposure times (~0.2 s) yield smoother surfaces when compared to a corresponding cycle with lower ion energies (<80 eV) and longer exposure times (~5 s).[2] The reason for these results is not entirely understood. In this work, we use classical molecular dynamics (MD) in order to provide atomistic-level insight behind this phenomenon. We have previously demonstrated the ability of classical MD to accurately reproduce experimental silicon-chlorine-argon ALE data.[3] However, in the aforementioned work we focused on a bombardment step with argon ion energies only up to 100 eV. In this work, we extend our simulations to include higher argon ion energies and use the results to explain why high energy ion bombardment with short exposure times yield smooth surfaces.

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8:40am **PS2+MS-TuM-3 Analysis of RF Sheath Dynamics in Dual-Frequency Capacitively Coupled Ar Plasmas Using a Two-Dimensional Particle-in-Cell Simulation***, **Ji Hyun Shin**, H. Kim, C. Kim, S. Choi, H. Lee,* Pusan National University, Republic of Korea

With dual-frequency (DF) driving, ions' energy and flux can be controlled by high-frequency (HF) and low-frequency (LF) voltage waveforms, of which periods are faster and slower than ion transit time, respectively. DF capacitively coupled plasmas (CCP) are widely used in semiconductor etching processes because of effective ion energy control. In addition, various types of electrode structures are requested to improve the uniformity of the ion flux to the wafer. In this presentation, we report the effect of the electrode and the dielectric structure under DF driving conditions. The large computation load in two-dimensional particle-in-cell (PIC) DF CCP simulation was overcome using a parallelization with a graphics processing unit (GPU). We observed the time-dependent sheath dynamics with the change in structure to find a way to improve the spatial uniformity of the ion flux. The low-frequency driving enhances the plasma density in the peripheral region by the inward ion transport and improves the spatial uniformity of ion flux on the wafer. The ion transport is also controlled by the dielectric structure.

9:00am **PS2+MS-TuM-4 Incorporation of Match timing in a Global Plasma Circuit Model***, **Carl Smith**,* North Carolina State University*; S. Nam, K. Bae, J. Lee,* Samsung Mechatronics R&D Center, Republic of Korea*; S. Shannon,* North Carolina State University

Pulsed inductively coupled plasmas have been of interest over the past couple of decades due to reduced charge buildup [1], improved etch uniformity [2], and enhanced control over plasma chemistry [3]. Control over transients in n_e *and* T_e has been of keen interest in semiconductor processes where control over the duty cycle and pulse length have useful in controlling time averaged plasma parameters by continuously operating outside of steady state conditions.

One method of transient control that has been demonstrated is match timing, where the match is selectively tuned to deliver power at a specific point in the ON-Cycle, leveraging electrical impedance mismatch due to plasma transients to control the rate of power delivery and charged particle formation in the plasma. Control over dn_e/dt in an Argon discharge has been measured in a cylindrical inductively coupled reactor and compared against a Matlab based Global Plasma Circuit Model (GPCM) with good agreement. GPCM couples plasma parameters to an equivalent circuit model where match feedback has been accounted for. Control over power delivery at requested match points has been achieved through the incorporation of integrated match feedback and subsequent time dependent power delivery to the plasma. Modulation of the electron temperature spike in the early ON-Cycle has been observed in GPCM via match setpoint control. Matching model results with experimental results required particular attention to the effective area of the plasma (A_{eff}) and treatment of the plasma skin depth and will be presented. Center-point time-resolved electron densities were taken with a hairpin resonator probe while time-resolved power measurements from the matching network are taken with directional couplers placed at the matching network input port.

This work is supported by the North Carolina State University and the Samsung Mechatronics R&D Center.

9:20am **PS2+MS-TuM-5 Nanosheet GAA Transistor Manufacturing Modeling Study: Build Fundamental Knowledge of SiGe to Si Selective Etching in ClF_3 Gas***, **Yu-Hao Tsai**, M. Wang,* TEL Technology Center, America, LLC **INVITED**

The gate-all-around field-effect transistor (GAAFET) is a promising candidate for improving the performance of MOSFET beyond FinFET. Manufacturing the Si-SiGe stacked nanosheet GGAFET involves the highly selective SiGe and Si etching, in order to create the uniform inner spacers required for robust device performance. To achieve the ultrahigh selectivity, fundamental understandings of the origin of the selectivity in the process is crucial. We conduct an atomic-level investigation on how Ge atom impacts on the SiGe etching rate. The plasmaless dry etching process in ClF_3 gas is considered in this study. We perform the density functional theory (DFT) to model the elementary reactions of etchant molecule fluorinating Si/Ge atom. Based on the modelling results, the activation energy (E_a) of single-F-transfer breaking Ge-Ge bond is 0.4 eV lower than the Si-Si bond, with the E_a of Si-Ge cases fall between. The overall smaller

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

E_a suggests that the relatively active fluorination reaction enabled by Ge atom facilitates the selective etching. In addition, a unique double-F-transfer from ClF_3 is identified, which simultaneously fluorinates two adjacent Ge atoms. The reaction enhances the selective etching with the drastically lowered E_a and more negative total energy change. We modelled different locations of Ge atom with respect to the fluorinated Si atom. The results show that the effect of Ge atom on lowering the Si fluorination E_a has a long-range nature. The calculation predicts a reduced E_a even when the Ge atom is on the second-nearest-neighbor site to the fluorinated Si atom. The finding implies that the Ge-induced E_a reduction can continuously assist the selective etching with a Ge-percentage as low as 6 at. %. Details of the surface chemical reactions and byproducts formation are discussed in the report.

11:00am **PS2+MS-TuM-10 Study on Spatiotemporal Evolution of Plasma Arcing in Low-Temperature Plasma***, **Si-jun Kim**, C. Cho, M. Choi, Y. Lee, I. Seong, W. Jeong, Y. You,* Chungnam National University, Republic of Korea*; J. Lee,* Samsung Electronics Co., Inc., Republic of Korea*; S. You,* Chungnam National University and Institute of Quantum Systems (IQS), Republic of Korea

Since arcing is a ubiquitous phenomenon in high-voltage applied systems and marks damages on surfaces where arcing arises, it has attracted attention from research fields as well as industries. Its formation mechanisms however have not been fully understood yet, especially under low-temperature plasma environments. Recently, we have reported electrical and optical characteristics of arcing, especially the observation of light emission from arcing occurred early than arcing current initiation under low-temperature plasma and brief explanations about formation mechanisms of this prior light. In this research, to elucidate the mechanism deeply, we analyzed a spatiotemporal behavior of arcing with a high-speed camera with various conditions (radio frequency (rf) power and voltage of an arcing inducing probe (AIP)). We found dependency of surface and bulk emission regions on the conditions; those regions are characterized by light emission positions on the AIP. In this talk, an improved arcing formation mechanism based on spatiotemporal analysis is discussed.

11:20am **PS2+MS-TuM-11 Instabilities in Low Pressure Magnetized Capacitively Coupled Plasmas***, **Sathya Ganta**, K. Bera, S. Rauf,* Applied Materials, Inc.*; I. Kaganovich,* Princeton University Plasma Physics Lab*; D. Sydorenko,* University of Alberta, Canada*; A. Khrabov, T. Powis,* Princeton University Plasma Physics Lab*; L. Xu,* Ruhr Universität Bochum, Germany

Low pressure (< 50 millitorr) capacitively coupled plasmas are commonly used for etching and deposition in the semiconductor industry. The plasma transport at low pressures is high causing significantly non-uniform steady state plasma density profiles. Static magnetic field is one option that can be used to improve plasma uniformity **[1]**. With the appropriate magnetic field profile, one can improve spatial uniformity in plasma density or adjust the plasma density profile to one that is desirable for the processing application. However, at high magnetic field intensity and low gas pressures, instabilities have been observed in plasmas which change the transport coefficients of electrons. This has been reported before by Boeuf **[2]**. In this paper, we examine such instabilities using a 2-dimensional particle-in-cell plasma simulation where plasma particle kinetics equations are coupled with the Poisson equation solver while incorporating a high intensity external static magnetic field. The code has been developed at the Princeton Plasma Propulsion Laboratory (PPPL). Using the code, Argon only capacitively coupled plasma simulations are performed at different process conditions (e.g., pressure, RF voltage), and for different intensities of external magnetic field. The simulation results for varying magnetic field intensities and for various processing conditions are analyzed to elucidate the physical reason behind the magnetic field induced plasma instability.

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11:40am **PS2+MS-TuM-12 2D Hybrid Simulation of a CF4 Plasma in a DF CCP Reactor: Influence of Operating Conditions on Plasma Bulk Properties and Fluxes on the Wafer***, **Pierre Ducluzaux**,* LTM/CNRS-UGA, France; STmicroelectronics, France*; D. RISTOIU,* STmicroelectronics, France*; C. Gilles, E. Despiau-Pujo,* LTM/CNRS-UGA, France

Image sensors used in smartphones have seen a lot of technological development over the past decade aiming pixel size reduction to improve photography resolution. One of the main component of these image sensors are microlenses, which focus the light incident on the photodiode, thus improving the quantum efficiency of the sensor. The manufacture of resist microlenses necessitates an etching step in a fluorocarbon plasma, during which a semi-spherical resist pattern must be transferred into a subjacent resist layer. Due to the complex chemico-physical processes taking place during etching, it is difficult to predict the final 3D shape of the microlenses. Thus, a better understanding of the link between the process conditions, the plasma properties, and the final microlens shape can assist the development of such new technology.

In this paper, we propose to numerically investigate the influence of different tunable process parameters on the plasma properties and the fluxes incident on the wafer. The CF4 plasma is simulated using a 2D hybrid model (Hybrid Plasma Equipment Model) in a dual-frequency capacitively coupled plasma reactor. We first investigate the impact of pressure (10-100 mT), RF power (100-1500 W) and gaz flow (100-500 sccm) on plasma bulk properties such as the electron and ion densities, the radical composition and the electronic temperature. In agreement with experiments reported in literature, F, CF3, CF and CF2 are shown to be the main radicals in the plasma. Increasing the low-frequency (13,56 MHz) power increases the ion energy at the wafer, while increasing the high-frequency (40 MHz) power allows to control the plasma density and the ion flux at the wafer. The detailed impact of process parameters on the fluxes and energy distribution functions of species (radicals, ions) impacting the wafer will be discussed during the presentation.

12:00pm **PS2+MS-TuM-13 Investigation of N_2 Plasma in Plasma Enhanced Atomic Layer Deposition of Silicon Nitride Using First Principles Calculation***, **Tsung-Hsuan Yang**, T. Wang, G. Hwang,* University of Texas at Austin*; P. Ventzek, T. Iwao, J. Zhao,* Tokyo Electron America Inc.,*; K. Ishibashi,* Tokyo Electron Ltd., Japan

Plasma-enhanced atomic layer deposition (PEALD) has been demonstrated to be a promising technique for the controlled growth of silicon nitride (SiN) thin films. The benefits of PEALD include excellent conformality, precise thickness control, and high quality at relatively low temperatures (<400°C). In this work, density functional theory (DFT) was applied to study the surface reaction mechanism when a Si-rich surface is exposed to N_2 plasma. The reactive species in N_2 plasma, atomic N, tends to react with a undercoordinated N or a tertiary amine by forming a N_2-dimer. After subtle surface reconstruction, three types of N_2-dimer (Si-N-N-Si, Si_2-N-N-Si_2, and Si_2-N-N-Si_2) were created, depending on the abundance of neighboring Si. These N_2-dimers were relatively stable and can remain after N2 plasma half cycle. The reactions between silane (SiH_4) and trisilylamine (TSA, $(SiH_3)_3N$) precursors and N_2-dimers were then examined and compared. Results show that one H from the Si precursor will first migrate to one N in the N_2-dimer, saturating the undercoordinated N and rendering a Si dangling bond in the precursor. The other N in the N_2-dimer will then initiate a nucleophilic attack toward the Si dangling bond in the precursor and forms a Si-N bond. Meanwhile, the N-N in the N_2-dimer is broken. The whole reaction is highly exothermic due to the destruction of weak N-N single bond and formation of strong Si-N bond. Most importantly, the Si precursor remains intact during the reaction, indicating that using a bulkier precursor with three silyl ligands such as TSA can guarantee a higher growth rate rather than silane. These findings agree well with previous experimental results.

Manufacturing Science and Technology Group
Room Ballroom A - Session MS-TuP

Manufacturing Science and Technology Poster Session

MS-TuP-2 Materials Metrology Using in-Line SIMS System for Improved Manufacturing Process Control in Advanced Nodes*, **Ganesh Vanamu**, J. Hoffman, L. Rooney, S. Okada,* Nova Measuring Instruments

As the semiconductor industry transitions more rapidly towards advanced technology nodes, devices are getting more complex and process challenges are increasing dramatically. Moreover, an abundance of new materials requires inline control of critical parameters, such as composition, dopant, thickness and local variations within the device.

For example, Germanium content in SiGe correlates to channel stress, and the Ge fraction has been increasing steadily as technology rapidly advances towards 3D structures. When stress is high, epi layers can suffer from multiple problems such as defect formation, facet formation, non-uniform strain. To enable process control on the Ge%, and Boron doping concentration in the complicated SiGeB epi stacks is critical in high-volume manufacturing (HVM), and there is no single in-line metrology technology that can perform the measurement.

Ion implantation, mainly Boron, Phosphorous, and Arsenic, has a long history of use in semiconductor manufacturing. After implantation, the concentration distribution of the implanted ions within the material will resemble a Pearson IV distribution., Secondary Ion Mass Spectroscopy (SIMS) is the only metrology method capable of measuring the peak concentration, peak depth, and dose simultaneously.

Contamination introduced during semiconductor processing is another critical concern because it can degrade device performances and can eventually cause device failures. Contaminants like Chlorine (Cl– ions) cause Al-Cu corrosion and metal cross- contamination in integrated circuits that could lead to wafer scraps. Integration and reliability issues can result from diffusion of Fluorine into underlying films or substrates. Therefore, there is a need for in-line monitoring of these contaminants.

The metrology goal is to enable automated in-line measurements that can be used for process monitoring of material concentrations, with vertical resolution. This paper explores the use of in-line SIMS technology, enabling depth profiles of the materials composition in the critical deposition steps in HVM, previously limited to a lab environment. This paper describes how in-line SIMS can be used to measure SiGe epi material composition profiles (such as thickness, Ge% and Boron concentration) as a function of depth. This study also shows measurements of peak concentration, peak depth, and dose of Boron implantation simultaneously to provide better implant process control. This paper also evaluates the detection sensitivity levels of contaminants like C, F, Cl in positive and negative ion mode with an Oxygen primary ion beam, as well as the use of proxy species or alternate isotopes for improved results.

Thin Films Division
Room 316 - Session TF3+MS-WeM

Simulations and Machine Learning Applications for Thin Films

Moderator: Angel Yanguas-Gil, Argonne National Lab

11:00am **TF3+MS-WeM-10 What an Experimentalist Needs from Computational Materials Science (Including Machine Learning) – Studies in Semiconductor Processing and Metrology***, **Rafael Jaramillo**,* MIT **INVITED**

I will present a view on computational materials science and machine learning, from the perspective of an experimentalist working primarily on compound semiconductors. I will first present uses of computation within my own group. These include computational thermodynamics to guide materials design and synthesis, atomistic modeling of deep levels in semiconductors, finite-element modeling of mechanical and acoustic phenomena, and machine learning models of optical metrology to improve materials discovery and microelectronics manufacturing. In many cases, our computations are limited by challenges that are beyond our expertise as experimentalists. With these challenges in mind, I will then highlight several outstanding needs from the computational science community, illustrated by ongoing research projects:

(1) We pioneered the synthesis of chalcogenide perovskite thin films by gas-source molecular beam epitaxy (MBE). Our successes pose questions of process optimization, particularly related to connections between precursor selection, processing temperature, and crystal quality. There is a need for multi-scale modeling of crystallization at solid-vapor interfaces, including highly-non-thermodynamic conditions such as plasma processing, to de-risk the development of manufacturing-compatible deposition methods.

(2) We discovered that chalcogenide perovskites have the strongest low-frequency dielectric response among VIS-NIR semiconductors. The only other family of semiconductors with comparable dielectric response are halide perovskites. We also discovered that chalcogenide perovskites have, in common with their halide cousins, slow non-radiative excited-state recombination. These observations pose the question of how, exactly, soft phonon spectra affect Schottky-Read-Hall (SRH) recombination rates. Polarons may be relevant. Exact calculations of SRH capture cross sections for particular materials, coupled to a Fröhlich model of electron-phonon interactions, would shed light on these open questions in solar cell materials physics.

(3) Native oxidation of chalcogenide layered and two-dimensional semiconductors (notably including transition metal dichalcogenides, TMDs) needs to be well understood for microelectronics fabrication, and presents unique opportunities for ultra-scaled logic and memory devices. We have used theory and experiment to describe TMD native oxidation processes. However, reactive molecular dynamics simulations combined with advanced data analytics are needed to accelerate progress towards device technology that would be advanced and manufacturable.

11:40am **TF3+MS-WeM-12 Computational Analysis and Design of Precursors for ALD and CVD of Metals***, S. Elliott, A. Chandrasekaran, S. Tiwari, A. Fonari, D. Giesen,* Schrödinger*;* ***Casey Brock***, Schrödinger

Understanding a deposition process depends to a large extent on understanding the chemical and physical properties of the precursor molecules. Volatility, reactivity and thermal stability are the three key precursor characteristics needed for chemical vapor deposition (CVD) and atomic layer deposition (ALD), although properties such as melting point, viscosity, synthetic cost and nucleation behavior are also important. Quantifying these characteristics for known precursors can help trouble-shoot an existing process, and designing novel precursors with optimum characteristics is a robust way to improve a process. We illustrate these points on the example of beta-diketonate-based Pd(II) precursors for the deposition of palladium metal. The aim is to find the optimum ligand combination in both homoleptic and heteroleptic complexes.

Precursor volatility often dictates the lower limits of temperature and pressure at which a process can be run. We use a machine-learning model of volatility to see the effect of ligand identity on this property. Specifically, cyclopentadienyl and allyl ligands are found to lower the evaporation temperature to <100 degrees C in the 1-5 Torr pressure range. The other end of the process window is determined by thermal decomposition. For Pd(hfac)2 and formalin experiments show a narrow ALD window between 200 and 230°C, followed by decomposition at higher temperatures. We therefore use density functional theory (DFT) to assess the thermal stability of candidate complexes. We exclude those heteroleptic complexes that DFT predicts to be impossible to synthesize because of ligand exchange. We find that the poor stability of thd complexes can be overcome by switching to fluorinated ligands. We also present quick and approximate measures of the reactivity towards reduction to metallic Pd, whether by CVD or ALD, and compare these with more time-consuming DFT calculations of the surface chemistry.

The computational tools for these properties have been automated to the level where they can be integrated into a team's R&D workflow for routinely assessing current precursors or discussing new ones, so that lists of molecules can be generated and ranked according to the key characteristics for a particular process and application area.

12:00pm **TF3+MS-WeM-13 Dopant-selective Atomic Layer Deposition of Metals for Bottom-up Nanoelectronics***,* ***Nishant Deshmukh****,* Georgia Institute of Technology, USA*; D. Aziz, A. Brummer, M. Filler,* Georgia Institute of Technology

The entirely bottom-up fabrication of nanoelectronic devices promises electronics with an unprecedented combination of performance and scalability. A long-standing challenge has been the bottom-up fabrication of nanoscale features on nanoscale semiconductors. Bottom-up methods can create suitable semiconductor structures, but top-down methods are needed for other important device features, such as contacts or gate stacks. For example, Si nanowire pn diodes can be readily fabricated with the vapor-liquid-solid (VLS) growth method; however, lithography is still necessary to define contacts to the p and n segments. Here, we report a dopant-selective atomic layer deposition (ALD) process to deposit metal thin films suitable for constructing fully bottom-up pn diodes. Briefly, undecylenic acid, a bifunctional self-assembled monolayer (SAM), is blanket attached to the Si surface. Exposure to KOH removes it from the surface of heavily-doped (~10^{20} cm^{-3}) p-type and n-type Si while it remains on lightly-doped (~10^{14} cm^{-3}) Si. Subsequent Pt ALD yields deposition only on the heavily-doped Si. X-ray photoelectron spectroscopy (XPS) shows that the ratio of Pt deposition on the heavily-doped to lightly-doped Si can be as high as 130. We suspect that this high selectivity results from undecylenic acid attaching to lightly-doped Si through its alkene group, and to heavily-doped Si through its carboxylic acid group. This difference in attachment results in KOH being able to remove undecylenic acid only from the heavily-doped Si, thus allowing Pt to deposit.

Applied Surface Science Division
Room 320 - Session AS+2D+EM+MS+NS+SS+TF-ThA

Probing Defects at Surfaces and Interfaces

Moderators: Michaeleen Pacholski, The Dow Chemical Company, **Zachary Robinson**, SUNY Brockport

2:20pm **AS+2D+EM+MS+NS+SS+TF-ThA-1 Controlling InP Quantum Dot Surface Defects Using ALD-inspired Surface Chemistry and Phosphorus Kα and Kβ X-ray Emission Spectroscopy**, ***Nayon Park,*** University of Washington **INVITED**

Colloidal InP quantum dots are a leading heavy-metal-free semiconductor material for spectral downconversion in current generation display technologies and future generation energy efficient LEDs. Achieving the brightest and narrowest photoluminescence (PL) relies on the synthesis of structurally and electronically defect-free quantum dots. InP quantum dots' high propensity for oxidation and the inherent oxidative defects arising from commonly used synthesis methods therefore motivates a systematic approach to probe InP oxidation as a function of synthesis and surface treatments and correlation with the resultant optical properties. Phosphorus X-ray Emission Spectroscopy (XES) presents itself as an exceptional tool in this regard. In this talk, I will show recent results from computational modeling where we find that native InP surface oxides give rise to dark states near the band edge. Replacing the surface indium with zinc to form a monolayer ZnO shell results in the reduction of dark states. Using ALD-inspired successive ionic layer adsorption and reaction (SILAR), we developed the colloidal, layer-by-layer growth strategy of metal oxide shells (i.e. ZnO, CdO, GaO_x, AlO_x) on InP quantum dots at room temperature using common ALD precursors (*i.e.*, metal alkyls and water). Metal oxide-shelled InP QDs generally show enhanced PL and evidence of bulk and local structural perturbations arising from the metal oxide as determined by X-ray diffraction and X-ray absorption spectroscopy. Further, we explore the impact of these metal oxide interfaces on the PL QY and emission linewidth of InP/ZnSe core/shell QDs. Upon growing a thin ZnSe shell, we observe improved PL properties, which we hypothesize to be attributable to the inhibition of phosphorus migration to the shell due to the presence of the metal oxide interlayer, as supported by X-ray emission spectroscopy. Taken together, these results suggest a clear path forward in the control and design of complex QD interfaces with atomistic insight for optoelectronic technologies.

3:00pm **AS+2D+EM+MS+NS+SS+TF-ThA-3 Characterization of MAX Phases using a Combination of Micro-spot XPS, HAXPES and C60 Cluster Depth Profiling**, ***Kateryna Artyushkova,*** Physical Electronics USA*; M. Anayee, Y. Gogotsi,* Drexel University

Two-dimensional (2D) transition metal carbides, carbonitrides, and nitrides (MXenes) have seen significant increases in the number of research areas and publications. MXenes have a unique combination of properties that have led to many applications.[1] MXenes are usually synthesized by etching “A” layers that interleave “MX” layers in the bulk MAX precursors. MAX are represented by Mn+1AXn, where M denotes early transition-metals (Ti, V, Cr, Mo, etc.), X is N or C, and A is an A-group element such as Al, Si and others. During synthesis, impurities and defects may be introduced, which significantly impact the properties of the resulting materials. It is therefore critical to detect and quantify these defects and impurities.

X-ray Photoelectron Spectroscopy (XPS) has the advantages of being easily quantifiable and providing chemical information such as surface termination and oxidation. However, there are many challenges in using XPS for analyzing MAX and Mxene. The first is a very small size of MAX, less than a few tens of microns. With the development of focused scanning micro-probe X-rays, these limitations can be overcome. The other challenge is the extreme surface sensitivity of XPS. It is challenging to separate surface adventitious carbon and oxygen from possible oxygen incorporation in the carbon site. Depth profiling using a monatomic Ar ion beam is not suitable as it can introduce damage to the structure of MAX.

In this work, we are presenting two approaches to address this challenge. The first involves the application of Hard X-ray Photoelectron Spectroscopy (HAXPES), in which a monochromated Cr X-ray source is used to probe ~3 times deeper than a soft Al X-ray. The second utilizes a cluster ion gun source, such as C60, for damage-free depth profiling through individual MAX particles using ~8µm X-ray spot for probing if oxygen is present in the MAX structure.

3:20pm **AS+2D+EM+MS+NS+SS+TF-ThA-4 Unusual Trend in Thermal Stability of Alanine Different Ni Surfaces***, J. Ontaneda,* Queen Mary University of London, UK*; R. Grau-Crespo,* University of Reading, UK*; **Georg Held**,* Diamond Light Source, UK

Chirally modified heterogeneous catalysts promise massive savings of cost and toxic waste in the production of enantiopure precursors for high-value chemicals such as pharmaceuticals, fertilizers, or fragrants [1]. A key aspect is the thermal stability of chiral modifiers, which generally are chiral organic molecules bound to a chemically active metal surface. The enantioselective hydrogenation of methylacteoacteate (MAA) is a topical reaction, which is catalysed by nickel modified with chiral carboxylic acids, such as alanine, tartaric acid, or aspartic acid [2]. The components of this catalytic system have been investigated using various surface sensitive techniques [3,4,5]. Here we present a study of the thermal stability of alanine on the three most common Ni surfaces, {111}, {100}, and {110}, using synchrotron-based temperature-programmed photoelectron spectroscopy and X-ray absorption spectroscopy. In contrast to common experience with smaller molecules, alanine is more stable on the more open {110} and {100} surfaces compared to {111}. Comparison with a detailed DFT study identifies structural and electronic effects that play a role in this unusual behaviour.

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3:40pm **AS+2D+EM+MS+NS+SS+TF-ThA-5 Correlative Theoretical and Experimental Study of the PC | X Interfacial Bond Formation (X = TiN, AlN, TiAlN) During DC Magnetron Sputtering**, ***Lena Patterer**, P. Ondračka, D. Bogdanovski, S. Karimi Aghda, J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany

Due to their outstanding oxidation and wear resistance, cubic (Ti,Al)N is widely used as protective coatings on forming and cutting tools. These characteristics make (Ti,Al)N also an attractive candidate for the protection of polymer components. The composition-induced changes in the interfacial bond formation of DC magnetron sputtered TiN, AlN, and $Ti_{0.25}Al_{0.25}N_{0.5}$ onto polycarbonate (PC) substrates are systematically investigated by correlating theory and experiment. In order to simulate the sputtering condition by *ab initio* molecular dynamics, a periodic structural model of bulk PC consisting of 394 atoms was bombarded by several Ti, Al, and N atoms with a kinetic energy of 1 eV. While both Ti and N atoms show high reactivity towards all functional groups of the polymer during the surface bombardment, Al atoms selectively react only with the carbonate group of PC or other reactive functional groups that have formed during previous bombardment events (e.g. C-N groups). At the PC | TiN and PC | TiAlN interfaces, Ti and N contribute equally to the interfacial bond formation, whereas the PC | AlN interface is defined mostly by C–N groups with Al-rich clusters forming on top of these groups. X–ray photoelectron spectroscopy data of the PC | X interfaces (X = TiN, AlN, TiAlN) show a very good agreement with the above-discussed predictions as the formation of C-N, C-(Ti,Al), and (C–O)–(Ti,Al) bonds is experimentally verified. This shows that the here employed computational strategy enables predictions of the interfacial bond formation between polycarbonate and metal nitrides, and it is reasonable to assume that the here proposed research strategy can be readily adapted to other polymer | inorganic material interfaces.

4:00pm **AS+2D+EM+MS+NS+SS+TF-ThA-6 Using Resonant Photoemission Spectroscopy to Probe the Electronic Structure of Complex Oxides with Elemental and Orbital Specificity**, ***Jessica McChesney**, D. Fong, H. Hong,* Argonne National Laboratory, USA

Understanding the role of defects and interfaces is necessary in order to realize many of the promising novel properties of complex oxide heterostructure devices. To this aim, we employ resonant angle-resolved photoemission spectroscopy to probe the electronic structure with elemental and orbital specificity of complex oxide heterostructure $LaTiO_3/SrTiO_3$ (LTO/STO).Combining these spectroscopy measurements with in-situ growth characterization we are able to determine the minimum thickness required to achieve high quality heterostructures with abrupt interfaces and to correlate the formation with the 2DEG with the

interface termination LTO/STO vs STO/LTO.In addition, we explore the role of oxygen vacancies in formation of the 2DEG on the bare substrate and reveal that contrary to expectations, the 2DEG is Ti^{4+} in character while the oxygen defects are Ti^{3+} in character.

Plasma Science and Technology Division
Room 305 - Session PS1+MS+SS-FrM

Modelling of Plasmas and Plasma Driven Processes, and Plasma-Surface Interactions II

Moderators: Tetsuya Tatsumi, Sony Semiconductor Solutions Corporation, Japan, **Yu-Hao Tsai**, TEL Technology Center, America, LLC

8:20am **PS1+MS+SS-FrM-1 Helium and Hydrogen Plasmas Interaction with Si-Based Materials for Advanced Etch Applications: Insights from MD Simulations***, **Emilie Despiau-Pujo**, V. Martirosyan, F. Pinzan,* Univ. Grenoble Alpes, CNRS, LTM, France*; F. Leverd,* ST Microelectronics, France*; O. Joubert,* Univ. Grenoble Alpes, CNRS, LTM, France

Featuring ultrathin layered materials in complex architectures, advanced nanoelectronics structures must be etched with a nanoscale precision and a high selectivity to preserve the electronic properties of active layers. Plasma-induced damage and reactive layers formed during the etch process must thus be carefully controlled, a challenge which cannot be addressed by conventional continuous-wave plasmas.To achieve uniform and damage-free etching, one possible route is to use sequential ion modification and chemical removal steps. In the first step, the material to be etched is exposed to a hydrogen (H_2) or helium (He) CCP or ICP plasma; in a second step, the modified layer is selectively removed by wet cleaning (HF bath) or exposure to gaseous reactants only (eg. NF3/NH3 remote plasma). In this paper, Molecular Dynamics (MD) simulations are performed to study the interaction between He and H_2 plasmas with Si, Si_3N_4 and SiO_2 materials. The objective is to better understand the light ion implantation step, and clarify the influence of the ion energy and ion dose on the structural and chemical modifications of the surface. Simulations of low-energy (15-200 eV) He^+ and H_x^+ bombardment lead to a self-limited ion implantation, followed by the formation of a modified layer of constant thickness at steady state. The modified layer thickness increases with the incident ion energy and only few sputtering is observed in the ion energy range considered here. The detailed structure of the modified materials at steady state will be discussed and compared during the presentation. Simulation predictions will also be confronted to experimental results of He^+ and H^+ implantation of Si_3N_4 and SiO_2 layers, followed by HF wet cleaning.

8:40am **PS1+MS+SS-FrM-2 Efficient Parametric Nonlinear Model Reduction of Low Temperature Plasma Applications***, **Abhishek Verma**,* Applied Materials Inc.*; K. Bera, S. Rauf,* Applied Materials, Inc.

Low temperature plasma simulations are playing an increasingly important role in system discovery, design and decision making in industrial applications, with greater demands for model fidelity. Often, high fidelity simulation models necessitate fine spatiotemporal resolution, coupled multiphysics etc., leading to higher computational cost. This precludes the integration of such models for many important scenarios where the models are required to be simulated very rapidly and multiple times. To overcome this challenge, we present a deep learning based non-linear model order reduction method used to develop surrogate models for low temperature plasma applications. We propose a computationally practical approach for model order reduction that is non-intrusive and purely data driven in nature, using convolutional autoencoders and recurrent neural networks from deep learning. Our numerical experiments on radio frequency powered capacitively coupled plasmas shows that deep learning-based model can learn an efficient latent space representation of spatial and temporal features of plasma dynamics. The learning data is generated by the full order model that includes continuity equations for charged and neutral species, drift-diffusion approximation for electron flux, momentum conservation equation for ions coupled with Poisson's equation. The proposed method is extended to parametric model by embedding parametric information into the latent space for broader applications. Finally, we demonstrate the effectiveness of proposed approach over linear-subspace method for low temperature plasma applications.

9:00am **PS1+MS+SS-FrM-3 Novel Approaches to Generate Missing Data for Plasma Chemistry Modelling** *, **Sebastian Mohr**,* Quantemol Ltd., UK*; M. Hanicinec, A. Owens, J. Tennyson,* University College London, UK

Plasma simulations are a standard method in both industrial and academic settings to optimise plasma processes and gain a better understanding of the underlying physical and chemical processes. To get useful results, comprehensive and reliable data on chemical processes in the plasma are vital. These usually need to be collected from multiple sources including journal articles. To shorten this process, several centralised plasma chemistry databases were collected in recent years. The Quantemol-DB database [1] started as simply a collection of reaction data. Since then it has been enhanced by tools to quickly collect and test data for specific gas mixtures such as an automatic set generator and a global model. Here, we introduce new additions to this tool set.

While for some commonly used gases such oxygen or CF4, vast data on heavy particle reactions are available, they are missing for more exotic or newly used gases. In such cases, reactions are usually included by analogy to known gases, including the rate coefficients for these estimated reactions. However, the rate coefficients can actually differ significantly for similar reactions between different molecules. This is especially true for neutral-neutral reactions which can have a significant influence on the chemical composition of the plasma. *Ab initio* calculations are very time-intensive if possible at all, so to get better estimates of missing rate coefficients, we developed and tested a machine learning regression model [2] which gives rate coefficients for binary heavy particle reactions based on fundamental physical and chemical properties of the reactants and products.

Apart from reactions between particles, radiative transitions of excited states also play an important role in plasmas. They determine the density of excited states and provide the flux of photons to surfaces which might induce additional surface reactions. Furthermore, optical emission spectra are an important diagnostic to obtain plasma parameters. In order to incorporate radiative transitions into our set generation tools, we have created a new database of atomic and molecular lifetimes called LiDa which is linked to QDB and enhances our global model to allow for excited state lifetimes. In due course we will also provide plasma emission fluxes.

[1] Tennyson et al., *Plasma Sources Sci. and Technol.***26**, 055014 (2017)

[2] https://github.com/martin-hanicinec-ucl/regreschem

9:20am **PS1+MS+SS-FrM-4 Particle-in-Cell Modeling of Electron-Beam Generated Low Electron Temperature Plasma***, **Shahid Rauf**,* Applied Materials, Inc.*; D. Sydorenko,* University of Alberta, Canada*; S. Jubin, W. Villafana, S. Ethier, A. Khrabrov, I. Kaganovich,* Princeton University Plasma Physics Lab

Plasmas generated using energetic electron beams are known to have low electron temperature and plasma potential, attributes that are particularly useful for atomic-precision plasma processing. [1] It has been demonstrated that electron beam plasmas cause significantly lower degradation of single layer carbon nanotubes than conventional radio-frequency plasmas. [2] In addition, they have been used to etch materials with atomic precision. [3] Electron beam produced plasmas are typically confined using a static magnetic field and operated at low gas pressures. Previous hybrid modeling of these plasmas confirmed that plasma transport can be non-classical in this parameter regime. [4] The electron transport coefficients were empirically tuned in this hybrid model using experimental measurements, and this hybrid model is only expected to be valid over a narrow range of gas pressure and magnetic field. A self-consistent 2-dimensional particle-in-cell model of electron beam produced plasmas is described in this paper. The model examines the creation and evolution of plasma in low pressure (10 – 40 mTorr) Ar gas on injection of an energetic electron beam (2 keV). Low frequency waves are initially observed as the plasma forms and expands across the magnetic field. These waves radiate outwards from the beam axis towards the chamber walls. The waves gradually disappear as the plasma fills the chamber volume. The final steady-state plasma is well-confined by the magnetic field with the plasma more constricted around the beam axis at lower pressure and higher magnetic field. The electron temperature is less than 1 eV for the range of conditions examined. Physical and energy transport in the plasma (i.e., ambipolar diffusion and thermal conduction) are observed to scale differently with magnetic field and gas pressure. The charged species density is, for example, found to be more confined near the electron beam axis than the electron temperature. The effect of gas pressure, magnetic field and beam current are examined in the paper. The impact of these parameters on electron density, plasma potential and electron temperature are found consistent with probe-based experimental measurements. [4]

[1] Walton *et al.*, ECS J. Solid State Sci. Technol. 6, N5033 (2015).

[2] Jagtiani *et al.*, J. Vac. Sci. Technol. A 34, 01B103 (2016).

[3] Dorf *et al.*, J. Phys. D: Appl. Phys. 50, 274003 (2017).

[4] Rauf *et al.*, Plasma Sources Sci. Technol. 26, 065006 (2017).

9:40am **PS1+MS+SS-FrM-5 Modeling Edge Effects in Wafer Etching with VSim**, ***Daniel Main,*** *J. Cary, T. Jenkins,* Tech-X Corporation

Plasma processing chambers for the etching of wafers are often used to create a uniform etch along most of the wafer. In such a chamber, a plasma is created using a RF source via Capacitive Coupling (CCP) or Inductive Coupling (ICP). The source region is often far from the wafer (thousands of electron Deybe lengths) so that the plasma is nearly uniform for most of the chamber.Therefore, the physics that requires a kinetic approach occurs near the wafer (within a few hundred Debye lengths).An important part of the process is the acceleration of the ions due to the sheath that forms near the wafer. However, the discontinuity in the boundary near the edge of the wafer leads to a non-uniform sheath and hence non-uniform ion velocities impacting the wafer.One way to make the sheath more uniform is to place a "focus ring" (FR) near the wafer edge. To model the essential physics near the wafer, including the effect of the FR on the sheath dynamics, we have used the electromagnetic, fully kinetic, particle-in-cell simulation package VSim.The simulation includes electrons, argon ions and neutral argon gas. We also include collisions between electrons and neutral species, secondary emission off the wafer, and the self-consistent calculation of the electric field, including a proper inclusion of the wafer and FR dielectric constants. Since the electric field is determined by Poisson's equation, including a full kinetic treatment of the electrons is essential for computing the sheath physics, and hence ion dynamics, correctly.Because of the small spatial and time steps required for a fully kinetic model, we include about half the wafer up to the edge and about 200 Deybe lengths above the wafer. We inject both electrons and ions (modeled as drifting Maxwellians) at the boundary opposite the wafer using incoming-flux boundary conditions, which ensure a smooth transition from the assumed infinite plasma reservoir outside the simulation into the simulation domain. We use Rejection-Sampling theory to compute the correct incoming-flux velocities of the injected particles. The boundary that includes the wafer is an absorbing boundary; electrons and ions accumulate on the dielectrics at this boundary. We show that elastic collisions tend to create a more symmetric Ion Angular-Energy Distribution (IAED) function about the normal. Finally, we demonstrate the role the focus ring has on the IAED and sheath dynamics.

10:00am **PS1+MS+SS-FrM-6 A Study on Dielectric Material Etching in Cryogenic Process Based on Atomistic Simulation**, ***Junghwan Um,*** Yonsei University, Korea*; S. Cho,* Samsung Electronics Co., Inc., Republic of Korea*; K. Kang,* Yonsei University, Korea

The adsorption of H2, H2O and HF in each membrane was calculated using molecular dynamics and DFT as parameters necessary to know the adsorbate concentration on the surface according to the temperature of SiO2 and Si3N4. After obtaining the parameters for reaction rate of the pathway in which the chemical reaction of each film material appears, the reaction rate according to the surface temperature of the film material was calculated using an analytic model and previously reported experimental results. As a result, the reaction rate according to the surface temperature of SiO2 and Si3N4 was obtained, and the reaction rate increased by decreasing the temperature was presented as a quantitative value. Finally, through the results of this study on the temperature dependence of the surface reaction, the understanding of the cryogenic process was helped, and the overcoming of aspect ratio dependent etching in deep contact was considered.

10:20am **PS1+MS+SS-FrM-7 Machine Learning Based Model for a RF Hollow Cathode Discharge**, *K. Bera, A. Verma,* ***Sathya Ganta****, S. Rauf,* Applied Materials, Inc.

Radio-frequency (RF) hollow cathode discharges (HCD) at low to moderate pressures have gained significance for advanced plasma processes in the semiconductor industry. HCDs form in cylindrical cavities in the cathode, and one can use an array of such cavities to create large area HCDs. A neutral-network based reduced order model for HCDs is discussed in this paper, where this reduced order model is trained using results from Particle-in-Cell/Monte Carlo Collision (PIC/MCC) simulations of single hollow cathode holes. 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 PIC/MCC code considers particle collisions with each other and with neutral fluid using a Monte Carlo model. RF hollow cathode behavior is simulated and characterized for different hole size, pressure, RF voltage, frequency, and secondary electron emission coefficient. The plasma penetrates inside the hollow cathode hole with increase in pressure, leading to plasma enhancement. The synergistic effect of RF sheath heating and secondary electron acceleration on hollow cathode discharge has been observed. For improved computational efficiency, a reduced order modeling framework has been developed based on neural network using plasma model parameters. Different methodologies have been explored in selecting and preprocessing physical data to train and validate the neural network. The temporal variation of voltage-current characteristics as well as that of spatial profile of plasma variables (density, temperature, etc.) have been used to train the neural network model. The predictions of trained neural network model compare reasonably well with that of the underlying physical model observations in PIC/MCC simulations. The neural network framework is being applied to determine the collective behavior of an array of RF hollow cathode holes for large area HCDs.

10:40am **PS1+MS+SS-FrM-8 Molecular Dynamics Simulations of Plasma-Enhanced Atomic Layer Etching of Silicon Nitride Using Hydrofluorocarbon and Oxygen Plasmas**, ***Jomar Tercero,*** 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 simulations were performed to study the influence of oxygen (O_2) in the hydrofluorocarbon (HFC) plasma-enhanced atomic layer etching (ALE) of silicon nitride (Si_3N_4). ALE is known to etch a surface with atomic-scale control and precision. Its in-depth understanding is essential for the advancement of fabrication technologies for semiconductor devices. It was presented earlier that such a Si_3N_4 ALE process can lead to an etch stop due to the accumulation of C atoms on the surface [1]. It was then shown that, by introducing an O_2 plasma irradiation step, a stable etch was observed and the etch stop was prevented [2]. In this study, molecular dynamics (MD) simulations were used to clarify the interaction mechanisms of an O_2 plasma with the modified Si_3N_4 surface during the HFC-based ALE process. To do this, CH_2F radicals were used in the adsorption step. It was then followed by Ar^+ bombardment in the desorption step. Subsequently, O_2 plasma was introduced as an additional step to help the removal of the remaining HFC species. This series of steps corresponds to one ALE cycle. Our simulations have shown that, during the desorption step of the first ALE cycle, HFC species assist the removal of the Si and N atoms of the Si_3N_4 by the formation of volatile by-products such as SiF_x, CN_x, and NH_x species. On the other hand, due to the momentum transfer from incident Ar^+ ions, some HFC species were pushed into the bulk layer, forming chemical bonds with Si and N atoms therein. By the addition of the O_2 plasma irradiation step, it was observed that HFC species interact with O atoms adsorbed on the surface. The removal of C atoms was also enhanced by the formation of CO_x. In this way, our MD simulations have shown that the additional O_2 plasma irradiation step prevents the etch stop and allows stable Si_3N_4 ALE cycles.

References

[1] A. Hirata, M. Fukasawa, K. Kugimiya, K. Nagaoka, K. Karahashi, S. Hamaguchi, and H. Iwamoto, *Journal of Vacuum Science & Technology A*, **38**, 062601 (2020).

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

11:00am **PS1+MS+SS-FrM-9 Understanding Plasma Etch Mechanism of Low-k Materials Under Low Temperature Substrates with Fluorine-Based Precursors**, ***Daniel Santos,*** Tokyo Electron America*; C. Vallee,* SUNY Polytechnic Institute, Albany*; P. Wang,* Tokyo Electron America

Plasma etching of ultra-low-k materials at aggressive back end of line (BEOL) nodes has become increasingly challenging as plasma induced damage becomes a significant challenge to overcome. Conventional reactive ion etch (RIE) processes usually occur at a temperature near room temperature in which diffusion of radicals will damage low-k materials surface. Alternatively, to limit diffusion mechanisms and prevent damage, cryogenic cooling of a substrate sub <-100 C can be used. The purpose of this research is to understand how to leverage the range between room temperature and cryogenic temperatures when using fluorine-based plasmas.

For this work we use a 300mm dual frequency TEL CCP chamber equipped with a low-temperature electrostatic chuck to conduct our experiments. Furthermore, we use in-situ OES, ex-situ XPS, and ellipsometry to understand the plasma surface interactions and observe change in etch rates, fluorine content and composition. We find the choice of between different Fluorine molecules plays a critical role in changing the surface fluorination in dielectric materials, and opposite results have been observed. When using NF_3 the etch rate of low-k 3.0 increases from 200 nm

min^{-1} at 15C to 350 nm min^{-1} at -40C but the etch rate of thermal oxide remains 10 nm min^{-1} at all ranges between which displays an increase in selectivity between the films. Opposite of that, when using C_4F_8 we observe the etch rate decrease from 135 nm min^{-1} at 15C to 90 nm min^{-1} at -40C with decreasing temperature suggesting that we enter a higher polymerization regime. We have concluded that different temperature threshold can be obtained, for same plasma parameters, for switching from deposition to etching regime and this behavior depends on fluorine molecule and substrate material composition, which also induces a modification of the selectivity. Using this approach, we try to understand the plasma surface reactions for the fluorine molecules as a function of their triple point temperature, surface saturation with F atoms, and condensation mechanisms.

11:20am **PS1+MS+SS-FrM-10 Plasma-Assisted Atomic Layer Etching of Silicon Nitride with Unfragmented Fluorocarbons***, **Chon Hei Lam**, M. Carruth,* University of Texas at Austin*; Z. Chen, J. Blakeney, P. Ventzek, S. Sridhar,* Tokyo Electron America Inc.*; J. Ekerdt,* University of Texas at Austin

The self-limiting behavior in atomic layer etching (ALE) processes promise to deliver atomic scale fidelity for three-dimensional device fabrication. Plasma-assisted ALE processes typically alternate cycles of chemical modification to weaken the surface bonds followed by ion bombardment to remove a limited amount of material. ALE may provide fine control over the etch rate through the “layer-by-layer” process and can limit physical damage to the substrate. Since silicon nitride films are a likely component in self-aligned multiple patterning schemes, we explore silicon nitride ALE by utilizing undissociated fluorocarbon (CF_4 and CHF_3) adsorption followed by argon ion bombardment. The impact of gas precursors, energetic ion energy, substrate temperature, and the nature of the surface chemical modification are discussed. We follow the surface chemistry and monitor structural damage during ALE with various *in situ* probes (X-ray photoelectron spectroscopy and spectral ellipsometry). Using CHF_3 to illustrate surface modification and argon ion bombardment to affect removal in concert with the spectroscopic probes we demonstrate changes to the adsorbed layer during bombardment. The ALE steps are performed at 100 °C (Fig 1). The silicon nitride films were exposed to CHF_3 at 4 mTorr for 60 s in the fluorocarbon adsorption step followed by argon ion bombardment. The F 1*s* peak appears after argon ion bombardment (4 min, 200 eV) at 100 °C. After the first ALE cycle, a C-F bond was detected in C 1*s* spectra at high binding energy (300 eV) (Fig 2a). The energetic argon ions fragment the fluorocarbon and activate the interaction between fluorine and silicon. The ALE process also leads to nitrogen depletion which is shown in the N 1*s* spectra (Fig 2d). After extended ALE cycles, the Si 2*p* peak shifts to higher binding energy and it might indicate that SiO_x and SiF_x formed through the ALE cycles. The intensity of O increases and the intensity of N decreases along the ALE cycles. The fluorine signal was detectable and the signal in C 1*s* spectra was barely noticeable, which suggest fluorine remains after the ALE process and it combines with silicon in the process. The ellipsometry result (Fig 1) shows a consistent removal amount per cycle of 1.4 Å/cycle over the 20 ALE cycles.

11:40am **PS1+MS+SS-FrM-11 Time Resolved Ion Energy Distribution in Pulsed Inductively Coupled Argon Plasma with/without DC Bias***, **Zhiying Chen**, J. Blakeney, M. Carruth, P. Ventzek,* Tokyo Electron America Inc.

Pulsed plasmas have emerged as promising candidates as means for precise control of ion energy/angle dependent surface processes and surface chemistry during plasma process, which are the key to 3nm and beyond device fabrication. The ion energy distribution functions (IEDFs) and ion fluxes over a pulsed period are important to understand as they directly influenced feature profile, damage and selectivity. We have developed an advanced plasma diagnostics (APD) system with advanced pulsing capability, including source, bias and synchronous pulsing. It is a compact inductively coupled plasma system with RF source frequency of 13.56 MHz intended to diagnose the general behavior of biased high-density plasmas. We report the effect of pulse frequency, RF duty cycle and power, DC duty cycle and voltage, and discharge pressure on the IEDFs and ion flux over a pulse period on the APD system. The time-resolved IEDFs and ion flux were measured using a retarding field energy analyzer. The ion energy transitions in a pulsed period from plasma ignition stage to stable stage and from plasma in glow period to afterglow period are studied. The results indicate the ion energy and ion flux are tailored by RF pulsing and RF-DC pulsing. The time-resolved IEDF demonstrates the merits of pulsing to precise control ion energy and flux, and the ion energy spread narrowed by pulsed plasma.

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Karimi Aghda, S.: AS+2D+EM+MS+NS+SS+TF-ThA-5, 10
Kessels, E.: AP+AS+EL+MS+SS-MoA-4, 3
Khrabov, A.: PS2+MS-TuM-11, 7
Khrabrov, A.: PS1+MS+SS-FrM-4, 12
Kim, C.: PS2+MS-TuM-3, 6
Kim, H.: PS2+MS-TuM-3, 6
Kim, S.: PS2+MS-TuM-10, **7**
King, S.: AP+AS+EL+MS+SS-MoA-3, 3
Knoops, H.: AP+AS+EL+MS+SS-MoA-4, 3
— L —
Lam, C.: PS1+MS+SS-FrM-10, **14**
Lee, H.: PS2+MS-TuM-3, 6
Lee, J.: PS2+MS-TuM-10, 7; PS2+MS-TuM-4, 6
Lee, Y.: PS2+MS-TuM-10, 7
Leverd, F.: PS1+MS+SS-FrM-1, 12
Liu, Y.: MS+AP+AS+TF-MoA-5, **4**
— M —
Mackus, A.: AP+AS+EL+MS+SS-MoA-4, **3**
Madison, E.: MS+HI-MoM-5, 1
Main, D.: PS1+MS+SS-FrM-5, **13**
Mane, A.: AP+AS+EL+MS+SS-MoA-6, **3**
Martirosyan, V.: PS1+MS+SS-FrM-1, 12
McChesney, J.: AS+2D+EM+MS+NS+SS+TF-ThA-6, **10**
McClain, J.: MS+HI-MoM-10, 2
McDow, J.: MS+HI-MoM-10, **2**
Minnich, A.: AP+AS+EL+MS+SS-MoA-5, 3
Mohr, S.: PS1+MS+SS-FrM-3, **12**
— N —
Nam, S.: PS2+MS-TuM-4, 6
— O —
Okada, S.: MS-TuP-2, 8
Ondračka, P.: AS+2D+EM+MS+NS+SS+TF-ThA-5, 10
Ontaneda, J.: AS+2D+EM+MS+NS+SS+TF-ThA-4, 10
Owens, A.: PS1+MS+SS-FrM-3, 12
— P —
Paquette, M.: AP+AS+EL+MS+SS-MoA-3, 3
Park, N.: AS+2D+EM+MS+NS+SS+TF-ThA-1, **10**
Park, S.: AP+AS+EL+MS+SS-MoA-1, **3**
Patterer, L.: AS+2D+EM+MS+NS+SS+TF-ThA-5, **10**
Pinzan, F.: PS1+MS+SS-FrM-1, 12
Powis, T.: PS2+MS-TuM-11, 7
— R —
Rauf, S.: PS1+MS+SS-FrM-2, 12; PS1+MS+SS-FrM-4, **12**; PS1+MS+SS-FrM-7, 13; PS2+MS-TuM-11, 7
RISTOIU, D.: PS2+MS-TuM-12, 7
Rooney, L.: MS-TuP-2, 8
— S —
Sankaranarayanan, S.: MS+AP+AS+TF-MoA-3, **4**
Santos, D.: PS1+MS+SS-FrM-9, **13**
Schmitt, R.: MS+HI-MoM-10, 2
Schneider, J.: AS+2D+EM+MS+NS+SS+TF-ThA-5, 10
Seong, I.: PS2+MS-TuM-10, 7
Shannon, S.: PS2+MS-TuM-4, 6
Shin, J.: PS2+MS-TuM-3, **6**
Shinagawa, J.: MS+HI-MoM-3, **1**
Smith, C.: PS2+MS-TuM-4, **6**
Soares, J.: AP+AS+EL+MS+SS-MoA-10, 4
Sorinto, E.: AP+AS+EL+MS+SS-MoA-11, 4
Sridhar, S.: PS1+MS+SS-FrM-10, 14
Sydorenko, D.: PS1+MS+SS-FrM-4, 12; PS2+MS-TuM-11, 7
— T —
Taira, S.: PS2+MS-TuM-1, 6
Tennyson, J.: PS1+MS+SS-FrM-3, 12
Tercero, J.: PS1+MS+SS-FrM-8, **13**
Thapa, R.: AP+AS+EL+MS+SS-MoA-3, 3
Tiwari, S.: TF3+MS-WeM-12, 9
Tsai, Y.: PS2+MS-TuM-5, **6**
— U —
Um, J.: PS1+MS+SS-FrM-6, **13**
— V —
Valentine, B.: MS+AP+AS+TF-MoA-10, **5**
Vallee, C.: PS1+MS+SS-FrM-9, 13
Vanamu, G.: MS-TuP-2, **8**
Vandalon, V.: AP+AS+EL+MS+SS-MoA-4, 3
Vanfleet, R.: AP+AS+EL+MS+SS-MoA-11, **4**
Vella, J.: PS2+MS-TuM-2, **6**
Ventzek, P.: MS+HI-MoM-3, 1; PS1+MS+SS-FrM-10, 14; PS1+MS+SS-FrM-11, 14; PS2+MS-TuM-13, 7
Verheijen, M.: AP+AS+EL+MS+SS-MoA-4, 3
Verma, A.: PS1+MS+SS-FrM-2, **12**; PS1+MS+SS-FrM-7, 13
Villafana, W.: PS1+MS+SS-FrM-4, 12
— W —
Wang, H.: AP+AS+EL+MS+SS-MoA-5, **3**
Wang, M.: PS2+MS-TuM-5, 6
Wang, P.: PS1+MS+SS-FrM-9, 13
Wang, T.: PS2+MS-TuM-13, 7
Wensel, J.: AP+AS+EL+MS+SS-MoA-10, 4
Wiwi, M.: MS+HI-MoM-5, 1
— X —
Xu, L.: PS2+MS-TuM-11, 7
— Y —
Yang, T.: PS2+MS-TuM-13, **7**
You, S.: PS2+MS-TuM-10, 7
You, Y.: PS2+MS-TuM-10, 7
— Z —
Zhao, J.: PS2+MS-TuM-13, 7